VAPOUR-LIQUID EQUILIBRIA OF THE AMMONIA-CARBON DIOXIDE-WATER SYSTEM

P. VERBRUGGE

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Voor Marion, Joost en Saskia

VOORWOORD

Dit proefschrift is tot stand gekomen met de medewerking van een groot aantal personeelsleden en studenten. Langs deze weg wil ik hen voor hun inzet hartelijk danken.

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CONTENTS

1 INTRODUCTION

Urea is today a very important chemical product. While the world production of urea in 1974 was 67 million tonnes, in 1977 it had risen to 99 million tonnes (1). Its most important application is as nitrogenous fertilizer (75%). Other applications are as a feedstock in the production of resins (15%) and as a supplement in cattle feed (10%) (3).

Urea is industrially synthesized from ammonia and carbon dioxide. It is an advantageous coincidence that the latter compound is a by-product of the ammonia production from hydrocarbon feedstocks. It is estimated that about 35% of the world's ammonia production is used in the production of urea (2). In order to provide some insight in the principles of urea production, a brief discussion of the fundamentals is presented. A comprehensive treatment can be found in Ref. 4.

The formation of urea proceeds via two reversible consecutive reactions:

$$2NH_{3_G} + CO_{2_G} \rightleftarrows NH_2CO_2NH_{4_L} \qquad (1\text{-}1)$$

$$NH_2CO_2NH_{4_L} \rightleftarrows NH_2CONH_{2_L} + H_2O_L \qquad (1\text{-}2)$$

The formation of ammonium carbamate (eq. 1-1) is strongly exothermic and goes practically to completion. The fact that it is a gas-liquid reaction is one of the main features in urea technology. The second reaction, in practice occurring only in the liquid phase, is slow, endothermic and does not proceed to completion. Under practical conditions the equilibrium conversion is in the order of 50-70%. Because the NH_3 price forms 75-80% of the urea manufacturing costs and because processing of the non-converted ammonia to other products is economically unfavourable, it is necessary to separate the unconverted reactants from the urea produced and to recycle these to the urea reactor. The equilibrium depicted in eq. 1-1, being a two-phase reaction, provides in principle a simple mechanism for the separation. Lowering the partial pressures of NH_3 and CO_2, achieved by lowering the total pressure or by stripping (see below), will result in a dissociation of ammonium carbamate and in a decrease the amount of excess NH_3 dissolved in the urea synthesis solution. By stepwise reduction of the pressure of the urea synthesis solution under supply of heat it is possible to recover practically all of the unconverted NH_3 and CO_2. Recirculation of the evolved vapours takes place by absorbing them in water or ammonium carbamate solutions and pumping the resulting solution back to the reactor. This recirculation method (solution recycle) has several drawbacks. Because recovery of NH_3 and CO_2 necessarily takes place at low pressures, hence low temperatures, the large heat of formation of ammonium carbamate cannot be recovered at a high temperature level (necessary for production of valuable steam). Absorption at low pressures also requires a relatively large amount of water. This water is also introduced into the reactor, thereby decreasing the urea conversion (eq. 1-2). Excess NH_3 can counterbalance this effect, but the excess leads to a larger reactor volume and a larger recirculation section. Furthermore the added water has to be removed in the urea finishing section, requiring more steam.

To overcome the above-mentioned disadvantages the stripping processes were introduced. By simultaneously heating the urea synthesis mixture and contacting it with CO_2 (DSM) or NH_3 (SNAM) at reactor pressure the partial pressure of the other volatile component is decreased, leading to dissociation of ammonium carbamate. About 85% of the unconverted reactants is recovered at synthesis pressure. Condensing the gases at this pressure results in the production of medium-pressure steam. A lower H_2O content in the urea reactor is also obtained. Separation of the remaining unconverted reactants from the urea synthesis solution remains necessary, but a much smaller recirculation unit suffices.

It is seen that vapour-liquid equilibria play an essential role in urea synthesis processes. In every piece of equipment (reactor, condensors, absorbers, decomposers, strippers) a vapour phase and a liquid phase are present. Recently the high pressure equilibria have been studied extensively. Lemkowitz (4) studied the phase behaviour of the system NH_3-CO_2-H_2O at and above urea synthesis conditions. These conditions imply that an equilibrium concentration of urea is present. Durisch (5) measured phase equilibria of the same system in the urea-rich concentration region. For the design and optimization of low-pressure absorbers, condensors and rectifiers the vapour-liquid equilibria of the system NH_3-CO_2-H_2O (no urea present) are needed. These equilibria are also indispensable for the process design of the production of melamine (2,4,6-triamino-1,3,5-triazine) from urea.

Melamine is produced from urea according to:

$$6H_2NCONH_2 \rightarrow C_3N_6H_6 + 6NH_3 + 3CO_2 \qquad (1-3)$$

For 1976 a production of 300.000 tonnes was estimated (6). Melamine is mainly used with formaldehyde to produce resins, applied in paints, lacquers, glues and plastics.

It is advantageous to reconvert the produced NH_3 and CO_2 (formed with a NH_3/CO_2 ratio corresponding to that required for urea synthesis) into urea. To achieve this aim separation and recirculation problems must be solved for this process. Because in various melamine processes water is introduced for the separation, the phase behaviour of the NH_3-CO_2-H_2O system (no urea present) is also important for design and optimization of the separation and recirculation section. In the separation section a dilute carbamate solution is obtained. Since this solution contains a large amount of H_2O, recirculation to the urea reactor will lead to a decrease in conversion. Therefore, it is necessary to concentrate the solution. However, a rigid coupling between two synthesis units decreases flexibility and reliability, and even in a concentrated recycle stream water will of course still be present. For these reasons several proposals were made for a complete separation of NH_3, CO_2 and H_2O, present in the recycle solution. This type of separation provides a clear example of the relation between phase equilibria and process design (see Chapter 6).

The third illustration of the use of vapour-liquid equilibria of the NH_3-CO_2-H_2O system concerns sour-water stripping. Because of increasingly strict environmental regulations it is no longer possible to dispose of process waste water streams by simply draining them. Urea process condensates containing NH_3, CO_2 and some urea are formed in evaporators or crystallizers in the urea finishing section. Refinery effluents also present problems involving the removal of volatile compounds such as NH_3, H_2S, HCN and SO_2; removal is usually accomplished by so-called sour-water stripping techniques using steam (7). If urea is present, hydrolysis prior to stripping is necessary for the conversion of urea into NH_3 and CO_2. In particular the thorough removal (down to the ppm region) of the solutes is interesting. Because experimental data are difficult to obtain in this region, a mathematical representation of the phase behaviour is desirable for the process design.

In general such a representation is helpful in process design, also in case experimental data are available. Process calculations can be easily performed with a mathematical model. In particular, interpolation to the desired conditions is facilitated. Van Krevelen et al. (8) were the first to propose a model for the vapour-liquid equilibria of the NH_3-CO_2-H_2O system.

The aim of the study presented in this thesis was to determine the vapour-liquid equilibria of the NH_3-CO_2-H_2O system and to develop a suitable model to represent the measured equilibria. Initially it was the intention to perform measurements in a wide range of temperatures and pressures. It soon appeared, however, that the measurements were so difficult and laborious that it was decided to restrict them to 0.1 MPa (0.987 atm, 1.020 kg/cm^2, 14.50 psia) and 40-90°C, also because reliable measurements at these conditions should provide a clear, though qualitative, insight into the phase behaviour of the system at higher pressures.

The organization of the thesis is as follows. Chapter 2 presents a general outline of the phase behaviour of the system at the conditions of interest. In particular the literature concerning vapour-liquid equilibria and equilibria involving solids is reviewed. The phase equilibria at 0.1 MPa are semi-quantitatively sketched. A discussion of the experimental apparatus, the experimental method and the analysis methods is given in Chapter 3. Chapter 4 presents the results of the experimental measurements. A proposal for a mathematical description of the measurements is given in Chapter 5. Experimental and calculated results are compared and limitations of the model are discussed. In Chapter 6 various processes related to the phase equilibria of the NH_3-CO_2-H_2O system are considered. In particular the coupling of melamine and urea synthesis and the complete separation of NH_3 and CO_2 is discussed.

References

1. G.P. Golovinskii, *Sov. Chem. Ind. (Engl. Transl.)* 9 (1977) 310.
2. D.M. Gorlovskii, V.I. Kucheryavyi, L.V. Petrov, B.P. Melnikov, *Sov. Chem. Ind. (Engl. Transl.)* 9 (1977) 203.
3. B.F. Greek, W.F. Fallwell, *Chem. Eng. News* 55 (4) (1977) 8.
4. S.M. Lemkowitz, *Phase and corrosion studies of the* NH_3-CO_2-H_2O *system at the conditions of the hot gas recirculation process for the synthesis of urea*, PhD thesis, Delft University of Technology, The Netherlands, 1975.
5. W. Durisch, *Experimentelle und thermodynamische Untersuchung des Siedegleichgewichts des Systems* $CO_2/NH_3/H_2O$ *unter Harnstoffsynthese-Bedingungen*, PhD-thesis nr. 6238, Eidgenössischen Technischen Hochschule Zürich, Switzerland, 1978.
6. A. Shiroishi, Y. Takakuwa, *Chem. Econ. Eng. Rev.* 8 (1976) 35.
7. R.C. Darton, P.F.A. van Grinsven, M.M. Simon, *Chem. Eng. London* (339) (1978) 923.
8. D.W. van Krevelen, P.J. Hoftijzer, F.J. Huntjens, *Recl. Trav. Chim. Pays-Bas* 68 (1949) 191.

2 PHASE EQUILIBRIA IN THE NH_3-CO_2-H_2O SYSTEM

2.1 Introduction

The phase equilibria of the NH_3-CO_2-H_2O system are complicated because chemical reactions may occur between the system's components. Although the system is composed of rather simple chemical species, the occurrence of chemical reactions leads to interesting phenomena such as azeotropy, liquid-liquid immiscibility, unusual critical behaviour and complicated equilibria involving solids.

In studying phase equilibria one investigates the relations that exist between the intensive thermodynamic properties of a system which is in complete equilibrium. Examples of these properties are the composition of the phases, pressure and temperature. For a thermodynamic description of a system in equilibrium it is not necessary to have complete information of all of the state variables of the system. Determining the value of a certain number of properties is necessary and sufficient to determine the equilibrium state. This so-called number of degrees of freedom is determined with Gibbs' phase rule, derived in many textbooks. The derivation can take place via logical reasoning (1, 3a) or with the use of strict thermodynamic relationships (2). In formula the phase rule reads:

$$F = C - P + 2 \qquad (2\text{-}1)$$

in which F is the number of degrees of freedom, P is the number of phases and C is the number of components. Although P is always easy to determine, problems may arise in determining the number of components, especially when chemical reactions occur. In can be shown that for a system in which chemical reactions are occurring the number of components can be found by subtracting the number of independent equilibria which occur from the number of constituents (chemical species present in the system) (2). It should be noted that although the number of components is definite, there is no clear definition of the term component. Any constituent can be chosen as a component, its choice being a matter of preference. Generally, it is preferable to choose the simplest species present as components.

Applying the phase rule as presented in eq. 2-1 sometimes results in values of F greater than observed. This phenomenon is caused by the occurrence of restrictive or additional equations. Examples are a given gross composition (3b) or the occurrence of azeotropy. Therefore a better way of expressing the phase rule is:

$$F = C' - R - P + 2 - Z \qquad (2\text{-}2)$$

where C' is the number of constituents, R is the number of reversible chemical reactions occurring in the system and Z is the number of additional equations.

To determine the number of components in a system containing ammonia, carbon dioxide and water, it is necessary to know which equilibria may occur. Possible independent equilibria are:

$$2NH_3 + CO_2 \rightleftarrows NH_4CO_2NH_2 \qquad (2\text{-}3)$$

$$NH_3 + H_2O + CO_2 \rightleftarrows NH_4HCO_3 \qquad (2\text{-}4)$$

$$NH_4HCO_3 + NH_3 \rightleftarrows (NH_4)_2CO_3 \qquad (2\text{-}5)$$

$$NH_4CO_2NH_2 \rightleftarrows NH_2CONH_2 + H_2O \qquad (2\text{-}6)$$ × > 140°

$$NH_2CONH_2 \rightleftarrows NH_4OCN \qquad (2\text{-}7)$$

$$NH_2CONH_2 \rightleftarrows HOCN + NH_3 \qquad (2\text{-}8)$$ ×

$$2NH_2CONH_2 \rightleftarrows NH_2CONHCONH_2 + NH_3 \qquad (2\text{-}9)$$ ×

Eqs. 2-3 to 2-9 give 10 constituents and 7 equilibria, resulting in 3 components. However, it is possible that certain equilibria do not occur at the conditions at which the system is studied. At temperatures below 140°C equilibria 2-6, 2-8 and 2-9 do not occur. At these temperatures a system initially composed of NH_3, CO_2, H_2O and urea therefore has 4 components. With no urea or ammonium cyanate present equilibrium 2-7 cannot occur and thus the system is again ternary. Therefore there are two separate ternary systems possible, one at lower temperatures, at which formation of urea does not occur, and one at higher temperatures with equilibrium concentrations of urea, biuret, isocyanic acid and ammonium cyanate. If, at temperatures below 140°C, it is assumed that electrolytic dissociation occurs in the equilibria 2-3 to 2-5 the number of constituents increases to 7. Still, the number of components remains 3 because then there is an additional equation, expressing the electroneutrality of the solution.

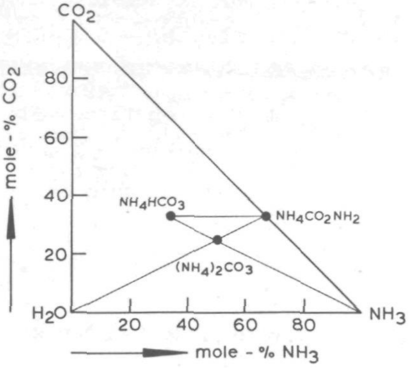


Fig. 2-1 Ternary composition triangle with composition points of three compounds.

The composition of a particular phase in a ternary system is determined by the concentrations of two of the system's components. Therefore, this composition can be represented on a plane, the coordinates of a point on that plane giving a particular composition. Although in principle various coordinate systems can be used, the equilateral and the rectangular triangle are mostly used. Because of reasons of symmetry, Lemkowitz et al. (4) proposed a rectangular triangle with corner points $2NH_3$, CO_2 and H_2O (right angle) for the system NH_3-CO_2-H_2O containing an equilibrium concentration of urea. The advantage of this proposal is that the composition of pure urea is found in a corner point diagonally opposite the H_2O corner point, forming a square with the other corner points. Because in the present system no compositions occur outside the triangle, a triangle with NH_3, CO_2 and H_2O as corner points is used. To express the character of water as a solvent a rectangular triangle with H_2O as right angle corner point is preferred. Fig. 2-1 depicts such a triangle and represents some compounds which may be present in the system.

The systems NH_3-CO_2-H_2O, with or without urea, and NH_3-CO_2-H_2O-urea have been studied for various reasons. Early studies were aimed at the conditions at which various salts were formed from NH_3 and CO_2 containing solutions. The vapour-liquid equilibria were investigated for their relation to the treatment of coal gas and coke oven gas. This implied a dilute concentration range and pressures up to 0.1 MPa. When the industrial synthesis of urea became important, the design of synthesis and recirculation equipment required equilibrium measurements at the relevant conditions. An extensive review of the literature up to 1936 is given in Ref. 53. Chao (54), who was apparently not aware of Ref. 53, summarized again the most important results and some more recent investigations.

Lemkowitz (5) presents a thorough study on the phase equilibria of the ternary system at chemical equilibrium at urea synthesis conditions, including a ternary space model to represent the measurements. Kaasenbrood (6) discussed a quaternary model of the NH_3-CO_2-H_2O-urea system. This model also contains the ternary equilibria. With the model it is possible to follow the path to complete chemical equilibrium in a urea reactor and to show the operation of a stripper. However, only little quantitative information is given in this study.

In general the literature on vapour-liquid equilibria of the NH_3-CO_2-H_2O system without urea is scarce and the experimental conditions are limited to small ranges of concentrations, pressure and temperature. Often the accuracy is doubtful.

The purpose of this chapter is to review the literature for the ternary system without urea present. Because of their importance for the system's characteristics the binary boundary systems are also taken into account. The occurrence of solid-liquid equilibria at lower temperatures is discussed in a separate section. Finally, a sketch is given of the system's behaviour at a pressure of 0.1 MPa.

2.2 Boundary systems

The ternary NH_3-CO_2-H_2O system is bound by three binary systems: NH_3-H_2O, CO_2-H_2O and NH_3-CO_2. The two water-containing systems exhibit a rather simple behaviour, whereas the NH_3-CO_2 system is more complicated and differs greatly from the other two.

The NH_3-H_2O system consists of two species which are quite similar. Both are polar and thus dissolve well in each other, ammonia being more volatile than water. The vapour-liquid behaviour is therefore normal, i.e. without azeotropy (except in a very dilute range due to ionization (7)) or liquid demixing and with a continuous critical curve. Various authors measured the vapour-liquid equilibria to a maximum pressure of 2 MPa (8 - 12). In only one reference (13) the measurements are extended to the critical range. However, the results are only presented in a small graph. The results of Refs. 8 and 9 at 0.1 MPa are presented in Fig. 2-2. It is seen that mutual agreement is excellent.

The H_2O-CO_2 system is more complicated than the NH_3-H_2O system. It is com-

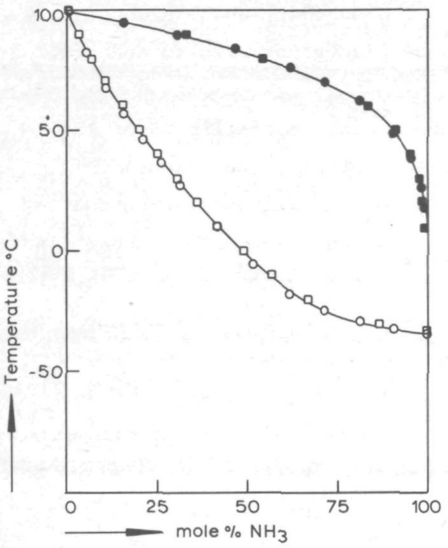


Fig. 2-2 Vapour-liquid equilibrium of the NH_3-H_2O system at 0.1 MPa. Open symbols: liquid phase. Closed symbols: vapour phase. Squares: Ref. 9. Circles: Ref. 8.

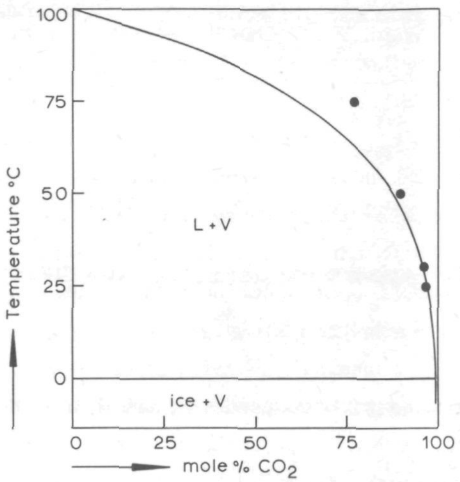


Fig. 2-3 Dewpoint line of the H_2O-CO_2 system at 0.1 MPa. Line: calculated. Points: Ref. 17.

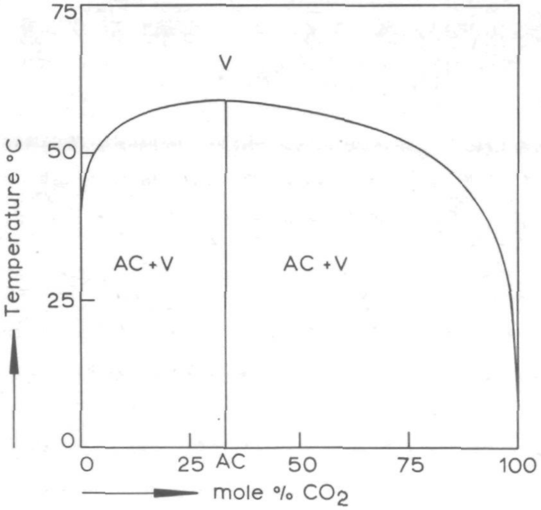


Fig. 2-4 Solid-vapour equilibrium of the NH_3-CO_2 system at 0.1 MPa, calculated with eq. 2-12. AC = solid ammonium carbamate. V = vapour.

posed of two dissimilar components, one polar, the other not. A comprehensive review of the system is presented in Ref. 18. At normal conditions water and carbon dioxide are poorly soluble in each other. Due to the great difference in critical conditions and the occurrence of a chemical compound (the hydrate $CO_2.6H_2O$) the critical curve of the system is divided into two parts, the high temperature part having a minimum temperature (14, 15). This phenomenon leads to exceptional phase behaviour, as is illustrated by a P-X section of the system at temperatures below the minimum critical temperature (265^oC). Contrary to the closed two-phase area normally found in systems with a supercritical component, the two-phase area is open to higher pressures. The solubility of carbon dioxide in water and the vapour-liquid equilibria have been extensively studied (14 - 17, 19). Due to its geochemical importance, the system has been especially studied in the region of high temperatures (up to the critical point of water) and high pressures (up to 350 MPa). Fig. 2-3 depicts results of Ref. 17 together with calculations, based on Dalton's law and on the assumption of pure water as liquid phase. (A complete T-X section at 0.1 MPa can be found in Ref. 3c). At low temperature the two phase equilibrium ends in the three phase equilibrium ice-liquid-vapour (-0.15^oC) At this temperature, the solubility of carbon dioxide in water at 0.1 MPa has a maximum value of 0.144 mole-% (19). At higher temperatures agreement between Wiebe's results and calculations is poor. Referring to experimental results discussed in Chapter 3 of this thesis, pointing to ideal behaviour of the vapour phase, it is believed that the discrepancy is due to the experimental technique, with which Wiebe's results were obtained (33). A constantly flowing stream of carbon dioxide had to be saturated in one equilibrium cell, making attainment of the equilibrium state unlikely.

Contrary to the two binary systems discussed above, the system NH_3-CO_2 exhibits considerable deviations from the normal phase behaviour. This unusual behaviour is caused by the formation of a compound, ammonium carbamate, which is much less volatile than CO_2 and NH_3. The influence of this compound on the phase behaviour is not limited to the binary system NH_3-CO_2; the phase behaviour of the ternary system $NH_3-CO_2-H_2O$ is also strongly influenced by this compound. At temperatures well below its maximum sublimation point (153^oC) solid-vapour equilibria, typical of a dissociating compound, occur. Above 147^oC, a binary minimum pressure azeotrope exists. It should be noted, however, that at these temperatures the system is not stable, because the urea formation reaction is fast enough to change the system to the ternary system $NH_3-CO_2-H_2O$ with an equilibrium concentration of urea (eq. 2-6).

A comprehensive discussion of the system NH_3-CO_2 is given by Lemkowitz (5) and Lemkowitz et al. (20). It appears that at a total pressure of 0.1 MPa only solid-vapour equilibria occur. Various researchers (21 - 25) have studied the vapour pressure of the dissociating compound ammonium carbamate. Up to 80°C the results agree well. At higher temperatures the experiments are difficult to perform because the formation of urea and water impedes accurate pressure measurement.

The equilibrium constant for eq. 2-3 (equilibrium between gaseous NH_3 and CO_2 and solid ammonium carbamate) gives a relation between the vapour composition and the total pressure at constant temperature:

$$K_p = y_{CO_2} \, y_{NH_3}^2 \, P^3 \tag{2-10}$$

in which y denotes mole fraction, P total pressure and K_p the equilibrium constant. The equilibrium constant K_p of this mass law (49) can be found from the dissociation pressure of ammonium carbamate, dissociating with known stoichiometry:

$$K_p = \frac{4}{27} \, P_{AC}^3 \tag{2-11}$$

in which P_{AC} is the dissociation pressure at a given temperature. The validity of eq. 2-10 was experimentally confirmed by Briggs and Migrdichian (21). A temperature-composition section at a constant pressure of 0.1 MPa can be constructed using eqs. 2-10 and 2-11 and an empirical relationship between dissociation pressure and temperature as given by Egan et al. (22). This leads to:

$$\log \left(y_{NH_3}^2 (1 - y_{NH_3})\right) = - 8225.7 \, T^{-1} + 23.9628 \tag{2-12}$$

The calculations performed with eq. 2-12 are presented in Fig. 2-4. A comparison with calculations, based on results of Bennett et al. (23) gives differences of 0.2 and 1°C in equilibrium temperature at the ammonium carbamate composition and at 1 mole-% NH_3, respectively. It is seen from Fig. 2-4 that the maximum temperature at which solid ammonium carbamate can exist at 0.1 MPa is 58.6°C.

From the review of the literature concerning the three binary systems, it can be concluded that their phase behaviour at low pressures is well known. The results at 0.1 MPa can be used to obtain a qualitative insight into the phase behaviour of the ternary system. Furthermore, the vapour-liquid equilibria of the NH_3-H_2O and the CO_2-H_2O system are important in testing the experimental apparatus and checking the ternary measurements.

2.3 Ternary equilibria

2.3.1 Equilibria involving solid phases

In a study of vapour-liquid equilibria in a system in which chemical reactions, leading to non-volatile products, occur, it may be necessary to investigate the formation of solids. When solids are formed a solid-liquid-vapour equilibrium occurs, rather than the desired vapour-liquid equilibrium. Measurement of such a three-phase equilibrium is difficult because the apparatus may become clogged or the liquid phase sampled may contain solid material. For industrial purposes it is also important to know the conditions at which solids are formed, because solids disturb proper operation of pumps, valves, condensors etc.

The solubility behaviour of various NH_3-CO_2-H_2O containing compounds was already studied in the first part of this century. For various reasons, however, the experimental results are not very accurate. Generally, measurement of equilibria involving solid phases is difficult because of the slow attainment of equilibrium, especially at lower temperatures. Periods of weeks are mentioned in attaining equilibrium. The complete conversion of one solid into another is often not possible because crust formation covers the original crystals. The determination of the solids' composition is another problem, due to their volatility and instability in air. Another complication is the volatility of the equilibrium solution, leading to formation of a vapour phase at pressures at and below the solution's vapour pressure. Instead of a solid-liquid equilibrium a solid-liquid-vapour equilibrium is then determined. This may lead to erroneous results if the solubility is not determined by analysis of the solution but by application of a mass balance in which the vapour phase is neglected.

Solubility experiments were performed by Terres and Weiser (26) and Terres and Behrens (27), Jänecke (28, 29) and Guyer and Piechowicz (30). A comparison of some solubility measurements is given in Fig. 2-5. Equilibrium of one solid with a solution at constant temperature and pressure can be represented in a ternary diagram by a solubility line. Because the influence of pressure on solid-liquid equilibrium is very small the restriction of constant pressure can be removed without altering the system's behaviour. The discontinuities in the curves of Fig. 2-5 imply the transformation of one solid in equilibrium

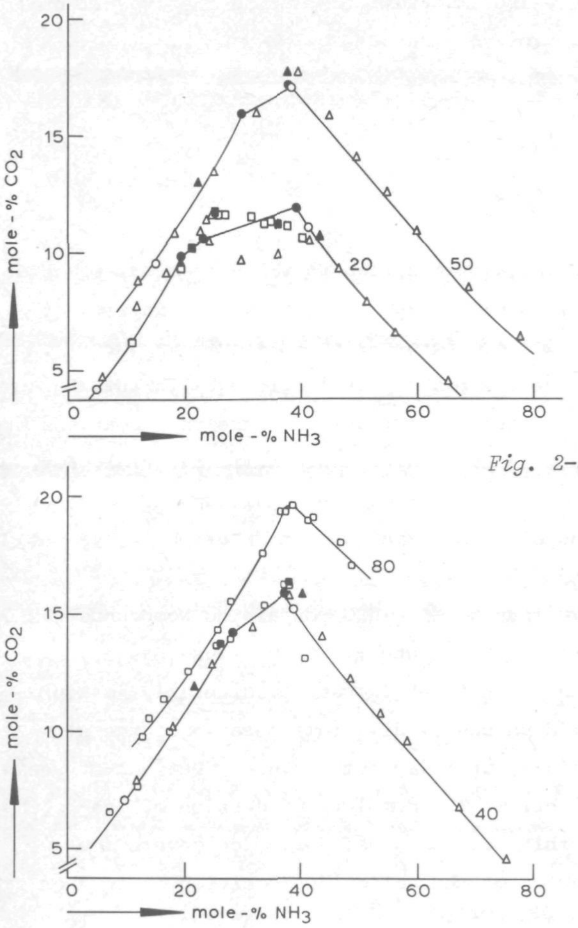


Fig. 2-5 Liquid compositions of solid-liquid equilibria of the NH_3-CO_2-H_2O system at various temperatures. Closed symbols: three-phase equilibria. Triangles: Ref. 29. Squares: Ref. 26. Circles: Ref. 30. Lines are drawn using Ref. 30 three phase equilibria (except for 80°C). Open circles: solid-liquid-vapour equilibria at 0.1 MPa. Numbers denote the temperature in °C.

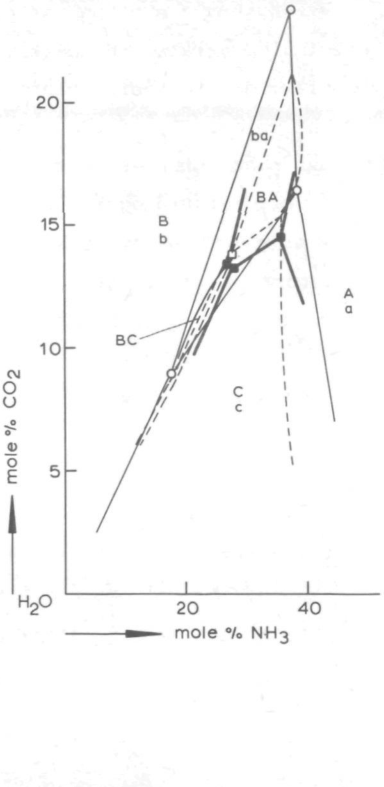


Fig. 2-6 Projection of three-phase lines and quadruple points. Bold line and closed squares: Ref. 30. Dashed line and open squares: Refs. 26 and 27. Thin line and circles: Ref. 29. The letters denote solubility regions. Capitals: Refs. 26, 27, 30. Small letters: Refs. 29. (For explanation see Table 2-1)

with the liquid phase, to another solid. At such a discontinuity the liquid is in equilibrium with two solid phases (triple point). It can be seen from Fig. 2-5 that agreement between the various sources is reasonable, at 20°C the deviations are most pronounced. On the CO_2-rich part of the solubility lines the equilibrium solid phase is ammonium bicarbonate, whereas on the NH_3-rich part ammonium carbamate is the solid phase. Concerning the intermediate part of the lines the authors do not agree as to the solid phases occurring in the equilibria. Terres et al. concluded that five solids can exist: ammonium bicarbonate, ammonium carbonate (with crystal water), ammonium carbamate and two double salts, $2NH_4HCO_3.(NH_4)_2CO_3.H_2O$ and $NH_4HCO_3.NH_2CO_2NH_4$, respectively. Jänecke (29) ignores the existence of the bicarbonate-carbamate salt and gives the composition of the other double salt without crystal water. His results tend to confirm this opinion. A close inspection of his experimental results, however, reveals that only a few measurements were made in the solubility field of the ignored double salt.

Because of the above mentioned contradictions Guyer and Piechowicz (30) reinvestigated the solubility behaviour of the system. They confirmed qualitatively the results of Terres et al. Fig. 2-6 presents a summary of the three-phase lines and quadruple points, given by the various authors. The quadruple points (liquid in equilibrium with three solids) are also given in Table 2-1. The position of the quadruple points, however, differs from those of Terres et al. It is believed that this difference is due to erroneous analyses of the solutions by Terres et al. A drawback of Ref. 30 is that only three-phase and four-phase equilibria are presented, obtained by interpolation of solubility curves. The fact that Jänecke's results differ greatly from the other investigations is probably caused by his experimental method. To overcome the difficult analysis of the liquid phase Jänecke prepared closed glass vessels with a known gross composition. The vessel's contents were prepared by mixing a particular salt with a known ammonia-water solution in different proportions. The mixture was heated until the salt was just dissolved. Under the assumption of a negligible vapour volume the liquid composition then equals the known gross composition. The temperature-composition curves so obtained may show discontinuities where a three phase equilibrium occurs. However, applying this method to Jänecke's results shows that it is impossible to find the triple points. This is due to the scatter of experimental points on such a curve, possibly caused by not attaining the equilibrium state.

For the temperature region of 20 - 50°C the experimental results of Guyer and Piechowicz will be used, being considered to be the most reliable data

Salts	Temperature	Liquid composition		Reference	
	°C	mole-% NH_3	mole-% CO_2		
B-BC-BA	33	27.5	13.7	27	*
	34	27.1	13.4	30	
C-BC-BA	33	27.9	13.8	27	
	29	27.9	13.4	30	
C-A-BA	33	36.0	15.3	27	*
	31	35.8	14.5	30	
B-A-BA	106	38	21.2	27	**
	85	37.8	23.8	29	
B-C-BC^-	5	17.8	8.9	29	
A-C-BC^-	43	38.6	16.4	29	

Table 2-1 *Composition of liquid phase and temperature at quadruple point conditions. B:* NH_4HCO_3. *C:* $(NH_4)_2CO_3.H_2O$. *A:* $NH_4CO_2NH_2$. *BA:* $NH_4HCO_3.NH_2CO_2NH_4$. *BC:* $2NH_4HCO_3.(NH_4)_2CO_3.H_2O$. BC^-: $2NH_4HCO_3.(NH_4)_2CO_3$. **: own interpolation. **: extrapolation.*

available. For higher temperatures the results of Terres and Behrens can be used. According to these authors the temperature of the quadruple point bicarbonate-double salt-carbamate-liquid is 106°C. Its liquid composition is not determined, but can be found by extrapolation of the three phase curves (Table 2-1). At this temperature the melting point of ammonium bicarbonate is also found. However, because in the experiments of Terres and Behrens a considerable vapour phase is present, this "melting point" is a point of the three phase line solid-liquid-vapour. The minimum melting point of ammonium bicarbonate is given by Zernike (32) as 114°C at 200 - 300 atm. It is unlikely that at 120°C liquid bicarbonate is in equilibrium with a solution, as Terres and Behrens state. Because of the good solubility of ammonium bicarbonate in water, apparently vapour-liquid equilibrium was measured at this temperature.

At temperatures above 106°C the three-phase line bicarbonate-carbamate-liquid goes to higher temperatures, passing through the bicarbonate-carbamate eutecticum. This eutecticum can be estimated at 110°C and 35 mole-% NH_3,

Temperature range °C	Pressure range MPa	Remarks	Reference
20 - 95	< 0.143	Amm. carbonate solutions	40
8 - 92	< 0.101		41
20 - 40	< 0.023		42
90	-	Ammonia partial pressures	43
20 - 60	< 0.075		44
10 - 40	< 0.067	Amm. bicarbonate solutions	45
60 - 120	< 1.2		50
20 - 100	< 0.320		46
40 - 160	0.101 - 4.05	Only graphs presented	35
70 - 120	0.203 and 1.52		34
40 - 100	0.010 - 1.32	Amm. carbamate solutions	36
40 - 100	0.010 - 3.43		37
39 - 93	0.101		47
70 - 140	2.026		38, 39
20 - 96	0.05 and 0.1		48

Table 2-2 Experimental conditions of ternary vapour-liquid equilibrium measurements.

33 mole-% CO_2 using Jänecke's measurements of the melting behaviour of bicarbonate-carbamate mixtures.

2.3.2 Vapour-liquid equilibria

The vapour-liquid equilibria of the NH_3-CO_2-H_2O system were studied by various authors. Especially in the older studies, providing data for the coal industry, the measurements were performed in the dilute concentration range and at pressures below atmospheric. Some authors only determined vapour pressures. The developing urea industry required data at higher pressures. At these conditions measurements were made by Frohlich (50), Takahashi (34) and Takahashi et al. (35), Jäger et al. (36, 37) and Yanagisawa et al. (38, 39). As in the low pressure work the number of experimental points is small. A summary of the experimental conditions of the various studies is given in Table 2-2.

According to the phase rule (eq. 2-2) a ternary two-phase equilibrium has three degrees of freedom, one more than for a binary system. Therefore there is considerable more choice in experimental conditions, compared to binary

Temperature	Liquid composition		Vapour composition		Reference	
^{o}C	mole % NH_3	mole % CO_2	mole % NH_3	mole % CO_2		
77.6	5.48	2.74	-	-	40	*
82.4	3.41	1.70				
87.2	3.32	1.66				
92.8	1.07	0.53				
60	17.31	4.85	81.58	0	46	
60	15.10	2.36	76.97	0		
80	5.75	2.04	20.79	18.95		
80	7.63	1.25	44.74	2.37		
80	8.91	2.71	35.53	15.79		
40	37.18	6.60	-	-	35	
60	31.37	6.62				
60	30.51	11.80				
80	17.24	6.67				
63	10.35	3.19				
50	23.06	11.82				
65	35.98	17.72				
80	3.30	1.65	-	-	36	*
60	25.36	12.68				
52	37.50	18.75				
84.3	2.15	1.07	-	-	41	
55.2	2.18	2.18				
76.9	2.16	1.62				
80.0	2.16	1.44				
80.5	2.15	1.18				
75.5	8.18	4.05	27.02	36.75		
71.6	9.87	5.42	24.84	44.08		
62.5	8.09	5.31	9.96	71.00		
78.5	9.57	4.10	44.29	19.65		
80.7	7.89	2.80	47.11	13.10		
78.8	5.49	2.57	24.09	31.14		
80.6	3.25	1.57	15.26	36.39		
87.6	1.23	0.56	7.74	29.21		
89.7	3.13	0.55	31.88	2.65		

84.1	5.29	1.64	39.14	10.85	
67.7	13.99	3.00	75.18	3.66	47
66.6	1.27	1.24	2.12	71.00	
55.6	2.10	2.13	1.83	84.58	
39.4	4.90	4.71	1.10	93.89	
45.6	3.94	3.91	1.02	89.79	
84.5	0.43	0.40	2.17	41.33	
80.2	7.73	2.10	54.36	5.83	
55.0	3.34	2.99	1.79	84.96	
84.3	5.43	2.02	31.27	14.63	
69.2	16.36	4.68	72.28	5.46	
84.6	5.81	1.42	43.75	4.48	
93.5	2.18	0.41	22.57	1.67	
59.5	8.43	6.14	8.01	79.40	
55.5	3.30	2.85	2.43	83.84	
67.1	18.04	9.66	37.01	42.31	
65.8	20.43	10.23	53.19	33.43	
65.9	20.38	10.50	52.07	32.13	
73.0	10.42	5.30	32.43	36.60	
78.8	4.45	2.02	23.10	33.82	
84.0	2.70	1.50	14.74	30.81	
87.7	3.00	1.12	25.21	12.62	48
68.9	19.08	9.08	60.90	21.27	
68.3	17.38	8.32	49.88	31.91	
70.5	14.87	5.62	74.11	3.17	
69.7	14.43	4.55	73.74	2.32	
68.6	18.99	8.72	66.17	17.22	
65.7	19.89	7.65	83.84	3.50	
48.2	22.63	3.53	90.80	0.23	
44.7	23.80	2.82	94.50	0	
92.5	2.13	0.62	18.32	7.86	
95.7	1.07	0.66	11.09	5.25	
92.8	0.42	0.29	6.30	3.33	

*Table 2-3 Experimental results from literature at 0.1 MPA. *: interpolations.*

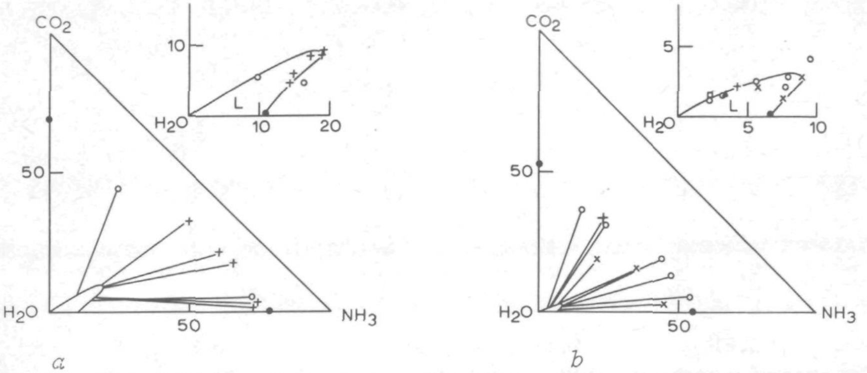


Fig. 2-7 Experimental liquid-vapour equilibrium results from literature at 0.1 MPa. Crosses: Ref. 48. Open circles: Ref. 47. Asterisks: Ref. 46. Triangles: Ref. 36. Squares: Ref. 41. Closed circles are taken from Figs. 2-2 and 2-3. For clarity the boiling point lines are presented separately. a: 70°C. b: 80°C.

systems, making comparison of the results obtained by various authors difficult. It is almost impossible to construct phase diagrams at constant temperature and pressure using literature data, because measurements at a given temperature differ greatly in pressure and vice versa. Also, a comparison can not be made by plotting the partial pressure of a given component against its liquid molar fraction at constant temperature. Because in the liquid phase the components exist as chemical constituents, the component concentration is not suited to correlate the partial pressures with the liquid composition. One needs to know the concentration of the actual constituent which is in equilibrium with the vapour, i.e., free (not bound) ammonia and free carbon dioxide. These concentrations can be calculated using a model that describes the chemical equilibria in the solution (44). Because in this study special attention is given to the equilibria at 0.1 MPa, Table 2-3 gives measurements made by various authors at this pressure. Although most data stem from studies covering a certain pressure range, Ginzburg (47) and Schmidt (48) performed experiments only at 0.1 MPa.

To compare the various sources and to check the accuracy of the measurements some data from Table 2-3 are presented in Fig. 2-7. (In the various phase diagrams presented in this chapter, the composition is expressed in molar fractions.) Because all of the measurements of Schmidt and Ginzburg were made at differing temperature, due to their experimental method, the variation in the temperature in each of the two figures is ± $2^{\circ}C$. It is seen that the liquid phase compositions agree rather well with each other and with the ammonia-water system (8). The vapour phase results show more scatter, however. Also the vapour phase water content is too low with respect to the water content of the binaries (for Otsuka's results the reverse holds). This may be caused by non-attainment of the equilibrium state or incorrect vapour analysis.

Takahashi (34) and Yanagisawa (38, 39) performed measurements at constant temperature and pressure at pressures above 0.1 MPa. Their results at some selected values of pressure and temperature are plotted in Fig. 2-8. In general, agreement with the NH_3-H_2O equilibria as measured by Wucherer (8) is good for the liquid phase results. Especially at higher temperatures there are discrepancies regarding the vapour phase compositions of the binary and ternary systems. Also, intersection of tie lines is observed, which is physically impossible. It can be concluded that the measurements give only a qualitative insight in the vapour-liquid equilibria of the system.

A clear insight in the equilibrium behaviour can be obtained only if the experimental conditions are systematically varied. Measurements can be performed at constant temperature and pressure, at constant water content of the liquid, or at a constant NH_3/CO_2 ratio in the liquid. Using the two constant composition methods, temperature or pressure can be chosen as the second constant variable. The isothermal-isobaric method is preferred, because with this method the position of the tie-lines is also found.

Due to the lack of systematic studies, it is difficult to obtain an insight into the vapour-liquid behaviour of the system. Some references contain graphs which qualitatively or semi-quantitatively show this phase behaviour. Jänecke (29) presented boiling point curves at 0.1 MPa without reference to measurements and without discussion. Otsuka et al. (46) presented graphs, giving partial and total pressures of solutions as a function of the ratio $(CO_2/(NH_3 + CO_2)$ at constant temperature and constant total $NH_3 + CO_2$ content. In the composition triangle (Fig. 2-1) this is represented by a straight line parallel to the hypotenuse. A sharp pressure minimum is found at about $NH_3/CO_2 = 2$ (molar), indicating formation of carbamate or carbonate. Takahashi et al. (35) constructed sections at constant temperature and pressure by interpolation.

According to Ginzburg (47) the isothermal-isobaric dew point lines are almost straight and parallel to the hypotenuse, indicating ideal behaviour and a constant water content at a given temperature. A p-T-section is given,

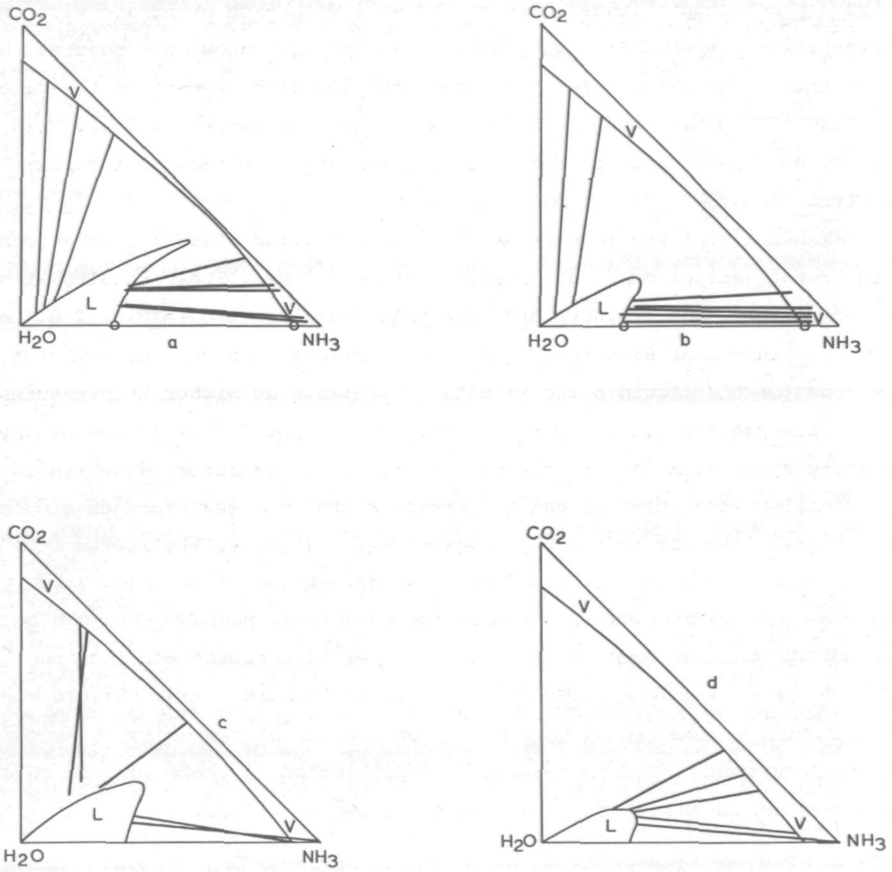


Fig. 2-8 Experimental liquid-vapour equilibrium results from literature at higher pressures. a: Ref. 34 at 1.5 MPa and 115°C. b: Ref. 34 at 1.5 MPa and 120°C. c: Ref. 38 at 2 MPa and 120°C. d: Ref. 38 at 2 MPa and 130°C. Thin lines denote qualitatively the expected phase behaviour.

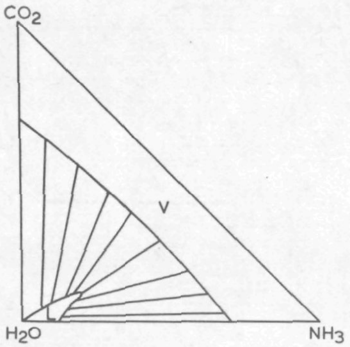


Fig. 2-9 Qualitative ternary phase diagram at 0.1 MPa and 70°C.

obtained by interpolation of a limited number of data and taking into account theboundary systems. Schmidt (48) used the same method to obtain sections at 0.1 MPa and several temperatures. Schmidt's dew point lines exhibit curvature as they approach the NH_3-H_2O system.

A semi-quantitative phase diagram of the vapour-liquid equilibria can be constructed based on the literature values. A semi-quantitative section at 0.1 MPa and 70°C is presented in Fig. 2-9, based on literature values presented in Fig. 2-7a. The behaviour of the dew point line deviates not much from the ideal case (a straight line). The boiling point line exhibits an unusual behaviour, enclosing the tongue-like liquid area, starting from the H_2O corner point. This behaviour is caused by the formation of chemical compounds of NH_3 and CO_2 in the solution, decreasing its vapour pressure. It can be shown that the shape of the boiling point lines at constant temperature and pressure implies a minimum pressure in isothermal boiling point lines at a constant water composition. Starting from the NH_3-H_2O system addition of CO_2 along such a line will lower the vapour pressure due to formation of non-volatile compounds. On continued addition of CO_2 the pressure will further fall, pass through a minimum and then rise abruptly. The pressure rise will occur when no free NH_3 is left to react with CO_2. Due to the low solubility of (excess) CO_2 the NH_3/CO_2 ratio cannot reach values below 1 (molar), except at extremely high pressures. A minimum pressure in an isothermal p-X section corresponds with a maximum temperature in a boiling point line at constant pressure and constant water composition. Going in the direction of the H_2O corner point, this maximum temperature will increase. Linking up several isobaric T-X sections at constant water content makes it possible to construct the p-T sections at the chosen pressure. The tongue-like boiling point lines are also found in the ternary system at urea synthesis conditions (4). At

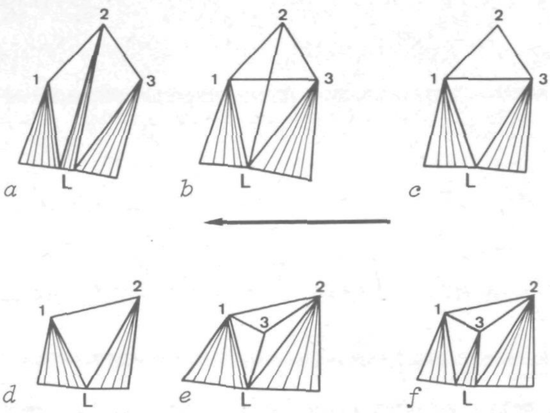


Fig. 2-10 Quadruple points of one liquid and three solids. b: Tetragonal. e: Triangular. The arrow gives the direction of increasing temperature. For explanation see text. 1, 2 and 3 denote solid phases.

these conditions the liquid area may reach the binary NH_3-CO_2 and extend through it to the urea-rich composition area.

2.4 Probable behaviour of the system at 0.1 MPa

Based on literature data and on extrapolations as discussed in the Sections 2.2 and 2.3 the probable phase behaviour of the NH_3-CO_2-H_2O system can be sketched at 0.1 MPa and various temperatures. At 20 - 50°C the results of Guyer and Piechowicz (30) are used for the equilibria involving solids. These authors also determined the three phase equilibria solid-liquid-vapour at 0.1 MPa, giving the connection between vapour-liquid and liquid-solid equilibrium. The vapour-liquid equilibria can be estimated, using the measurements of the binary systems and some results obtained for the ternary system (Table 2-3). Fig. 2-11 presents the behaviour of the system at temperatures from 20 to 70°C.

For a better understanding of the phase behaviour of the system in this temperature range it is necessary to discuss the phase behaviour of quadruple points. According to the phase rule (eq. 2-1) a four-phase equilibrium in a ternary system has one degree of freedom. If the pressure is fixed, the system is non-variant. Because the influence of pressure is negligible on equilibria involving solids and liquids a definite temperature for every quadruple point will be found. Supply or withdrawal of heat therefore cannot result in temperature change but can only lead to the occurrence of phase transitions.

These phase transitions depend on the relative composition positions of the phases in equilibrium (51, 52). The four compositions form a tetragon (Fig. 2-10b) or three of them may form a triangle, the fourth composition situated within this triangle (Fig. 2-10e).

For the former case the transition reaction is:

$$\text{solid 1} + \text{solid 3} \rightleftarrows \text{solid 2} + \text{liquid} \qquad (2\text{-}13)$$

On continuous supply of heat this phase equilibrium will shift to the right at constant temperature until one of the solids, 1 or 3, or both, disappear. Then three or two phases remain, resulting in the three-phase equilibria S_2S_3L, S_1S_2L or the two-phase equilibrium S_2L (Fig. 2-10a) and the temperature will rise. Which of these equilibria is reached, depends on the system's gross composition. Analogous reasoning for heat withdrawal leads to two three-phase equilibria (Fig. 2-10c) at a temperature below the quadruple point's temperature.

For a triangular quadruple point the conversion reaction is:

$$\text{solid 3} \rightleftarrows \text{solid 1} + \text{solid 2} + \text{liquid} \qquad (2\text{-}14)$$

On heat supply solid 3 will finally disappear, whereupon the three-phase equilibrium S_1S_2L is reached and the temperature can rise (Fig. 2-10d). Depending on the gross composition of the system, heat withdrawal will result in various two-phase and three-phase equilibria (Fig. 2-10f).

It can be concluded that at the quadruple point's temperature the number of two-phase solid-liquid equilibria changes from two to three or vice-versa. In the triangular case the third solid disappears on temperature increase, whereas in the tetragonal case the third solid is no longer taking part in solid-liquid equilibria at temperatures below the quadruple point's temperature.

At 20°C there are four salts which can be in equilibrium with a liquid: ammonium bicarbonate (B), ammonium carbonate (C), the double salt bicarbonate-carbonate (BC) and ammonium carbamate (A). It is assumed that the double salt bicarbonate-carbamate (BA) also exists at this temperature. Besides solid phase equilibria this salt can also give a solid-vapour equilibrium with a CO_2-rich vapour. The two-phase regions are separated from each other by three-phase equilibria.

From Fig. 2-11a it can be seen that at this temperature there are two vapour-liquid regions, each starting from a water containing binary system. The boiling point and dew point lines end in a three-phase equilibrium, on the ammonia side with A as solid phase, on the carbon dioxide side with B as solid phase. The solubility lines of these salts end in three phase equilibria solid-solid-liquid and the liquid becomes saturated with another salt. The salts B and A will also be in equilibrium with vapour, these two phase regions being extremely small, however.

At 29°C a tetragonal quadruple point BC-BA-C-liquid is found, indicating that above this temperature also salt BA will give a solid-liquid equilibrium. At 31°C the quadruple point C-A-BA-liquid is found. It appears that the liquid composition point is situated on the straight line connecting the composition points of C and BA. Therefore on supply of heat solid ammonium carbonate will disappear according to the transition reaction

$$C_S \rightarrow BA_S + \text{liquid} \tag{2-15}$$

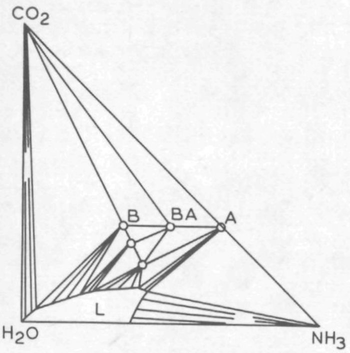
Equilibrium between a liquid and the solids BC, B and BA occurs at 34°C. It is of the triangular type, with double salt BC situated within the triangle. Therefore at temperatures above 34°C this salt will no longer be present at 0.1 MPa. The p-T-section at 50°C (Fig. 2-11b) contains only the salts B, BA and A. It can be seen that on temperature increase the liquid area narrows, because of the lower solubility of gaseous ammonia. Simultaneously, this area penetrates deeper into the ternary region, due to the greater solubility of the salts at higher temperature.

By extrapolation of the three-phase line carbamate-BA-liquid and the so-called NH_3-saturation curve (carbamate-liquid-vapour equilibrium at 0.1 MPa) as given in Ref. 30, a point of intersection is found at 51°C and 38 mole % NH_3, 17.2 mole % CO_2 (Fig. 2-11c). This is a tetragonal quadruple point, indicating that from this temperature on BA has also a solid-vapour equilibrium with an NH_3-rich vapour and that the equilibrium of solid A with liquid will disappear (Fig. 2-11d).

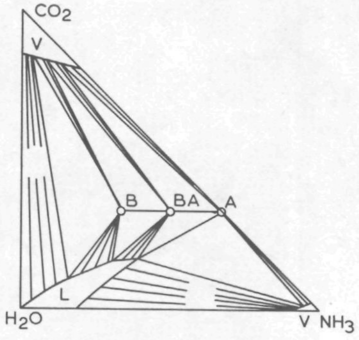
On further temperature increase the three remaining salts will successively disappear. According to Zernike (31) the three-phase equilibrium of pure ammonium bicarbonate at 0.1 MPa occurs at 57.7°C, giving the maximum temperature at which this salt will be present as solid at this pressure (Fig. 2-11e).

From the temperature-composition section of the NH_3-CO_2 system (Fig. 2-4) it is seen that at 58.6°C (checked by application of eq. 2-12) ammonium carbamate has a dissociation pressure of 0.1 MPa. This indicates that at this temperature the two vapour branches in the sections at constant pressure and temperature just meet at the carbamate composition. From this temperature on there is a continuous dew point line (Fig. 2-11f).

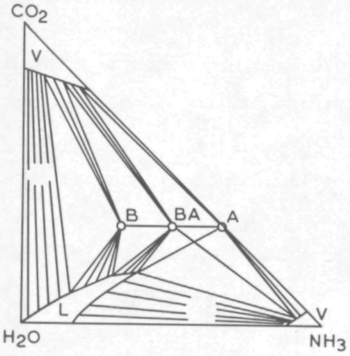
The two extrapolated saturation curves (carbamate-liquid-vapour and


CO_2
B
BA
A
L
H_2O
NH_3

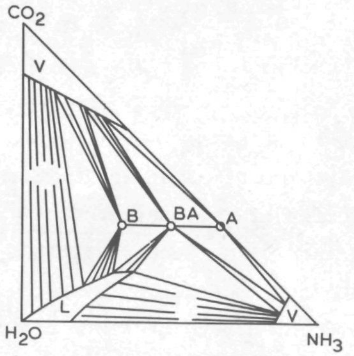
a


CO_2
V
B
BA
A
L
H_2O
V
NH_3

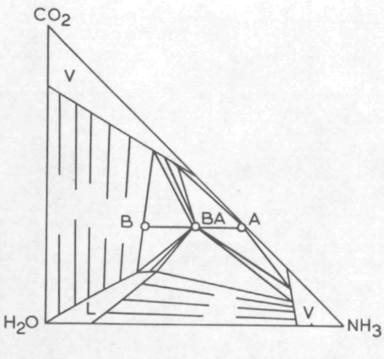
b


CO_2
V
B
BA
A
L
V
H_2O
NH_3

c


CO_2
V
B
BA
A
L
V
H_2O
NH_3

d


CO_2
V
B
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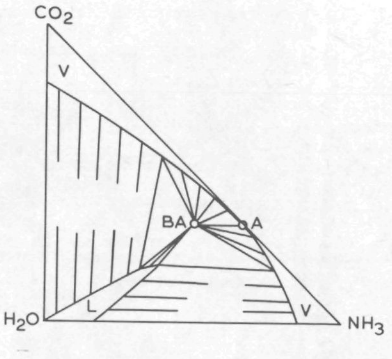
L
V
H_2O
NH_3

e


CO_2
V
BA
A
L
V
H_2O
NH_3

f

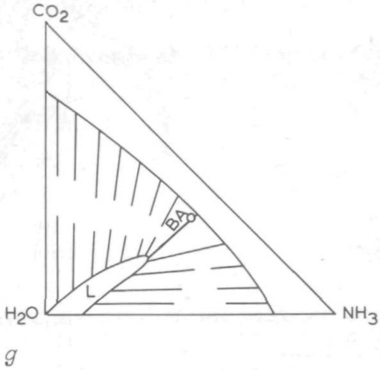


Fig. 2-11 Semi-quantitative phase diagrams at 0.1 MPa and various temperatures. a: 20°C. b: 50°C. c: 51°C. d: 55°C. e: 57.7°C. f: 58.6°C. g: 64°C.

bicarbonate-liquid-vapour at 0.1 MPa) will intersect at a composition of 35.5 mole-% NH_3 and 19.3 mole-% CO_2. This point is the liquid phase composition of the three phase equilibrium of the pure salt BA. It is difficult to estimate the temperature at which this equilibrium occurs at 0.1 MPa. Inspection of the estimated dew point curves shows that this temperature can not exceed 65°C, because at this temperature the dew point curve passes through the composition of BA. This would indicate the dissociation equilibrium of pure BA. Due to the lack of information concerning the phase behaviour of BA it is not known what actually happens in the temperature range 58.6 - 65°C. It is assumed that at 64°C the existence of BA at 0.1 MPa ends via a three phase equilibrium solid-liquid-vapour (Fig. 2-11g).

At higher temperatures a continuous boiling point line will be present (Fig. 2-9). On temperature increase the liquid area will move toward the H_2O corner point, with simultaneous increase of the vapour area. Finally, at 100°C only vapour will rest.

In conclusion it can be said that the system's behaviour at 0.1 MPa is at least qualitatively known. At 20 - 50°C the equilibria involving solids are known and can be extrapolated to higher temperatures. These extrapolations lead to the conclusion that from 65°C on no solids are present anymore in the system. The vapour-liquid equilibria of the binary systems offer a means for the construction of the possible behaviour of these equilibria in the ternary system. Due to the large scatter in literature data it is only possible to make qualitative sketches.

References

1. A. Findlay, *The phase rule and its applications*, 9th ed., Dover Publications, New York, 1951, p. 17.
2. M.W. Zemansky, *Heat and thermodynamics*, 4th ed., McGraw-Hill, New York, 1957, p. 451.
3. J. Zernike, *Chemical phase theory*, Uitgeversmij. Kluwer, Deventer, the Netherlands, 1955. a: p. 5, b: p. 14, c: p. 210.
4. S.M. Lemkowitz, G.A.M. Diepen, P.J. van den Berg, *J. Appl. Chem. Biotechnol.*, 27 (1977) 327.
5. S.M. Lemkowitz, *Phase and corrosion studies of the* NH_3-CO_2-H_2O *system at the conditions of the hot gas recirculation process for the synthesis of urea*, PhD thesis, Delft University of Technology, the Netherlands, 1975.
6. P.J.C. Kaasenbrood, *Chem. React. Eng., Proc. Eur. Symp. 4th, 1968*, Pergamon Press, Oxford, 1971, p. 317.
7. A.B. van Aken, J.J. Drexhage, J. de Swaan Arons, *Ind. Eng. Chem. Fundam.*, 14 (1975) 154.
8. J. Wucherer, *Z. ges. Kälte-Ind.*, 39 (1932) 97.
9. I.L. Clifford, E. Hunter, *J. Phys. Chem.*, 37 (1933) 101.
10. R.A. Macriss, B.E. Eakin, R.T. Ellington, J. Huebler, *Inst. Gas Technol. Res. Bull.*, 34 (1964) 3.
11. J. Polak, B.C. Lu, *J. Chem. Eng. Data*, 20 (1975) 182.
12. D. Hoshino, K. Nagahama, M. Hirata, *Bull. Jpn. Pet. Inst.* 17 (1)(1975) 9.
13. D.S. Tsiklis, L.R. Linshits, N.P. Goryunova, *Russ. J. Phys. Chem. (Engl. Transl.)*, 39 (1965) 1590.
14. K. Tödheide, E.U. Franck, *Z. Phys. Chem. (Frankfurt am Main)*, 37 (1963) 387.
15. S. Takenouchi, G.C. Kennedy, *Am. J. Sci.*, 262 (1964) 1055.
16. S.D. Malinin, *Geochemistry (USSR)*, (3)(1959) 292.
17. R. Wiebe, *Chem. Rev.*, 29 (1941) 475.
18. *Gmelin Handbuch der Anorganischen Chemie*, 14 C3, 8th ed., 1973, p. 36.
19. G. Houghton, A.M. McLean, P.D. Ritchie, *Chem. Eng. Sci.*, 6 (1957) 132.
20. S.M. Lemkowitz, J.C. van Erp, D.M. Rekers, P.J. van den Berg, to be published.
21. T.R. Briggs, V. Migrdichian, *J. Phys. Chem.*, 28 (1924) 1121.
22. E.P. Egan, J.E. Potts, G.D. Potts, *Ind. Eng. Chem.*, 38 (1946) 454.
23. R.N. Bennett, P.D. Ritchie, D. Roxburgh, J. Thomson, *Trans. Faraday Soc.*, 49 (1953) 925.
24. D. Janjic, *Helv. Chim. Acta*, 47 (1964) 1879.
25. M.J. Joncich, B.H. Solka, J.E. Bower, *J. Chem. Educ.*, 44 (1967) 598.
26. E. Terres, H. Weiser, *Z. Elektrochem. Angew. Phys. Chem.*, 27 (1921) 177.
27. E. Terres, H. Behrens, *Z. Phys. Chem. Abt. A*, 139 (1928) 695.
28. E. Jänecke, *Z. Elektrochem. Angew. Phys. Chem.*, 35 (1929) 332.
29. E. Jänecke, *ibid.*, 716.
30. A. Guyer, T. Piechowicz, *Helv. Chim. Acta*, 27 (1944) 858.
31. J. Zernike, *Recl. Trav. Chim. Pays-Bas*, 70 (1951) 711.
32. J. Zernike, *Recl. Trav. Chim. Pays-Bas*, 73 (1954) 95.
33. R. Wiebe, V.L. Gaddy, *J. Am. Chem. Soc.*, 63 (1941) 475.
34. T. Takahashi, *Kogyo Kagaku Zasshi*, 65 (1962) 837; *Chem. Abstr.*, 59 (1963) 2216h.
35. T. Takahashi, S. Yoshimura, K. Fujii, E. Otsuka, *Kogyo Kagaku Zasshi*, 65 (1962) 743; *Chem. Abstr.*, 57 (1962) 14485a.
36. L. Jäger, J. Nývlt, H. Kocová, J. Gottfried, *Chem. Prum.*, 15 (1965) 404; *Chem. Abstr.*, 63 (1965) 10718g.
37. L. Jäger, J. Gottfried, J. Nývlt, J. Sura, J. Havlicek, L. Sisler, *Chem. Prum.*, 15 (1965) 649; *Chem. Abstr.*, 64 (1966) 4324a.
38. Y. Yanagisawa, Y. Harano, T. Imoto, *Nippon Kagaku Kaishi*, (1973)(5) 917;

Chem. Abstr., 79 (1973) 35558.
39. Y. Yanagisawa, Y. Harano, T. Imoto, *Nippon Kagaku Kaishi*, (1975)(2) 271; *Chem. Abstr.*, 82 (1975) 129903.
40. E. Terres, H. Weiser, *J. Gasbeleucht. Verw. Beleuchtungsarten Wasserversorg.*, 63 (1920) 705.
41. R. Mezger, T. Payer, *Gas Wasserfach*, 68 (1925) 651.
42. S. Pexton, E.H.M. Badger, *J. Soc. Chem. Ind. London Trans. Commun.*, 57 (1938) 106.
43. E.H.M. Badger, D.S. Wilson, *J. Soc. Chem. Ind. London*, 66 (1947) 84.
44. D.W. van Krevelen, P.J. Hoftijzer, F.J. Huntjens, *Recl. Trav. Chim. Pays-Bas*, 68 (1949) 191.
45. E. Terres, W. Attig, F. Tscherter, *Gas Wasserfach*, 98 (1957) 512.
46. E. Otsuka, S. Yoshimura, M. Yakabe, S. Inoue, *Kogyo Kagaku Zasshi*, 63 (1960) 1214; *Chem. Abstr.*, 56 (1962) 9501c.
47. D.M. Ginzburg, *J. Appl. Chem. U.S.S.R. (Engl. Transl.)*, 38 (1965) 2157.
48. D. Schmidt, *Enthalpie-Zusammensetzungs-Diagramme für Dreistoffsysteme am Beispiel des Systems* NH_3-CO_2-H_2O, PhD thesis, Technische Universität Braunschweig, West Germany, 1973.
49. T.R. Briggs, *J. Chem. Educ.*, 20 (1943) 484.
50. G.J. Frohlich, *Vapor-liquid equilibria of aqueous systems containing ammonia and carbon dioxide*, PhD thesis, Polytechnic Institute of Brooklyn, 1957.
51. G. Masing, *Ternary systems*, Dover Publications, New York, 1960, p. 11.
52. D.R.F. West, *Ternary equilibrium diagrams*, MacMillan, London, 1965, Ch. 4.
53. *Gmelin Handbuch der Anorganischen Chemie*, 23, 8th ed., 1936, p. 327.
54. G.T. Chao, *Urea its properties and manufacture*, Chao's Institute, West Covina, California, 1967.

3 APPARATUS FOR THE DETERMINATION OF THE VAPOUR-LIQUID EQUILIBRIA OF THE AMMONIA-CARBON DIOXIDE-WATER SYSTEM

3.1 Introduction

The great importance of knowledge of vapour-liquid equilibria for the design of separation equipment has led to the development of various methods for the determination of these equilibria. For a given method numerous experimental designs are proposed in the literature. A comprehensive review of methods and apparatus is given by Hála et al. (1). These authors classify the methods in five groups, which can be found in Table 3-1. This table also includes a brief description of the essentials and some remarks.

Essentially, the determination of vapour-liquid equilibria consists of two parts. Firstly, the two phases are brought in equilibrium with each other; secondly, the compositions of both phases are determined. (In the dew- and bubble-point method this order is reversed.) In general, the method used to determine the compositions of the phases depends on the system under consideration, whereas the method used to attain equilibrium is much less dependent on the nature of the system. In evaluating apparatus for the measurement of vapour-liquid equilibria one has to take into account several factors. The more important ones are the accuracy of the temperature and pressure measurements, the sampling method used to obtain representative samples of both phases, the rate at which equilibrium is reached, possible entrainment of liquid phase in the vapour and the possibility of superheating of the liquid phase (1).

In analysing the phases in equilibrium, disturbance of the equilibrium condition should be avoided as much as possible. Therefore an analysis technique which does not require sampling is the best answer to this problem. However, possibility of application of such techniques, which include the various spectroscopic methods, depends strongly on the system under consideration and on the type of equilibrium apparatus used, and in most cases sampling is necessary. The samples should be equal to the phases in equilibrium an should also be as small as possible in order to avoid disturbing the equilibrium state. On the other hand, the sample size should be great

Method	Principle	Remarks
Distillation	Continuously distilling off a small amount of liquid	Simple; no isothermal equilibrium data are found
Circulating	Boiling of liquid and separation of phases in equilibrium chamber; phases return to boiling flask.	Widely used; good establishment of equilibrium
Static	Equilibrium in closed vessel	Only suited for high pressures
Dewpoint/bubblepoint	Varying isothermally the pressure of a given mixture	No analyses necessary; no tie-lines are found
Flow	Feeding a stream of constant composition to equilibrium chamber	Easy change of composition; accurate control of feed necessary

Table 3-1 Methods for the determination of vapour-liquid equilibria

enough to allow for an accurate determination of the composition. Care must be taken not to change the sample's composition after sampling. For vapour samples condensation may occur; liquid samples may partially evaporate due to pressure decrease. Careful control of the sample's temperature and pressure is necessary.

The above-mentioned general remarks concerning measurement of vapour-liquid equilibria can be applied to the development of equilibrium and analysis apparatus for measurement of these equilibria in the system ammonia-carbon dioxide-water. As discussed in chapter 2, this system exhibits unusual behaviour, due to reactions occurring between the components. The fact that ammonia and carbon dioxide react to form compounds, either solid or in solution, influences the choice of experimental method in the determination of the vapour-liquid equilibria. This fact also has to be taken into consideration in developing analysis methods, especially for the liquid phase. Therefore, the organisation of the rest of this chapter is as follows. In section 3.2 the literature concerning the equipment used in the measurement of vapour-liquid equilibria of the present system is reviewed and a suitable method is chosen. Also design and experimental procedure are discussed, together with some preliminary results. The same organisation is applied in the two following sections concerning the analysis of the vapour phase and the liquid phase, respectively, i.e. review of literature, design of apparatus and experimental procedure.

3.2 Equilibrium apparatus

3.2.1 Review of literature

3.2.1.1 General

Due to its importance to the chemical industry, the system ammonia-carbon dioxide-water has already been studied for more than 70 years. In former years this importance was based on the coal-based chemical industry (coal gas and coke-oven gas) and the soda industry. More recently, the system has become important for the urea and melamine industry and for the purifying of process waste water streams containing ammonia, carbon dioxide and their reaction products.

A literature survey reveals that two methods are most used for the determination of the vapour-liquid equilibria of the present system: the so-called saturation method and the static method (see Table 3-1). The former method resembles the flow method, but differs from it in using an inert carrier gas, e.g., nitrogen or air, that must be saturated with the equilibrium vapour. Hála et al. (1) mention this method only as a less frequently used one in determining vapour pressures. Some authors used both methods, depending on the temperature and pressure of the system.

3.2.1.2 Saturation method and flow method

A sketch of the apparatus used in the saturation method is presented in Fig. 3-1a. The solution under investigation is placed in one or more washing bottles contained in a thermostat. A stream of air or nitrogen is passed through the bottles to saturate it with ammonia, carbon dioxide and water. The contents of the saturated gas stream are analysed by absorbing them in suitable absorbents, contained in an absorption train. The absorbents can be liquids, e.g., concentrated or diluted sulfuric acid solution, barium-hydroxide solution, or solids, such as soda asbestos. Because the vapour phase composition is determined by means of the weight increase of the absorbents during an experiment, also the amount of gas, which has flowed through the

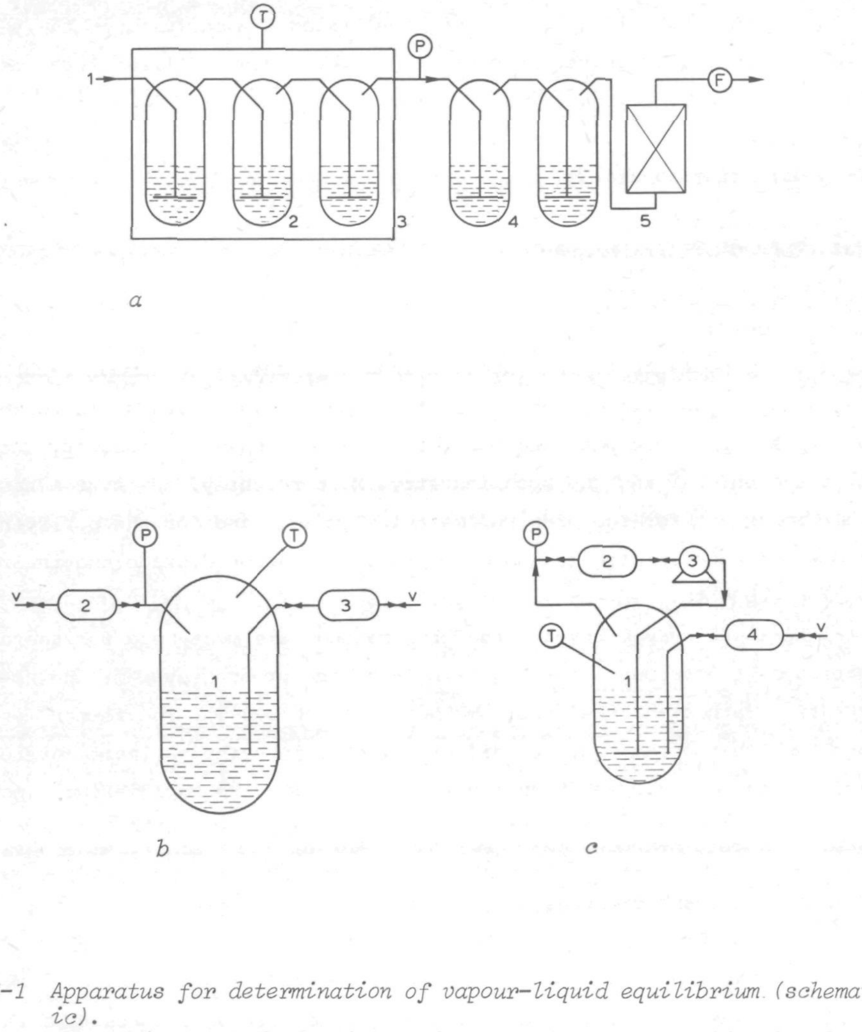


Fig. 3-1 Apparatus for determination of vapour-liquid equilibrium (schematic).

- *a. Saturation method. 1: Air or nitrogen stream. 2: Washing bottles with solution under investigation. 3: Thermostat. 4: Washing bottles with liquid absorbent. 5: Tube with solid adsorbent. T, P, F: temperature, pressure and flow measurement, respectively.*
- *b. Static method. 1: Equilibrium vessel. 2: Vapour sample. 3: Liquid sample. P, T: pressure and temperature measurement, respectively. V: vacuum line.*
- *c. Vapour recirculation method. 1: Equilibrium cell. 2: Vapour sample. 3: Recirculation pump. 4: Liquid sample. Letters: see Fig. 3-1b.*

apparatus, has to be accurately known. In order to know the equilibrium liquid composition it is necessary to analyse the solution in the last washing bottle.

The saturation method for the ammonia-carbon dioxide-water system was first used by Terres and Weiser (2) at temperatures from 20 to 80°C. Pexton and Badger (3) used wash bottles and so-called Winkler worms as equilibrium cells. They correctly analysed the contents of the last cell. An extension to this investigation was made by Badger and Wilson (4), who changed from saturation method to flow method, using an ammonia-carbon dioxide-water mixture as vapour. This mixture was continuously fed to the equilibrium cell. Equilibrium is reached when the vapour leaving the equilibrium vessel has the same composition as the vapour entering it. An advantage of this method is that there is no need to determine the amount of gas which has flowed through the apparatus. However, the flowing vapour mixture is prepared by mixing the components via calibrated flow gauges, making it difficult to obtain a constant composition.

In the important work of Van Krevelen et al. (5) the saturation method was used with three washing bottles and nitrogen as the carrier gas.

For the low pressure part of their investigation, Otsuka et al. (6) used the saturation method. The authors describe the possibility of purging the apparatus to obtain a steady state. This is necessary for accurate vapour phase analysis, because this analysis takes place in a certain amount of gas flowed through the apparatus. Also, after the termination of the air stream, the saturated air remaining in the absorption train was swept through by a separate air stream in order to absorb the remaining vapour components. In Refs. 2-5 no mention is made of purging the apparatus before the experiment and of sweeping the contents of the absorption train afterwards. Also, Refs. 3-5 do not mention the determination of water in the vapour. It is, however, not clear in Ref. 6 whether the solution is analysed at the end of an experiment.

A flow method with the system's components ammonia and carbon dioxide as the flowing gas mixture was used by Takahashi (7). This mixture was prepared in an 5 l autoclave at 5 MPa and 150°C.

According to Jäger et al. (8), who studied the system ammonium carbamate-water, the solution composition did not change during an experiment. Thus the composition of the liquid phase is known, being the same as the composition initially prepared.

3.2.1.3 Static method

The static method, used by various authors in combination with the saturation method, is illustrated in Fig. 3-1b. The experimental apparatus is simple, as is the experimental procedure. A solution is charged into the equilibrium cell, preferably evacuated. The cell is brought to the desired temperature and equilibrium is established. To attain equilibrium in a reasonable time it is necessary to mix the cell's contents in some way, e.g., by rotation, shaking or stirring. In obtaining an amount of vapour sufficient for accurate determination of the composition it is practically inevitable that disturbance of the equilibrium occurs, especially at low pressures. Therefore this method is only suited for above ambient pressures, for which the saturation method cannot be used.

Mezger and Payer (9) determined vapour pressures of carbon dioxide containing ammonia solutions. A given solution was introduced into an evacuated vessel and brought to the desired temperature. Pressure was determined via a small mercury manometer and a compensating nitrogen pressure. The composition of the liquid followed from its preparation out of solid ammonium bicarbonate and a known ammonia solution.

In addition to the saturation method Van Krevelen et al. (5) used the static method with a 5 l vessel containing the equilibrium mixture. A vapour sample was prepared by introducing the equilibrium vapour in an evacuated 1 l flask. Pressure and temperature then determine the total number of moles introduced.

The work of Terres and Weiser (2) was completed by Terres et al. (10) using a static apparatus. The vapour phase is sampled in the same way as in Ref. 5. For one experimental point two measurements had to be performed, because in the vapour phase analysis only one component per measurement was absorbed, either ammonia or carbon dioxide.

Complementary to the saturation equipment Otsuka et al. (6) made use of a stirred autoclave for measurements at temperatures of 80°C and above. The reason for this is that the solution's vapour pressure became too high for the saturation method. The measured pressure is corrected for the pressure of the air, present in the autoclave during filling.

Yanagisawa et al. (36) avoided this correction by introducing the components in an autoclave cooled with a methanol-dry ice mixture. After filling vacuum was applied to remove the air.

Contrary to Refs. 6 and 36, Takahashi et al. (11) did not analyse the liquid phase in determining vapour pressures. They assumed that the gross composition introduced into the autoclave equalled the liquid composition.

Because of the small loading density (0.6 gr/ml, the introduced mass divided by the autoclave's volume) a large vapour phase was present, making the results very unreliable.

Ginzburg (12) used the static method in a rather peculiar way. Instead of using one equilibrium vessel and analysing the two equilibrated phases, two separate vessels were applied. One was used for the determination of the liquid composition, the other for the vapour phase analysis. Thus two compositions are found, for which it is assumed that they form one experimental liquid-vapour equilibrium point. According to the author this procedure is correct if the two cells have the same vapour-liquid ratio at a given gross composition. Isobaric, non-isothermal results were obtained because the vessels' temperature was increased until the pressure equalled 0.1 MPa.

In a study concerning the separation of ammonia-carbon dioxide gas mixtures by fractional absorption in ammonium nitrate solutions Othmer and Frohlich (13) measured vapour-liquid equilibria of the ammonia-carbon dioxide-water-ammonium nitrate system up to 150°C and 2.5 MPa. Because of these conditions the static method was adopted. The equilibrium mixture, contained in a stainless steel cell, was mixed using a perforated disk, mounted on the lower end of a shaft with a permanent magnet on top. The disk was moved up and down through the vapour-liquid interface by means of a solenoid. The cell was not placed in a thermostat but wound with heating tape. The temperature was manually controlled. Vapour samples were taken using the same procedure as Van Krevelen et al. (5). A liquid sample was diluted with a given amount of cold water (14).

Jäger et al. (15) extended their measurements at sub-ambient pressures (8) to higher pressures with the aid of a glass autoclave (pressures around 0.1 MPa, no details are given) and a stainless steel autoclave for pressures of 0.2-3.5 MPa. Mixing was achieved by swinging the autoclave around a horizontal axis. The mixing action was augmented using a stainless steel ball, which rolled inside the autoclave.

The most recent investigation concerning vapour-liquid equilibria of the ammonia-carbon dioxide-water system was made by Schmidt (16). His first experiments were performed in an apparatus of the vapour and liquid recirculation type. As can be expected, difficulties were encountered with recirculation and subsequent condensation of the vapour. Due to the low water content of the equilibrium vapour phase, solids were formed in the condensate. Therefore a new apparatus was developed, which resembles the devices used in Refs. 5 and 10. Although the equilibrium cell is shaken, it still took 8 hours to reach equilibrium.

3.2.1.4 Other methods and discussion

In the description of Schmidt's work in section 3.2.1.3 it was already mentioned that a recirculation method with condensation of recycling vapour cannot be used, especially at lower temperatures. However, according to two references a vapour recirculation method without condensation can be applied (Fig. 3-1c). Mezger and Payer (9) determined ammonia partial pressures using a mechanically operated balloon as "compressor" in the recirculation line. Pexton and Badger (3) made use of a gas pump. They mention that 14 - 18 hours were necessary to reach equilibrium.

With the material presented in the sections 3.2.1.2 and 3.2.1.3 and in the present section a comparison of the methods applied can be made.

The saturation method is especially suited for lower temperatures. The vapour phase analysis is performed by absorption, as is inherent to the method. Equilibrium can be easily attained, due to the gas flowing through the apparatus. There are, however, various disadvantages, which can already be concluded from the fact that most authors use a second method in addition to the saturation method.

The main drawback is the use of a carrier gas. The amount of gas which has flowed through the apparatus in a given time has to be accurately measured in order to obtain a reliable vapour phase analysis. Displacement of air with a known amount of water is an elegant solution to this problem (2, 6). Applying a flowing gas mixture, consisting of the system's components (the flow method), like Takahashi (7) and Badger and Wilson (4) changes the above mentioned problem to that of accurately mixing two or even three gas flows or to containment of a gas mixture at high temperature and pressure. Also the saturation method limits the vapour pressure and thus the temperature of the solution under investigation.

Another disadvantage concerns the applied vapour phase analysis. By using an absorption method to determine the composition of the outcoming gas stream it is difficult to control the attainment of equilibrium. Repeated sampling is then necessary. The time-consuming character of the analysis methods used, however, discourages repetition.

Concerning the static method the main problem is attaining equilibrium in a short time. Stirring is more efficient than swinging or shaking the equilibrium cell. As is already mentioned (section 3.2.1.3) this method is only applicable at higher pressures, due to the fact that removal of a vapour sample changes the equilibrium state at low pressures. Especially at higher pressures care must be taken in sampling to avoid evaporation or condensation of liquid and vapour samples, respectively. Ginzburg's method (12) using two cells, must be rejected because of uncertainty in obtaining the same experimental conditions in both cells. The apparatus of Othmer and Frohlich (13) is especially suited for higher pressure work and has an excellent mixing device. Temperature control can be improved by application of a thermostat.

The vapour recirculation method has the advantage over the static method that the recirculating vapour intensively mixes with the liquid, thereby giving a rapid attainment of equilibrium. By using appropriate equipment the method is also suitable for high pressure work. In general, sampling the vapour phase will disturb the equilibrium state, as in the static method. Therefore, if attainment of equilibrium is to be followed, only analysis methods which require small samples can be used. A sample volume, e.g., a gas chromatographic gas sample valve, can easily be inserted in the vapour recirculation line.

It can be concluded that the vapour recirculation method is the most suitable method for the present investigation, provided that small vapour samples are sufficient for analysis.

3.2.2 Experimental apparatus

The experimental determination of the vapour-liquid equilibria of the ammonia-carbon dioxide-water system at 0.1 MPa was performed according to the vapour recirculation method (Fig. 3-1c). As is discussed in the preceding section, this method can be used with gas chromatographic determination of the vapour phase composition. By providing a sufficient vapour volume in the equipment repeated sampling will not disturb the equilibrium. This sampling procedure is advantageous in following the attainment of equilibrium and in improving the accuracy of the analysis by averaging out small differences between results, due to fluctuations in gas chromatographic conditions. Attention has to be paid to the temperature of the recirculation part of the equipment in order to avoid condensation or formation of solids. A temperature difference between recirculated vapour and equilibrium liquid may lead to superheating of this liquid. A low vapour-liquid ratio can prevent this phenomenon.

The apparatus is presented in Fig. 3-2. The critical part is the glass equilibrium vessel 1, with a volume of 2 l and a five neck cover. (Sovirel, France, article numbers 296-65 and 296-02, respectively). Vessel and cover are connected to each other with a flange containing 6 clamps. For sealing a rubber o-ring with Teflon coating is placed between vessel and cover. See

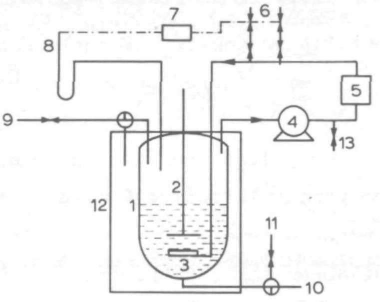


Fig. 3-2 Equilibrium apparatus. 1: Equilibrium cell. 2: Stirrer. 3: Vapour disperger. 4: Membrane compressor. 5: GC sample valve. 6: Electrical valves in NH_3 and CO_2 feeding lines. 7: Pressure controller. 8: Mercury manometer. 9: Water feeding line. 10: Connection for liquid sample flasks. 11: Nitrogen to purge sample line. 12: Thermostat. 13: Purge.

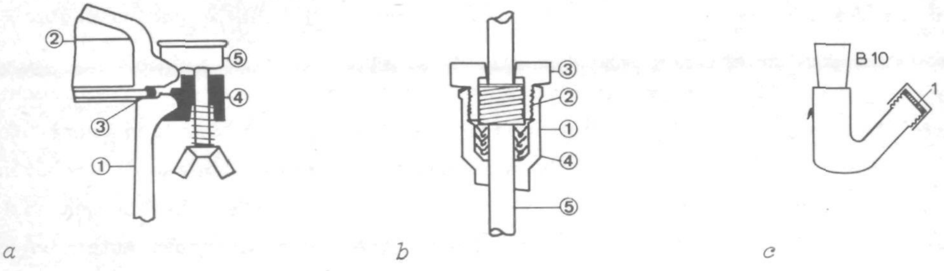


Fig. 3-3 Details of equilibrium vessel.

a. Sealing of vessel and cover. 1: Vessel. 2: Cover. 3: O-ring. 4: Flange. 5: Clamp.

b. Sealing of stirrer's shaft. 1: Neck. 2: Spring. 3: Nut. 4: Sealing rings. 5: Stirrer's shaft.

c. Sample flask. 1: Septum.

Fig. 3-3a. Connections to the vessel can be made via the threaded necks and Sovirel nuts. The mixer's shaft passes through the central neck (30 mm diameter). The shaft's sealing is mounted on the neck with a double sided nut. The sealing (Fig. 3-3b) consists of three rubber rings, pressed against the shaft by a spring, loaded by a packing nut. Two 15 mm necks are used as entrance and exit for the vapour flow. The recirculated vapour is introduced into the liquid via a stainless steel pipe (all stainless steel parts mentioned are SS 316) and a sintered stainless steel disk, which disperses the vapour. Connection to the recirculation lines is made with short butylrubber tubes. A 22 mm neck contains a stainless steel tube which connects vessel and mercury manometer 8. Another 22 mm neck can be used for filling or emptying the vessel. Stirrer 2 consists of a 10 mm diameter stainless steel shaft and a stainless steel turbine with six blades. The stirrer is driven by a variable speed electrical motor. The bottom of the vessel is fitted with a ball-joint to connect a stainless capillary (internal diameter 1 mm). This capillary protrudes through the wall of thermostat 12 for sampling of the liquid phase with a sample flask (Fig. 3-3c).

The equilibrium vessel is contained in a 70 l water-filled thermostat 12 (Tamson, the Netherlands, TXVB 70-100). Temperature is controlled by a contact mercury thermometer and an electronic circuit which refines the control of the moving mercury thread.

Recirculation of the vapour phase is achieved by means of a membrane compressor 2 (KNF Neuberger, Freiburg, West Germany, type NK 145 EK). The compressor has a Teflon coated rubber membrane and a Teflon valve plate. Maximum flow rate is 1.80 Nm^3/h. In the stainless steel recirculation line (4 x 6 mm) a 1 ml sample valve of the gaschromatograph is inserted (see section 3.3). Ammonia and carbon dioxide can be introduced into the system from commercial cylinders via electromagnetic valves 4. The introduction of the gases is controlled via open mercury manometer 6, with which pressure differences up to 100 mm mercury can be determined. In the open leg of the manometer two electrodes, insulated except for their tips, are fitted. The electrodes' lengths differ by about 10 mm. When the mercury touches one of the electrodes an electrical circuit is closed via a small platinum wire soldered in the manometer's wall at the bottom. With a specially wired electronic relay (level controller) one of the valves 4 is opened or closed, depending on the position of the mercury surface in the open leg. On increasing pressure the gas feed is shut off when the mercury reaches the higher electrode. Feed is restarted when the contact with the lower electrode is broken. To dampen pressure pulsations the lower part of the manometer has a narrow passage. With a switch either ammonia or carbon dioxide can be fed to the system. Changing the system's composition or decreasing the pressure can be achieved by purging via valve 5 and a heated purging line, ending in the atmosphere outside the laboratory.

The stainless steel lines of the apparatus are heated with electrical heating wire (Pyrotenax Ltd, Hebburn-on-Tyne, England) and insulated with glass wool. The compressor, manometer and valves are heated with infra-red heaters (Elstein, Northeim, West Germany). The sample valve is an integral part of the gas chromatograph, contained in a thermostat. The butylrubber tubes, connecting recirculation lines and vessel, and parts of the vessel's cover extending from the thermostat are heated by "Heat-by-the-yard" heating tape (Electrothermal, London, England). On various points of the equipment the temperature is measured with chromel-alumel thermocouples and registered on a strip-chart recorder. The accuracy of these measurements is $1^{o}C$. Control of the temperature is performed manually with variable transformers.

3.2.3 Experimental procedure

The materials used were commercial grade ammonia and carbon dioxide, obtained from 20 l cylinders (Hoekloos, the Netherlands) and ordinary distilled water. With gas chromatographic analysis a purity of the gaseous components of better than 99.9% could be determined, the remainder being water and air. The thermostat is adjusted to the desired temperature. The temperature of recirculation line, compressor, valves, manometer and the line to it is adjusted to $120^{o}C$.

The equilibrium vessel is filled with distilled water to about one-third of its volume. The system is then freed from air by feeding carbon dioxide and simultaneously purging the vapour phase with the compressor running to ensure rapid mixing. This purging process can be followed by gas chromatographic analysis. When the air content has fallen to about 0.2 mole % purging is terminated. System leakages are detected by a pressure decrease and a subsequent automatic carbon dioxide addition and by a decrease of the vapour's air content, as registered by the gas chromatographic analysis. Sources of leakage are the numerous connections in the system; careful inspection is necessary to locate leaks. In this inspection use is made of a leak detecting fluid (Snoop liquid leak detector, Nupro Company, Willoughby, Ohio). Tightening of nuts usually ends the leakage. If leakage occurs along the stirrer's shaft and tightening of nut 3 (Fig. 3-3b) does not solve the problem, then replacement of the sealing rings 4 is necessary.

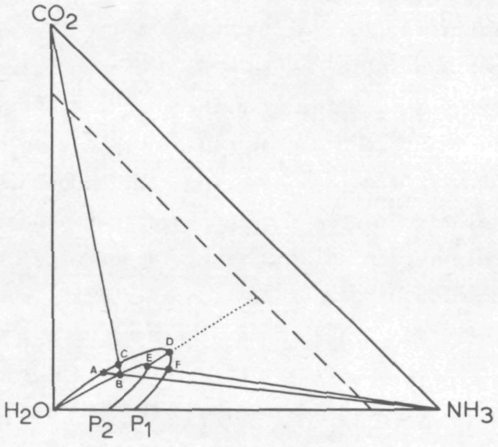


Fig. 3-4 Ternary isothermal composition diagram (qualitative) to show experimental change of composition. A-F: gross compositions (for explanation see text). p_1 *and* p_2*: boiling point lines at pressures* p_1 *and* p_2*, respectively.* $p_1 > p_2$*. Dashed line: dewpoint line at pressure* p_1*. Dotted line: tie line.*

If there are no leaks measurement of the binary system can be started. Generally 8 to 10 gas chromatographic determinations are made to average out fluctuations. Because the solubility of carbon dioxide in water is extremely small and therefore not detectable with the applied carbon dioxide analysis, no liquid sample is taken. The equilibrium pressure is determined by reading the mercury manometer and an accurate barometer (Lambrecht KG, Göttingen, West Germany) installed in the vicinity of the equipment. The combined error in reading the barometer and the manometer is 0.3%. The temperature of the thermostat liquid is measured using a platinum resistance thermometer with a digital display (CRL204, Control and Readout Ltd., Lancing, England). The complete temperature measuring unit is calibrated, giving an accuracy within 0.1°C. The temperature is read with a precision of 0.1°C. It was found that the temperature difference between thermostat liquid and the equilibrium vessel's content is less than 0.1°C for temperatures up to 80°C and 0.2°C for a temperature of 90°C.

A new experimental point can be found by addition of ammonia to the system. This will result in a rapid fall of pressure because of the high solubility of ammonia in water and the high solubility of carbon dioxide in the ammonia solution formed. Therefore the ammonia addition rate should be high enough so as not to decrease the system pressure more than 100 mm mercury, because of the manometer's dimensions and in order to prevent the leakage of ambient air in the system under sub ambient pressure. The decrease in vapour pressure can be eliminated by subsequent addition of carbon dioxide. Fig. 3-4 illustrates this addition procedure. Points A-F depict gross composition points, which practically coincide with liquid phase compositions because of the small mass of vapour phase, relative to the liquid phase in the system. Starting from point A at pressure p_1, point B at a lower vapour pressure p_2 is reached by adding ammonia. Addition of carbon dioxide shifts the system's composition from B to C, the new experimental point at pressure p_1 again. After several experiments, point D is reached, and in order to follow the lower part of the liquid line towards the ammonia-water axis the ammonia and carbon dioxide contents of the liquid must be decreased. This can be done by purging and simultaneously adding ammonia, as depicted by points D-F. Because the tie lines and the line to the ammonia corner point have about the same direction this composition change will be small. Therefore the ammonia-rich area of a given pressure - temperature section is measured faster by starting from the binary ammonia-water system and proceeding as described in the case of the carbon dioxide-rich area.

After 8-10 gas chromatographic measurements a liquid sample is taken. The liquid sample line is purged, either by a nitrogen stream displacing the liquid contained in the line back into the equilibrium vessel, or by discharging some milliliters liquid into a beaker. A sample flask, containing a known amount of distilled water is connected to sample line 10 (Fig. 3-3). About 1 gram of sample is taken, the mass of which is accurately determined by weighing with a precision of 0.1 mg.

The water present in the sample flask acts as diluent and also cools the incoming sample to reduce volatilization losses of ammonia and carbon dioxide. At higher equilibrium temperatures the sample flasks are cooled before sampling in a refrigerator.

3.2.4 Preliminary results

With the above-mentioned apparatus and using gas chromatographic vapour analysis (section 3.3) some preliminary measurements were performed to check the equilibrium apparatus. At a total pressure of 0.1 MPa the equilibrium vapour phase of the binary system water-carbon dioxide was determined. Results are shown in Fig. 3-5. The average total pressure was 0.1026 MPa with a standard deviation of 0.0007 MPa. These results can be compared with values

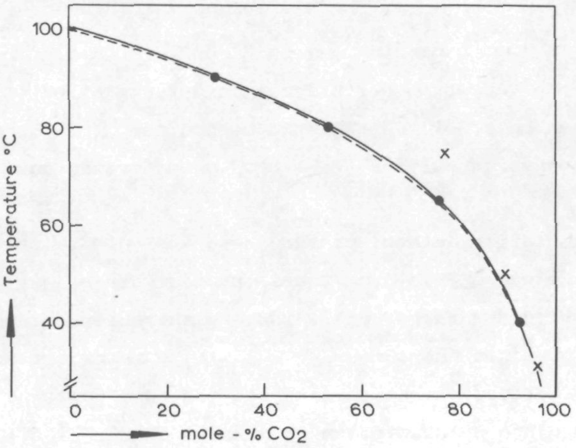


Fig. 3-5 Vapour phase composition of the H_2O-CO_2 *system at 0.1 MPa. Solid line: calculated at 0.1026 MPa. Dashed line: calculated at 0.1013 MPa. Crosses: Wiebe and Gaddy (40) at 0.1013 MPa. Closed circles: measured at 0.1026* ± *0.0007 MPa.*

of Wiebe and Gaddy (40) and calculations. Because of the very low solubility of carbon dioxide in water at the experimental conditions (41), the water content of the vapour phase can be calculated with Raoult's law, assuming pure water as liquid phase. Agreement of experimental results with calculations and Ref. 40 is good, except for Ref. 40's point at 75°C. An explanation for this deviation was given in section 2.2. Calculations show that a pressure difference of 1.3% between the present measurements and those of Wiebe and Gaddy has only a small influence, giving a composition difference of 0.1 mole % at 30°C to 0.5 mole % at 75°C for the vapour phase.

At higher temperatures the effect of pressure on the equilibrium composition becomes more pronounced (see Fig. 3-5). Therefore attention has to be paid to adjustment of the pressure difference between atmosphere and system. Variations in barometric pressure and pressure difference may cause large variations in composition, especially at higher temperatures. This matter is again discussed in chapter 4.

3.3 Vapour phase analysis

3.3.1 Introduction

In considering the vapour phase analysis in determination of vapour-liquid equilibria it can be concluded that the method used for the analysis of the vapour phase depends greatly on the method used for the equilibrium measurements.

Using the saturation method, vapour phase analysis is carried out by absorption of the components from the saturated carrier gas stream. This method of analysing the vapour phase is very suitable, because equilibration and analysis proceed in the same way, i.e., by passing a flow of carrier gas through washing bottles, first to saturate the gas, followed by absorption. Ammonia is determined by absorption in a known amount of dilute sulfuric acid and back titration of the excess acid (3,5). Carbon dioxide can be absorbed in barium hydroxide solution (5) or on solid sodium hydroxide (6) or magnesium perchlorate (8). Water is absorbed in concentrated sulfuric acid. However, various authors (3,5,12) do not mention a water determination method. They probably assume that the water partial pressure is the saturation pressure of pure water at the prevailing temperature. The amount absorbed can be determined by the weight increase or by titration methods in the case of liquid absorbents. The drawbacks of this absorption method are that it is time dependent, it is difficult to check the attainment of equilibrium, purging of the apparatus is necessary and the analysis procedure is tedious.

In the static method sampling is necessary for vapour phase analysis. This is almost always achieved by drawing an amount of vapour phase into an evacuated vessel of known volume. Using a vapour recirculation method the sample volume is part of the recirculation section and has to be withdrawn after the experiment is ended. Analysis can then take place by connecting an absorption tube (10) to the sample flask or by introducing dilute sulfuric acid to absorb ammonia, followed by carbon dioxide determination. The latter is achieved by sweeping the remaining contents into an absorption apparatus (5,16). Sweeping the complete contents into an absorption train (14) or direct titration in the sample flask (12) is also possible. Repeated sampling to check whether the equilibrium has been attained is not possible, due to the large sample volume, which disturbs the equilibrium. The laborious nature of the method is also a disadvantage.

In studies concerning vapour-liquid equilibria of the ammonia-carbon dioxide-water system various references mention other types of analysis methods for the vapour phase. Koren and Andreatch (18) made use of a near-infra-red spectrophotometric determination of ammonia and water, directly in the equilibrium cell. Carbon dioxide had to be determined in a separate infra-red gas analyser, due to interference of the near infra-red absorption bands of ammonia and carbon dioxide. Drawbacks of this method are the dependency of the molar absorbtivity on temperature and pressure and the low accuracy. The results show that the sum of partial pressures, determined with the spectra, deviated from the measured total pressure up to 10%.

Schmidt (16) developed a gas chromatographic method for analysis of the liquid phase. Such a method can also be applied for vapour phase analysis. The column material was a porous polymer, Porapak T, impregnated with 6% polyethyleneimine and 4% carbowax 600. For ammonia and carbon dioxide peculiar non-linear calibration curves are given.

Yanagisawa et al. (36) analysed both liquid and vapour phase with gas chromatography. Small samples were expanded in large volumes at 100°C, thereby evaporating the liquid phase. Porapak Q was used as column material. However, according to Ref. 17 ammonia exhibits irreversible adsorption on Porapak Q, leading to non-reproducible results.

A gas chromatographic analysis method was also used by Lemkowitz (17) in a study of dewpoints of ammonia-carbon dioxide-water mixtures at urea synthesis conditions. Porapak T and Chromosorb 104, also a porous polymer, were selected as column materials. Good separation of the system's components is possible and good quantitative results are also obtained. The accuracy of the analysis is to within 2% relative for all components, except water. Due to the low water content of the investigated mixtures, the accuracy for water amounts to 5% relative.

Because of its simple incorporation into the vapour recirculation equipment, the low sample volume and good accuracy it was decided to apply Lemkowitz' analysis method for the vapour phase analysis.

3.3.2 Experimental apparatus

A detailed description of the original experimental apparatus can be found in Ref. 17. Therefore only a concise description, but including the modifications which were made, will be given here.

Helium was used as carrier gas instead of hydrogen for reasons of safety. In order to minimize the influence of atmospheric pressure on the carrier gas mass flow and hence on the analysis results, a high inlet pressure and an above ambient outlet pressure were applied. A stainless steel capillary, contained in the chromatograph's thermostat serves as a pressure reducing device to obtain a normal pressure in the sample valve, column and detector. To obtain a carrier gas flow rate of 40 ml/min STP, using helium and a 4 m capillary with an internal diameter of 0.2 mm, required an inlet pressure of 0.96 MPa and an outlet pressure of 0.13 MPa. Fine control of the carrier gas flow can be achieved using the flow controller at the end of the carrier gas circuit. The column material was Chromosorb 104 (60 - 80 mesh). Column dimensions were 2.5 m long by 4 mm internal diameter. The originally used Ratfisch sample valve leaked often, probably due to its use of a reciprocatively moving slider made of reinforced Teflon. Sealing of the valve is difficult and the slider can easily exhibit creep under pressure. Therefore this valve was replaced with a valve employing rotation (Carle mini volume valve no. 5518, Carle Instruments, Fullerton, California). This sample valve functioned perfectly. Sampling was performed every 15 minutes using a timer mechanism. The bridge signal was integrated with an Infotronics CRS208 integrator.

Because of slow deterioration of the column's separation performance, giving especially a poor ammonia-water separation, after about two years a new column had to be prepared.

3.3.3 Calibration

Because of the great variation in the components' concentrations, the direct calibration method was used for the calibration of the gas chromatographic analysis system. For every component calibration lines have to be determined for the full concentration range. The calibration of nitrogen, carbon dioxide and ammonia was performed by analysis of the pure gaseous components. This was done by disconnecting the sample valve from the equilibrium apparatus and connecting the valve to a sample line, which in turn could be connected to lecture bottles or to the laboratory's gas supply system. Gas flows were about 20 ml/min STP. According to gas chromatographic detector theory (44) there is a linear relation between peak area and amount of component injected, up to a certain limiting amount. To check this linear relationship ammonium carbamate was used as a calibration substance. Pure ammonium carbamate dissociates stoichiometrically on heating into an ammonia-carbon dioxide vapour, thus yielding a second calibration point. This procedure was experimentally performed by gentle electrical heating of a glass vessel filled with ammonium carbamate, connected to the sample line. It appeared that straight calibration lines occurred for both ammonia and carbon dioxide, starting from the origin (Fig. 3-6). Because nitrogen is only present in very low concentrations in the mixtures to be analysed, no check on the nitrogen calibration line was made.

Calibration of water can be achieved by sampling water evaporated in the same apparatus as used in ammonium carbamate analysis. This yields the 100% point of the calibration line. Accurately measuring other points of this line is more complicated, however. Lemkowitz (17) reports that use of a saturator to obtain nitrogen-water mixtures of known composition gives an accuracy of about 10% relative. He also mentions the use of water-alcohol azeotropic mixtures as calibration substances. The use of azeotropes as standards in gas chromatography is discussed by Ioffe et al. (43). On evaporation liquid and vapour phase of these mixtures will have identical compositions. The liquid phase composition can be accurately determined using Karl Fischer's method. Using the water azeotropes of ethanol, propanol-1 and propanol-2 the calibration line of water can be obtained (Fig. 3-6). This line also appears to be completely straight, going through the origin.

There is evidence that polar compounds, analysed with the use of porous polymers, influence each other on analysis. This will result in a difference between calibration lines, obtained with mixtures of two or more polar substances, and calibration lines, obtained with mixtures of the polar substance with a non-polar component. More details concerning the interaction of polar substances on porous polymers can be found in Appendix 1. Because of this phenomenon it was attempted to prepare calibration lines for ammonia and water using ammonia-water mixtures of known composition. Due to experimental difficulties no definite conclusions can yet be drawn. It is found that the NH_3 calibration line is curved and gives smaller percentages at a given peak area relative to the straight calibration line. The difference with respect to the straight line obtained by analysing pure NH_3 and ammonium carbamate may amount to 3 mole %. In Chapter 4 this analysis problem is again discussed.

Because of slow aging of the katharometer, resulting in a lower sensitivity, it is necessary to recalibrate the gas chromatographic system regularly, e.g., once per three months.

3.3.4 Results and discussion

A typical chromatogram is presented in Fig. 3-7. It reveals that separation of nitrogen, carbon dioxide and ammonia is excellent. The separation of

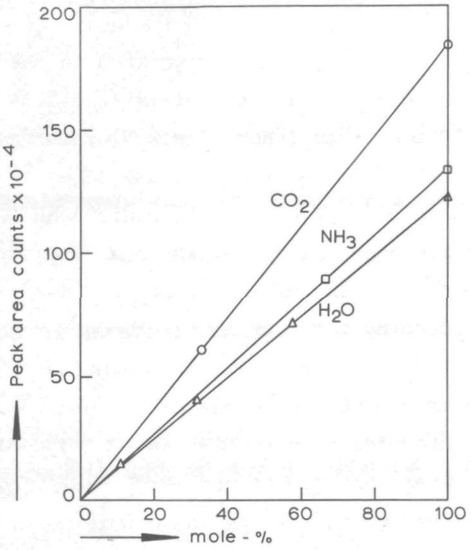


Fig. 3-6 Calibration lines for vapour phase analysis.

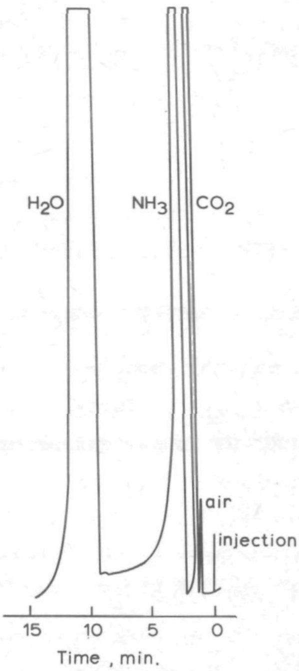


Fig. 3-7 Chromatogram of an air-CO_2-NH_3-H_2O-mixture as obtained on a 1 mV strip chart recorder. (unattentuated signal)

ammonia and water is, however, less good. Aging of the column material resulted in a further decrease of this separation performance, as illustrated by an increase of the tailing of the ammonia peak. This tailing also results in an incomplete integration of the ammonia peak, due to the integrator's characteristics. Because this effect happens as well in calibration as in analysis, however, it does not significantly decrease the accuracy of the analysis.

In determining the equilibrium vapour phase composition, the pressure in the sample volume is above atmospheric, as caused by recirculation of the vapour with the compressor. Therefore the sum of the component's mole percent's, calculated with calibrations made at atmospheric conditions, will be above 100%. Using the ideal gas law the composition can be normalized, giving a sum which equals 100%. Results obtained in the binary system water-carbon dioxide (see section 3.2.4) show that this correction is admissible, i.e., the mass of sample in the sample volume follows the ideal gas law at the prevailing conditions.

3.4 Liquid phase analysis

3.4.1 Introduction

In the preceding chapter it was explained that the ammonia-carbon dioxide-water system is a ternary system with the best choice of components being ammonia, carbon dioxide and water. The composition of a phase in the sense of the phase rule is determined by the concentration of two of the components, the third one following from the balance. A thermodynamic description of the vapour-liquid equilibria of this system implies determination of the composition in terms of components of both phases. Because chemical reactions do not occur in the vapour phase the components are here identical with the constituents. In the liquid phase, however, various reactions occur, leading to a number of constituents, i.e., ammonium carbamate, ammonium bicarbonate and ammonium carbonate.

To develop a model which correlates the measured equilibria it would be a great advantage if determination of these constituents were possibe. Durisch and Buck (45) determined the concentration of five constituents (CO_2, NH_3, H_2O, urea and ammonium carbamate) in the equilibrium liquid at urea synthesis conditions. Urea and the sum of ammonia and ammonium were determined by gravimetric methods. Using the vapour-liquid mixture's gross composition and the determined vapour phase composition, the remaining constituent concentrations can be found using mass balances. The main drawback of this method is that beforehand it has to be decided which constituents may be present in both phases. This results from the use of mass balances to calculate the concentrations. A'Campo (19) investigated the possibilities of spectroscopic techniques (particularly Raman and ultraviolet spectroscopy) in determining the constituents of the urea synthesis solution. Quantitative analysis is not possible because of calibration problems, due to the non-linear calibration behaviour of the concentrated solution and the impossibility to prepare calibration mixtures. It is believed that this problem will also hold for solutions under conditions of the present investigation. Christensson et al. (39) presented a study to determine the equilibrium constant of the bicarbonate-carbamate equilibrium. By freezing the equilibrium in cold alkaline solution carbamate could be determined. Firstly, carbonate is removed by precipitation. Boiling the solution and subsequent addition of bariumchloride gives the carbamate content by precipitation. This method is, however, very tedious and time consuming.

Because of the difficulties in analysing the constituents it was decided to determine only the two components ammonia and carbon dioxide, i.e. to determine the concentration of these two compounds in the solution as if no reactions had taken place. In the following the terms ammonia or carbon dioxide therefore refer to components.

In previous investigations of the vapour-liquid equilibria of the ammonia-carbon dioxide-water system several authors (9,10,11) did not analyse the liquid phase, assuming that no change in the known composition of the prepared solution took place during the experiment. Most authors determine ammonia directly by titration of a sample. No account is made for bound ammonia, nor for the effect of bound carbon dioxide on the titration. Schmidt (16) used a Kjeldahl procedure to expel free and bound ammonia from the solution. Carbon dioxide is determined either by precipitation in alkaline solution or by boiling of the acidified solution and subsequent volumetric or gravimetric determination of the expelled carbon dioxide. With these methods carbon dioxide as component will be found.

Gas chromatographic analysis of the liquid phase was suggested by Schmidt (16) and applied by Yanagisawa et al. (36). The latter authors analysed evaporated liquid samples, as in vapour phase analysis. Another possibility is direct injection of a liquid sample into the chromatograph. Because evaporation prior to injection is not suited with respect to the applied method of equilibrium measurement the direct injection method was investigated. A discussion of the results is given in Appendix 2.

In order to obtain the concentration of ammonia and carbon dioxide as components in the liquid phase two methods were developed. Special attention was paid to accuracy, ease of operation (automation) and short analysis time.

3.4.2 Determination of ammonia

3.4.2.1 Introduction

Determination of the total amount of nitrogen in a sample is discussed extensively in the literature. The Kjeldahl method (42) is most used, consisting of an acid digestion to convert the various nitrogen compounds to ammonia, transfer of ammonia out of the alkalified digest into excess acid and subsequent back titration. In the present investigation no digestion is necessary because of the inorganic nature of the solution, leaving distillation and subsequent determination of the ammonia. A review of these parts of the method is given by Bradstreet (20).

Transfer of the ammonia into the titration solution can be performed by simple distillation or by aeration; the latter technique, however, consumes considerably more time than distillation and quantitative recovery of the ammonia is difficult to achieve. The distilled ammonia is usually absorbed in a known excess amount of acid, followed by back titration. A drawback of this method is that two standard solutions must be available. Winkler (21) proposed to use a boric acid solution as absorbent. Because boric acid is a very weak acid it does not interfere with the determination. A mixture of indicators is proposed for a sharp indication of the end point. Potentiometric end point detection is not mentioned in Ref. 20.

Wilson (22) reviewed nitrogen determinations used in the fertilizer industry. It is pointed out that the distillation and titration method is very accurate, but rather time consuming. This is due to the use of a spray trap during distillation to prevent droplets of alkaline liquid reaching the receiver. Frey (23) suggested a method improved by Potrafke et al. (24), to shorten distillation time. Use was made of an electrically heated tube filled with metal wool, as spray trap. Potrafke et al. applied an inert carrier gas to transfer the ammonia more rapidly. Also a very fast heating method, simultaneously heating the distillation vessel and the spray trap, was used. Combined with reduction of the volume of solution to be distilled to a few milliliters, this procedure led to distillation times of 1 - 2 min. For the titration of ammonia a combined absorption-titration vessel was developed. In an accompanying article (25) an automatic apparatus for the determination was proposed, in which titration takes place potentiometrically, For ammoniacal nitrogen a standard deviation of 0.032% N is given, using this apparatus.

Concerning the titration of ammonia in boric acid solution, numerous references can be found (20). Malý (26) reported on the effect of boric acid and carbon dioxide on the accuracy of the determination. It was concluded that there is no difference between equivalence point and inflection point of the titration curve, when using boric acid solution. The effect of dissolved carbon dioxide on this difference is severely decreased by the presence of boric acid. It is also shown that the amount of ammonia to be determined has a minor influence on the pH of the equivalence point, using boric acid solution. A decrease of 0.02 pH-units is given for a change in ammonia concentration from 10^{-4} to 10^{-3} molar.

3.4.2.2 Experimental

Figure 3-8 presents the ammonia titration equipment. Its design is based on the work of Potrafke et al. (24). The distillation apparatus has a separate heating of the spray trap 2 and distillation vessel 1. Via rotameter 3 nitrogen (50 ml/min) is introduced above the liquid surface in 1, improving the transfer of ammonia to absorption spiral 4 and hence to titration vessel 5. From storage vessel 6 a 3% boric acid solution can be fed to the titration vessel to a level just above the inlet of the spiral. The absorption spiral also acts as a gaslift, mixing the contents of vessel 5 with ammonia containing liquid form the spiral and with introduced titrant. To remove carbon dioxide, nitrogen is continuously bubbled through the boric acid storage vessel. Control of the titration takes place via a potentiometric method. The pH of the solution is measured with a combined electrode and a pH meter (Metrohm E512, Metrohm, Herisau, Switzerland); the pH meter is connected to a control unit (Metrohm Impulsomat E473) which drives a recording motorburette (Metrohm Multidosigraph E425). After filling vessel 5 the pH of the boric acid solution (pH = 4.7) is measured and used as set point on the control unit. A pH increase, due to distilled ammonia, will result in introduction of titrant, 0.02 N hydrochloric acid solution (prepared with a Merck Titrisol ampul). The rate of delivery can be controlled by adjustment of the proportional band width and the sensitiviy (ratio electrical signal/number of milliliters). In the vicinity of the end point the titration rate is proportional to the distance from this end point, thereby assuring an accurate addition of titrant. The titration is recorded on a strip chart recorder, giving milliliters of titrant added as a function of time.

Initially, heating of the solution to be distilled took place with a heating wire spiral embedded in a circular glass tube at the bottom of vessel 1. Electrical current could be fed to the spiral via two platinum contacts soldered in the vessel's wall. This construction, however, functioned improperly, due to the corrosive action of the boiling strong alkaline solution. This corrosion caused leakage of liquid into the glass tube, containing the spiral, and along the platinum connections, leading to short-circuiting of the heater. Therefore a band heater was installed, closely fitting around the vessel 1. In about 10 ml of distilled water containing a few boiling stones 100 µl of the diluted sample was introduced, after which about 1.5 grams of water-free soda were added.

It was observed that a heating period of 9 minutes sufficed for quantitative boiling out of ammonia. The actual boiling time was about 4 minutes. To simplify the heating operation use was made of a push button electrical timer

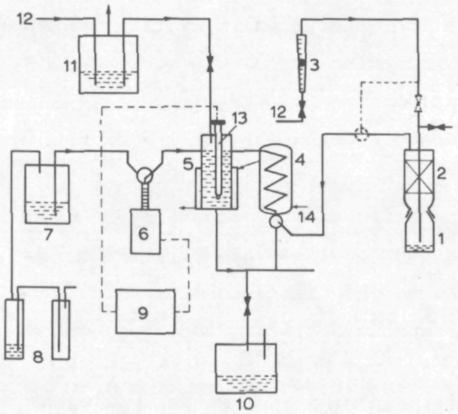


Fig. 3-8 *Equipment for analysis of ammonia. 1: Distillation vessel. 2: Spray trap. 3: Rotameter. 4: Absorption spiral with cooling mantle. 5: Titration vessel with cooling mantle. 6: Motor burette. 7: Vessel with titration solution. 8: Guard bottle with dilute sulfuric acid. 9: Titration control unit. 10: Waste. 11: Vessel with boric acid solution. 12: Nitrogen. 13: Combined electrode. 14: Cooling water.*

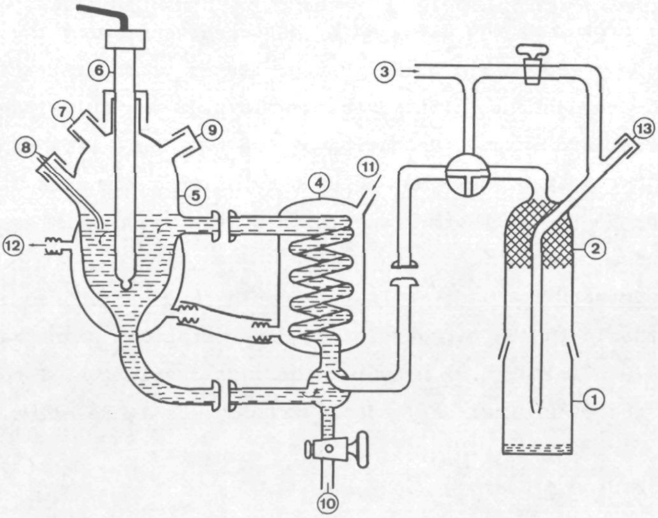


Fig. 3-9 *Detailed apparatus for ammonia determination. 1: Distillation vessel. 2: Spray trap, filled with glasswool. 3: Nitrogen flow. 4: Absorption spiral. 5: Titration vessel. 6: Combined electrode. 7: Boric acid solution inlet. 8: Titrant inlet via capillary tube. 9: Gas outlet. 10: Waste. 11: Cooling water inlet. 12: Cooling water outlet.*

(Suevia 108) inserted in the electrical heating circuit. The recorded titration curves (added titrant versus time) often showed a dragging end point, indicating that either the actual titration was slow or that the ammonia transfer to the titration vessel was slow. Reproducibility also was poor. Checking the titration time by titration of a known amount of alkaline solution revealed that the titration was not the disturbing step in the procedure.

Investigation of the distillation procedure by blank determinations resulted in high and non-reproducible values. Increasing the temperature of spray trap 2 and the line to absorber 4 to 120°C did not sufficiently improve the blank value and the reproducibility. Close inspection of the procedure used revealed that after removal of vessel 1 to prepare a new determination, thus interrupting the nitrogen flow through the apparatus, boric acid solution could rise into the hot transfer line. This solution could evaporate and condense in the spray trap. The wetted glass wool filling will absorb ammonia. The absorbed ammonia will be released some time after the nitrogen flow is restored, leading to poor reproducibility. To prevent this phenomenon the apparatus was modified, according to the dashed lines in Fig. 3-8. Before vessel 1 was disconnected, the nitrogen flow was bypassed the distillation equipment.

A further improvement was attained by better dimensioning the complete apparatus, as depicted in Fig. 3-9. Better mixing of the titration solution was achieved by tangential inlet of the liquid from the spiral and by reduction of the dead volume. Reduction of the residence time of the ammonia vapour in the spray trap could be achieved by halving the spray trap's volume. To improve the isothermal operation of the titration the spiral absorber was also cooled.

The time necessary for a determination could thus be reduced to 10 - 15 minutes, comparable to the carbon dioxide determination. Blank values were found of 0.04 - 0.07 ml of 0.02 N hydrochloric acid solution. The reproducibility of the determination (made in triplo) was 1% relative.

3.4.3 Determination of carbon dioxide

3.4.3.1 Introduction

In the determination of the carbon dioxide content of the equilibrium liquid phase laborious and time-consuming gravimetric or gas volumetric methods are used. Davies (27) reviews non-gravimetric methods for carbon dioxide determination. Aqueous titration methods suffer from incomplete absorption of carbon dioxide and inaccuracy. Organic solvents like pyridine or acetone are more suitable than alkaline solutions, leading to the development of non-aqueous titrimetric methods.

Blom and Edelhausen (28) developed a method using pyridine or acetone as solvent and sodium methoxide in a methanol-pyridine mixture as titrant. To absorb carbon dioxide completely a small amount of monoethanolamine has to be added to the absorption solution (29,30). This compound converts the carbon dioxide into 2-hydroxyethylcarbamic acid (37), which is then titrated. Various improvements of this method have been proposed (27), such as dimethylformamide/monoethanolamine as absorbent (31,32) and tetra n-butyl-ammoniumhydroxide in benzene/methanol (32) or methanol/isopropanol (33) as titrant. This organic titrant solves the problem of precipitation of potassium methyl carbonate when potassium methoxide is used as titrant. Also fading end points did no longer occur. Dimethylformamide has a greater odour limit than pyridine and is, contrary to acetone, not flammable. In a systematic study concerning the choice of absorbent, indicator and titrant, Braid et al. (34) concluded that application of a 5 vol % solution of mono-ethanolamine in dimethylformamide, thymolphtalein as indicator and tetra n-butylammoniumhydroxide in benzene/methanol was the best choice.

Determination of the end point takes place visually using thymolblue or thymolphtalein. Because it is necessary to keep the solution at its neutral point for complete carbon dioxide absorption and to reduce analysis time, an automated titration procedure is desirable. Snoek and Gouverneur (35) developed a photo-electrical titrator. Light of a suitable wavelength is sent through the solution to a photoresistor, which is part of an electronic relay to control a motorburette. Delivery of titrant is ended as soon as the solution's colour changes. A drawback of this on-off principle, as the authors state, is the non-proportional feed when the end point is approached. Introduction of the titrant near the light path, rapid stirring and a sensitive detector could overcome this problem.

Based on the above-mentioned discussion of proposed methods and on Ref. 35 concerning the practical design, an analysis apparatus for determination of carbon dioxide in the equilibrium liquid phase was developed.

3.4.3.2 Experimental

The equipment for the determination of carbon dioxide is presented in Fig.3-10. The critical part of the equipment is titration cell 4, whose design was based on Refs. 35 and 38. Fig. 3-11 gives a detailed drawing of the cell. It is placed in an aluminium holder, containing the lamp, interference filter

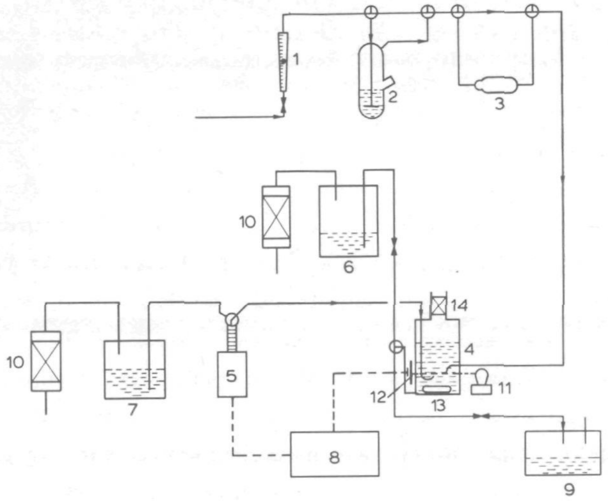


Fig. 3-10 Equipment for analysis of carbon dioxide. 1: Rotameter for nitrogen flow. 2: Strip vessel with concentrated sulfuric acid. 3: Oven for dissociation of calciumcarbonate. 4: Titration vessel. 5: Motor burette. 6: Vessel with absorption solution. 7: Vessel with titration solution. 8: Colorimetric titration unit. 9: Waste. 10: Guard tubes containing soda asbestos. 11: Lamp. 12: Filter and photo resistor. 13: Magnetic stirrer. 14: Active charcoal tube.

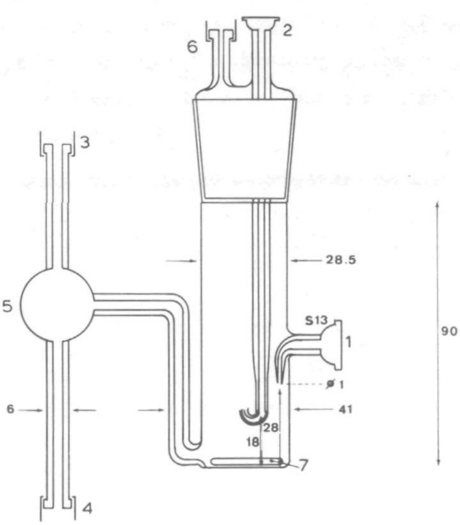


Fig. 3-11 Titration vessel for carbon dioxide determination. 1: Gas in. 2: Titrant. 3: Absorbent. 4: Waste. 5: Teflon three way cock. 6: Gas out. 7: Magnetic stirrer. Measures in mm. Except for gas in and titrant, connections are SQ13.

(Barr and Stroud MD4, 584 nm) and photoresistor (ORP 63). The photoresistor is connected to control unit 8. In this unit the filtered and amplified signal is fed to a comparator, which may actuate a relay to drive motorburette 5 (Metrohm E415). The colour change of the titration solution and the actuation point of the burette can be accurately matched by means of a variable resistor in the control unit. Adjustment of the titration addition rate is possible with the burette's variable speed motor. The cell is filled with absorption solution up to about 5 mm above the gas entrance from storage vessel 6. The solution is prepared by adding together 950 ml dimethylformamide, 50 ml mono ethanolamine and 5 ml thymolblue solution (120 mg thymolblue in 50 ml dimethylformamide).

Liberation of carbon dioxide from a sample takes place in stripper 2, containing concentrated sulfuric acid solution. Samples are introduced with a 100 µl syringe through a septum. Carbon dioxide is conducted to the titration vessel with a nitrogen flow of 50 ml/min measured with rotameter 1. Storage vessels 6 and 7 are protected from CO_2 in the air by soda asbestos tubes 10.

0.01 N tetra n-butylammoniumhydroxide in methanol/isopropanol is prepared by dilution of 0.1 N solution (Merck, Darmstadt, West Germany) with isopropanol. The fresh absorption solution is titrated to the neutral point (requiring about 0.7 ml of titrant), whereafter the sample is introduced into stripper 2. It was found that 12 minutes after this introduction titration was complete.

Standardization of titrant is performed with calciumcarbonate. About 5 mg (weighed on an electrobalance to within 0.002 mg) is introduced in furnace 3, a quartz tube, heated by resistance wire. Vessel 2 is bypassed and the nitrogen flow is led through oven 3, which is normally bypassed. Heating to $900^{\circ}C$ results in dissociation of the calciumcarbonate, giving a known amount of carbon dioxide. The stability of the titrant solution is good. Reproducibility was 2% and 1%, for low and high carbon dioxide contents, respectively.

References

1. E. Hála, J. Pick, V. Fried, O. Vilím, *Vapour liquid equilibrium*, 2nd ed., Pergamon Press, Oxford, 1967, p. 280.
2. E. Terres, H. Weiser, *J. Gasbeleucht. Verw. Beleuchtungsarten Wasserversorg.*, 63 (1920) 705.
3. S. Pexton, E.H.M. Badger, *J. Soc. Chem. Ind. London Trans. Commun.*, 57 (1938) 106.
4. E.H.M. Badger, D.S. Wilson, *J. Soc. Chem. Ind. London*, 66 (1947) 84.
5. D.W. van Krevelen, P.J. Hoftijzer, F.J. Huntjens, *Recl. Trav. Chim. Pays-Bas*, 68 (1949) 191.
6. E. Otsuka, S. Yoshimura, M. Yakabe, S. Inoue, *Kogyo Kagaku Zasshi*, 63 (1960) 1214; *Chem. Abstr.*, 56 (1962) 9501c.
7. T. Takahashi, *Kogyo Kagaku Zasshi*, 65 (1962) 837; *Chem. Abstr.*, 59 (1963) 2216h.
8. L. Jäger, J. Nijvlt, H. Kocová, J. Gottfried, *Chem. Prum.*, 15 (1965) 404; *Chem. Abstr.*, 63 (1965) 10718g.
9. R. Mezger, T. Payer, *Gas Wasserfach*, 68 (1925) 651.
10. E. Terres, W. Attig, F. Tscherter, *Gas Wasserfach*, 98 (1957) 512.
11. T. Takahashi, S. Yoshimura, K. Fujii, E. Otsuka, *Kogyo Kagaku Zasshi*, 65 (1962) 743; *Chem. Abstr.*, 57 (1962) 14485a.
12. D.M. Ginzburg, *J. Appl. Chem. U.S.S.R. (Engl. Transl.)*, 38 (1965) 2157.
13. D.F. Othmer, G.J. Frohlich, *Ind. Eng. Chem. Process. Des. Dev.*, 3 (1964) 270.
14. G.J. Frohlich, *Vapor-liquid equilibria of aqueous systems containing ammonia and carbon dioxide*, PhD thesis, Polytechnic Institute of Brooklyn, 1957.
15. L. Jäger, J. Gottfried, J. Nijvlt, J. Sura, J. Havlicek, L. Sisler, *Chem. Prum.*, 15 (1965) 649; *Chem. Abstr.*, 64 (1966) 4324a.
16. D. Schmidt, *Enthalpie-Zusammensetzungs-Diagramme für Dreistoffsysteme am Beispiel des Systems* NH_3-CO_2-H_2O, PhD thesis, Technischer Universität Braunschweig, West Germany, 1973.
17. S.M. Lemkowitz, *Phase and corrosion studies of the* NH_3-CO_2-H_2O *system at the conditions of the hot gas recirculation process for the synthesis of urea*, PhD thesis, Delft University of Technology, the Netherlands, 1975.
18. J.G. Koren, A.J. Andreatch, *Anal. Chem.*, 37 (1965) 256.
19. C.P.M.G. A'Campo, Internal Report Laboratory of Chemical Technology, Delft University of Technology, the Netherlands, 1979 (in Dutch).
20. R.B. Bradstreet, *The Kjeldahl method for organic nitrogen*, Academic Press, New York, 1965, p. 147.
21. L.W. Winkler, *Angew. Chem.*, 27 (1914) 630.
22. H.N. Wilson, *Proc. Fert. Soc.*, 62 (1960).
23. M. Frey, *Chim. Ind. (Paris)*, 70 (1953) 213.
24. K.A. Potrafke, M. Kroll, L. Blom, *Anal. Chim. Acta*, 31 (1964) 128.
25. G. Kateman, L.L.M. Willemsen, J.B.G. Wijenberg, P.J. Stornebrink, *ibid.*, 139.
26. J. Malý, *Talanta*, 23 (1976) 655.
27. D.H. Davies, *Talanta*, 16 (1969) 1055.
28. L. Blom, L. Edelhausen, *Anal. Chim. Acta*, 13 (1955) 120.
29. L. Blom, J.A. Stijntjes, J.A. van der Vliervoet, A.J. Beeren, *Chim. Anal. (Paris)*, 44 (1962) 302.
30. A.Patchornik, Y. Shalitin, *Anal. Chem.*, 33 (1961) 1887.
31. J.A. Grant, J.A. Hunter, W.H.S. Massie, *Analyst (London)*, 88 (1963) 134.
32. R.F. Jones, P. Gale, P. Hopkins, L.N. Powell, *Analyst (London)*, 90 (1965) 623.
33. H.F. Pronk, A.C. van der Geest, *CNRM Metall. Rep.* (11), (1967) 49.

34. P. Braid, J.A. Hunter, W.H.S. Massie, J.D. Nicholson, B.E. Pearce, *Analyst (London)*, 91 (1966) 439.
35. O.I. Snoek, P. Gouverneur, *Anal. Chim. Acta*, 39 (1967) 463.
36. Y. Yanagisawa, Y. Harano, T. Imoto, *Nippon Kagaku Kaishi*, (1973) (5) 917; *Chem. Abstr.*, 79 (1973) 35558.
37. D.W. Whymark, J.M. Ottoway, *Talanta*, 19 (1972) 209.
38. DSM, private communication.
39. F. Christensson, H.C.S. Koefoed, A.C. Petersen, K. Rasmussen, *Acta Chem. Scand. Ser. A*, 32 (1978) 15.
40. R. Wiebe, V.L. Gaddy, *J. Am. Chem. Soc.*, 63 (1941) 475.
41. W.S. Dodds, L.F. Stutzman, B.J. Sollami, *Chem. Eng. Data Ser.*, 1 (1956) 92.
42. H.D. Drew, *"Determination of total nitrogen"* in C.A. Streuli, P.R. Averell (eds.), *The analytical chemistry of nitrogen and its compounds, part 1*, Wiley-Interscience, New York, 1970, p. 1.
43. B.V. Ioffe, A.G. Vitenberg, A.N. Marinichev, L.M. Kuznetsova, *Chromatographia*, 9 (1976) 502.
44. A.B. Littlewood, *Gas chromatography*, 2nd ed., Academic Press, New York, 1970, p. 362.
45. W. Durisch, A. Buck, *Chimia*, 29 (1975) 437.

4 EXPERIMENTAL MEASUREMENTS

4.1 Introduction

Using the apparatus and experimental method described in the previous chapter measurements were made of the vapour-liquid equilibria of the NH_3-CO_2-H_2O system at 0.1 MPa and various temperatures.

In measuring vapour-liquid equilibria the compositions of the phases in equilibrium are usually determined by chemical analysis. The raw analysis results have to be transformed in order to obtain useful data. The composition of a phase can be expressed in various concentration units, such as mol/liter, molar fractions, weight fractions etc. Because the molar concentration (moles of a component per one mole mixture) is usually employed to express the phase composition, this concentration unit was adopted. Therefore the analysis results have to be transformed to molar concentrations. For the vapour phase measurements the transformation from peak area to mole fraction is straightforward. With the aid of calibration curves the mole fraction of a component in the mixture is directly found from its average peak area. Two corrections are applied on the results so-obtained. Due to the difference in sample loop pressure in calibration and analysis, the results have to be normalized to 100% (see also Section 3.3.4). Because only the three components NH_3, CO_2 and H_2O are of interest, an additional correction for the small amount of air in the mixture is made by normalizing the sum of the NH_3, CO_2 and H_2O mole fractions to unity. An example of this calculation procedure is found in Table 4-1.

The primary results obtained in the liquid analysis are the number of milliliters of titrant (with known normality) added in analyzing a given volume of diluted liquid sample. Because this method only gives the composition per unit volume of solution, the density of the diluted sample is needed for the transformation into molar units. This density is determined by weighing a given volume of solution (with a 100 µl syringe) with a precision of 0.1 mg. The density, together with the sample's degree of dilution (see Section 3.2.3), makes possible the calculation of the molar composition of the

Temperature : 90.1 °C
Barometric pressure: 761 mm mercury
Pressure difference: 56 mm mercury
→ Total pressure: 0.1089 MPa

<u>Vapour analysis</u>

Number of measurements: 7

Components:	air	CO_2	NH_3	H_2O
Average peak area, arbitrary units	1.87	428.4	451.0	1047.0
Relative standard deviation peak area, %	11	1.7	2.2	1.0
Uncorrected composition, mole-%	0.11	22.70	39.68	103.97
Composition, corrected for sample pressure	0.07	13.64	23.84	62.40
Composition, corrected for air content	-	13.6	23.9	62.5

Sum of partial pressures of NH_3, CO_2 and H_2O: 0.1088 MPa

<u>Liquid analysis</u>

Sample flask weighings: empty : 16.6024 gr
with water : 17.4442 gr
with water and sample: 18.4408 gr
→ Degree of dilution: 1.845

Density measurement: syringe with 100 μl diluted sample: 22.4043 gr
syringe empty : 22.3029 gr
density: 1.014 gr/ml

Titrations:

Injected 100 μl diluted sample

Normalities: NH_3 titration: 0.0216 eq/l. CO_2 titration: 0.00898 eq/l.

Number of milliliters:

NH_3	4.34 ml	CO_2	2.62 ml
	4.33 ml		2.56 ml
Blank	0.04 ml		2.53 ml
Average	4.30 ml	Average	2.57 ml

Calculated composition: 3.073 mole-% NH_3 and 0.764 mole-% CO_2.

A second sample of the same liquid yielded 3.085 mole-% NH_3 and 0.759 mole-% CO_2.

Table 4-1 Example of transformation of analysis results to molar equilibrium compositions.

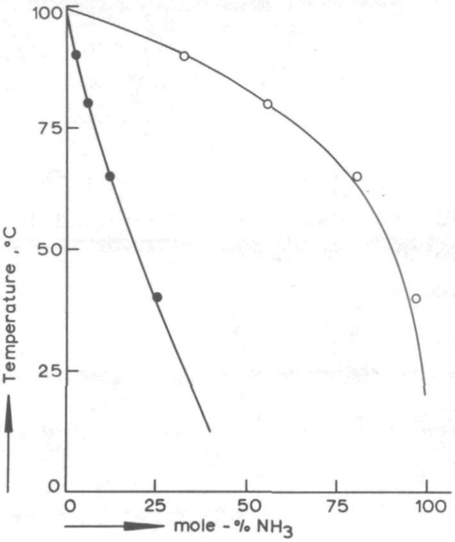


Fig. 4-1 Experimental measurements of the NH_3-H_2O system at 0.1 MPa. Lines are drawn using Refs. 1 and 2.

liquid phase. This part of the calculation procedure is also shown in Table 4-1.

Because the measurements of the binary systems NH_3-H_2O and CO_2-H_2O can be compared with literature values, they are presented separately. After the presentation of the ternary measurements some concluding remarks are made.

4.2 Binary measurements

Measurements of the two binary systems NH_3-H_2O and CO_2-H_2O were made to test the experimental procedure. In Chapter 3 the results of the H_2O-CO_2 equilibrium measurements were already mentioned (Fig. 3-5). These results were in good agreement with calculations, indicating the correct operation of the equilibrium apparatus and the gas chromatographic analysis system. Measurements of the NH_3-H_2O system can be used to test the liquid sampling procedure and the subsequent analysis for ammonia. The results are shown in Fig. 4-1 and

Temperature °C	Pressure MPa	Liquid mole-% NH_3		Vapour mole-% NH_3	
		exp.	lit.	exp.	lit.
40	0.1037	24.8	24.7	96.7	95.0
65	0.1019	12.0	12.4	80.6	79.0
80	0.1023	6.18	6.17	-	-
80	0.1023	5.62	6.17	55.7	55.7
90.1	0.1010	2.84	2.75	32.2	33.0

a.

Temperature °C	Pressure MPa	Vapour mole-% CO_2	
		exp.	lit.
40	0.1031	92.7	92.8
65	0.1027	76.7	75.6
80	0.1024	53.3	53.8
90.1	0.1014	29.8	30.6

b.

Table 4-2 Comparison of experimental results with literature values. a. NH_3-H_2O system. b. CO_2-H_2O system.

Temperature °C	Number of data points	Average pressure MPa	Standard deviation MPa	
40	17	0.1036	0.0003	1)
40	9	0.1016	0.0006	2)
65	21	0.1035	0.0006	3)
80	12	0.1022	0.0008	
81.5	14	0.1028	0.0004	
90.1	11	0.1009	0.0008	
90.1	13	0.1088	0.0002	

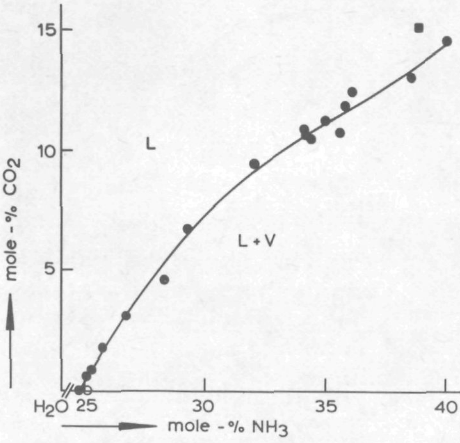
Table 4-3 Average pressure values for ternary measurements. 1: NH_3-rich side. 2: CO_2-rich side. 3: Pressure recorded for only 6 points.

tabulated, together with the results of the other binary system, in Table 4-2. The literature values in this table were found by interpolation of data from Clifford and Hunter (1) and Wucherer (2) for the NH_3-H_2O system or by calculation, assuming ideal behaviour, for the CO_2-H_2O system. It can be seen from Table 4-2 that the deviation from the literature data for the NH_3-H_2O liquid phase composition is within 3% relative, with the exception of an 80°C measurement, included for its vapour phase composition. For the vapour phase composition of both systems the deviation of the CO_2 or NH_3 content from the literature is less than 3% relative, the maximum absolute deviation being 1.7 mole %. The results at 40° and 65°C for the NH_3-H_2O system show a higher NH_3 concentration in the vapour than expected, corresponding with an insufficient water percentage. Because at higher temperatures such a systematic deviation was not found, it is believed that this difference is due to the non-attainment of equilibrium at these lower temperatures.

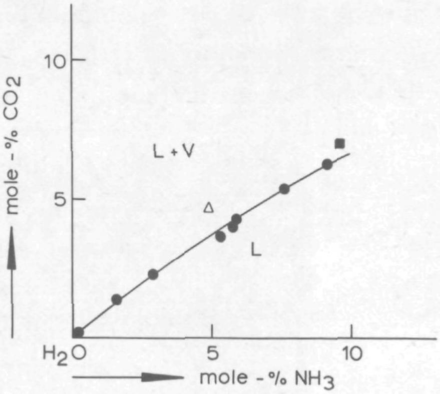
It can be concluded from these results that the interaction of NH_3 *and* H_2O in the gas-chromatographic analysis, as discussed in Section 3.3.3 and Appendix 1, does not influence the accuracy of the measurements. The probable reason for this is that the interaction effect is counterbalanced by the effect of a higher sample-loop pressure. This higher pressure in the actual analysis, compared with the calibration, results in an increase in the peak areas of both NH_3 and H_2O. Due to the insufficient programming possibilities of the digital integrator, a larger part of the tailing NH_3 peak is not integrated, resulting in a lower NH_3 peak area. This is a possible explanation for the fact that correct vapour phase compositions for the NH_3-H_2O system were found.

4.3 Ternary measurements

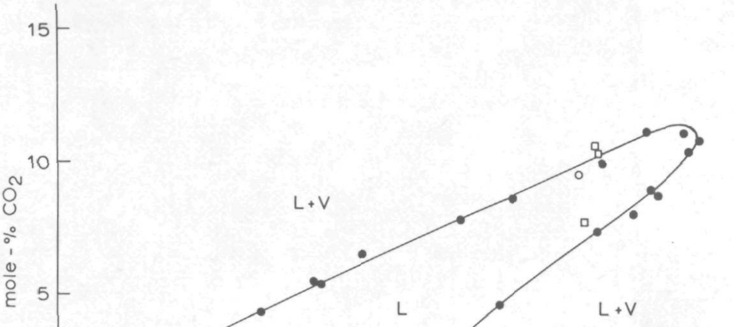
Measurements of ternary equilibria were made at 40, 65, 80, 81.5 and 90.1°C. For 80°C only the boiling point line was determined. To investigate the effect of pressure two series of measurements were made at 90.1°C with average pressures of 0.1008 MPa and 0.1088 MPa. The number of data points and the average pressure for each series can be found in Table 4-3. The measurements are presented in Figs. 4-2 and 4-3 and in Table 4-4. From this table it is seen that for the series at 65°C the pressure was recorded at only 6 points. Because the effect of pressure is rather low at this temperature (see Table 4-5), it can be assumed that the calculated average pressure also holds for the other measurements and that no large composition errors occurred because of varying pressure.


15
10
5
mole - % CO2
L
L + V
H2O
25
30
35
40
mole - % NH3

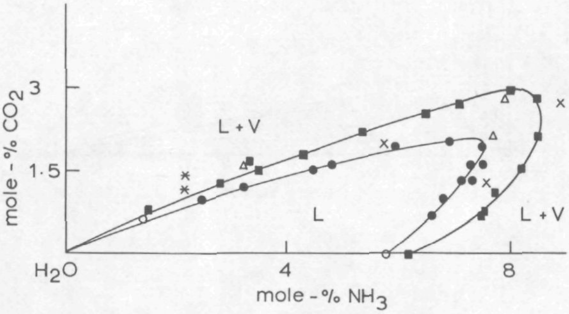
a


10
5
mole - % CO2
L + V
L
H2O
0
5
10
mole - % NH3

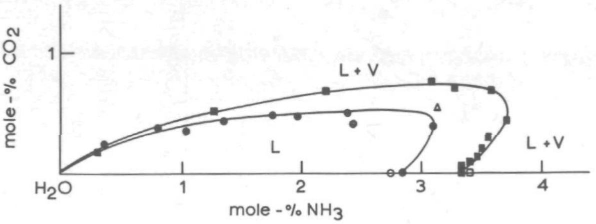
b


15
10
5
mole - % CO2
L + V
L
L + V
H2O
5
10
15
20
25
mole - % NH3

c

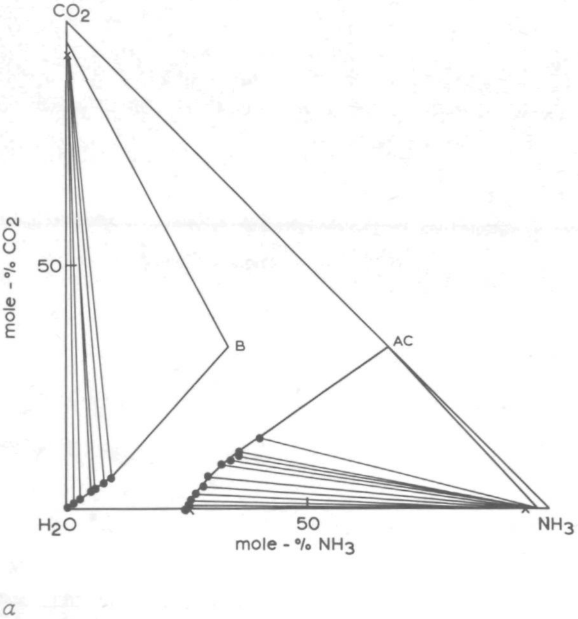

3
1.5
mole - % CO2
L + V
L
L + V
H2O
4
8
mole - % NH3

d

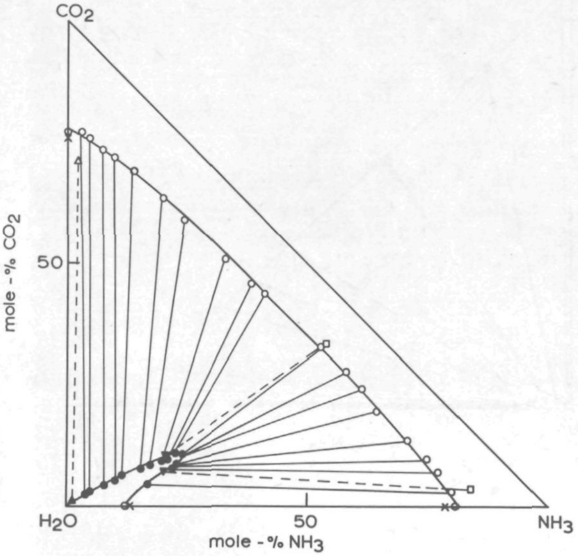


e

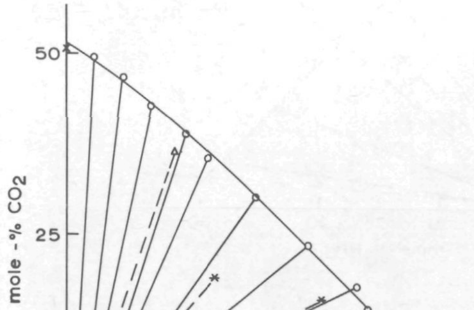
Fig. 4-2 Boiling points at 0.1 MPa and various temperatures. a: 40°C, NH_3-rich equilibria. Square: three-phase equilibrium, Ref. 3. b: 40°C, CO_2-rich equilibria. Square: three-phase equilibrium, Ref. 3. c: 65°C. d. 80°C (squares) and 81.5°C (circles). e: 90.1°C. Squares: 0.1088 MPa. Circles: 0.1009 MPa. Binary boiling points (open symbols) from Refs. 1 and 2. Triangles: Ref. 5. Open squares: Ref. 4. Crosses: Ref. 6. Asterisks: Ref. 7. Half-open square: Ref. 8.



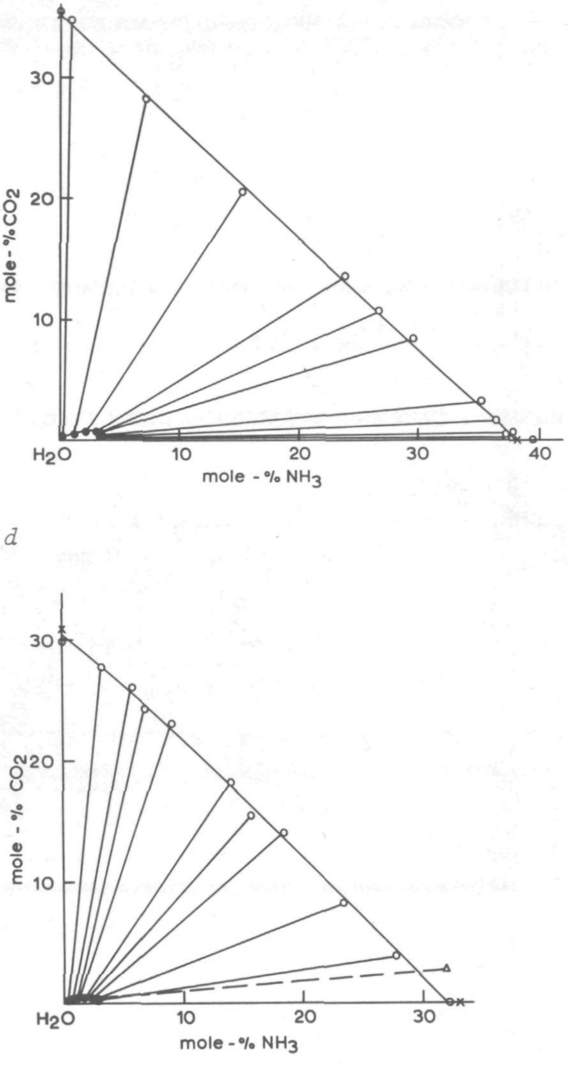
a


CO2
50
mole - % CO2
H2O
50
mole - % NH3
NH3

b


50
25
mole - % CO2
H2O
25
50
mole - % NH3

c



d

e

Fig. 4-3 *Measured vapour-liquid equilibria at 0.1 MPa and various temperatures. a: 40°C. AC: solid ammonium carbamate. B: solid ammonium bicarbonate. b: 65°C. c: 81.5°C. d: 90.1°C and 0.1009 MPa. e. 90.1°C and 0.1088 MPa. Crosses: literature values from Refs. 1 and 2 or calculated values. Triangles: Ref. 5. Squares: Ref. 4. Asterisks: Ref. 6. Open symbols denote dew points, closed symbols boiling points.*

The measurements at 40°C (Figs. 4-2a, 4-2b and 4-3a) show the behaviour which was expected (see Chapter 2). Two separate vapour-liquid regions are found, each ending in a three-phase equilibrium. Because the change in the liquid composition achieved by adding gaseous NH_3 and CO_2 was small in approaching the three-phase equilibria, these equilibria were measured by introduction of solid ammonium carbamate into the equilibrium vessel. For the CO_2-rich equilibrium a transformation of this compound into ammonium bicarbonate had to take place, because the latter salt is the equilibrium solid present. From Figs. 4-2a and 4-2b it is seen that the agreement of the measured liquid compositions of the triple points with values given by Guyer and Piechowicz (3) is reasonable. The ternary boiling points agree well with those of the binary systems.

Inspection of the dew points at 40°C shows that all of them are situated very close to the respective binary dew points. For the CO_2-rich equilibria the amount of NH_3 in the vapour was not detectable, whereas for the NH_3-rich equilibria a gradual increase in CO_2 content with increasing liquid CO_2 content was found (see Table 4-4). The equilibrium water content of the vapour is low compared to literature values for the binary systems. This error is probably due to non-attainment of equilibrium at this low temperature. Close inspection of the mole-% of H_2O in the vapour indicates a decrease with an increasing amount of the third component, starting from a binary system. This behaviour agrees with the qualitative behaviour, sketched in Chapter 2 (see Fig. 2-10b).

During these measurements formation of a thin layer of white solid occurred on parts of the equilibrium apparatus in contact with the vapour. This phenomenon is caused by the occurrence of a solid-vapour equilibrium with about the same equilibrium vapour phase as in the vapour-liquid equilibrium. The formation of the solid (ammonium carbamate for the NH_3-rich composition region and ammonium bicarbonate for the CO_2-rich composition region) took place at non-equilibrium conditions, i.e. during a change of the system's composition. Due to the low sublimation rate at this temperature the solid remained present in the subsequent equilibrium measurement, but for the same reason did not measurably influence this equilibrium.

Measurements at 65°C were made because it was expected that at this temperature and 0.1 MPa solids would no longer occur, and indeed a continuous boiling point line was found (Fig. 4-2c). The strong curvature of the boiling point line in the region of low water content is striking. In this region a small change in liquid composition causes a large change in vapour composition. This is seen from Fig. 4-3b, which shows the complete phase diagram at this temperature. The dew point line also exhibits curvature, although to a much smaller extent than the boiling point line. As was already discussed in the preceding section, the water content of the vapour is low with respect to literature values for the binary systems. The deviation is about 1 - 1.5 mole-%.

With temperature increase the liquid region will withdraw towards the H_2O corner point and the dew point line also moves in this direction, as is seen by comparing the results at 65°C with those at 81.5°C (Fig. 4-3c). The consistency of the ternary measurements with those of the boundary systems is good. The curvature of the dew point line is less than at 65°C, indicating vapour behaviour that is more ideal, as is to be expected at higher temperatures. The effect of temperature on the boiling points is shown in Fig. 4-2d, in which measurements of the liquid phase at 80°C and 81.5°C are presented. No accurate dew points are available at the former temperature. It is seen that on the CO_2-rich side there is an increasing difference between the two lines with increasing ammonia content. This is caused by the low solubility of CO_2 in water resulting in boiling-point lines starting from the H_2O corner point at every temperature at 0.1 MPa. The CO_2-solubility in the ternary liquid is determined by its ammonia content, which is temperature dependent. Therefore the two boiling point lines in Fig. 4-2d diverge with increasing NH_3-content.

In performing measurements at this temperature it was observed that the pressure also had a significant influence on the equilibrium compositions, especially for the vapour phase. To express this pressure dependency for every temperature the effect is given for the binary systems in Table 4-5. As in Table 4-3 the values were found by interpolation or calculation. It is seen that the effect on the vapour composition is of the same magnitude for both binary systems. The effect of pressure on the liquid composition is much less and decreases with increasing temperature. The pressure effect can be visualized by drawing pressure-composition figures at the temperatures of interest. Of the totality of the measurements at this temperature only those are presented here for which the deviation from the mean experimental pressure lay within values, corresponding with composition differences of the same order of magnitude as the errors in the vapour phase analysis.

This procedure was also followed for the measurements at 90.1°C. Two series of measurements were made, at 0.1009 and 0.1088 MPa. In the latter series special attention was paid to reducing the pressure differences between the various measurements, resulting in a lower standard deviation than in other

Temperature	Composition				Pressure
	Liquid		Vapour		
°C	mole-% NH_3	mole-% CO_2	mole-% NH_3	mole-% CO_2	MPa
40	24.8	0	96.7	0	0.1037
	25.1	0.63	96.7	< 0.01	0.1035
	25.3	0.85	96.7	< 0.01	0.1036
	25.8	1.81	96.7	0.03	0.1033
	26.8	3.12	96.8	0.04	0.1033
	28.4	4.57	97.0	0.08	0.1036
	29.3	6.73	97.0	0.13	0.1039
	32.1	9.41	97.2	0.24	0.1035
	34.1	10.8	97.3	0.33	0.1035
	34.2	10.6	97.3	0.34	0.1032
	34.4	10.4	97.4	0.29	0.1036
	35.0	11.2	-	-	0.1047
	35.6	10.7	97.3	0.31	0.1036
	35.8	11.8	97.3	0.37	0.1035
	36.1	12.4	97.4	0.40	0.1037
	38.6	13.0	-	-	0.1037
	40.1	14.6	97.5	0.5	0.1040
	0	0	0	92.7	0.1031
	0.25	0.17	< 0.01	93.3	0.1013
	1.6	1.4	|	93.6	0.1015
	2.9	2.3	|	93.8	0.1013
	5.3	3.73	|	94.1	0.1015
	5.83	4.04	|	94.1	0.1018
	5.89	4.26	|	94.1	0.1013
	7.63	5.35	|	94.3	0.1014
	9.20	6.29	< 0.01	94.6	0.1012
65	0	0	0	76.7	0.1027
	3.87	2.42	2.7	76.9	-
	4.9	3.0	4.2	75.6	-
	7.7	4.3	7.1	73.4	-
	9.73	5.38	9.9	72.3	-
	10.0	5.3	9.6	71.6	-
	11.5	6.36	13.5	69.1	-
	15.2	7.72	19.5	63.5	-
	17.2	8.46	24.2	59.1	-
	19.7	9.38	32.6	50.9	-
	20.6	9.82	38.0	45.9	-
	22.3	11.0	43.8	40.9	-
	23.7	10.9	52.9	32.7	-
	24.3	10.6	61.4	24.3	-
	23.9	10.2	57.9	27.6	-
	22.7	8.6	70.6	13.5	0.1031
	22.4	8.77	64.5	19.8	0.1031
	21.8	7.90	74.8	9.8	0.1033
	20.4	7.23	77.2	7.0	0.1035
	16.7	4.49	79.9	3.3	0.1032
	12.0	0	80.6	0	0.1019
	1.47	0.81	-	-	0.1013
	2.77	1.31			0.1013
	3.51	1.52	-	-	0.1026
	4.26	1.76	-	-	0.1014

80	5.38	2.16	–	–	0.1023
	6.50	2.50	–	–	0.1026
	7.10	2.69	–	–	0.1026
	8.02	2.87	–	–	0.1027
	8.48	2.76	–	–	0.1027
	8.55	2.08	–	–	0.1023
	8.25	1.54	–	–	0.1038
	7.67	0.80	–	–	–
	7.45	0.73	–	–	–
	7.71	1.06	–	–	–
	6.18	0	–	–	0.1023
81.5	1.39	0.62	3.9	49.5	0.1031
	2.46	0.95	7.7	46.8	0.1027
	3.22	1.19	11.7	42.8	0.1027
	4.49	1.53	16.6	39.0	0.1037
	4.85	1.63	19.6	35.7	0.1027
	5.95	1.93	26.4	30.3	0.1026
	6.92	2.02	33.4	23.4	0.1029
	7.50	1.94	40.2	17.8	0.1031
	7.52	1.62	45.4	11.9	0.1029
	7.31	1.60	41.8	14.7	0.1021
	7.32	1.33	51.0	6.1	0.1031
	7.17	1.32	49.8	6.3	0.1020
	6.79	1.02	50.7	3.4	0.1027
	6.63	0.71	52.8	1.8	0.1029
90.1	0	0	0	29.8	0.1014
	0.36	0.24	3.3	27.7	0.1014
	0.80	0.38	5.8	26.0	0.1002
	1.03	0.34	6.9	24.3	0.1010
	1.35	0.43	9.1	23.1	0.1009
	1.75	0.48	14.0	18.2	0.1010
	1.97	0.47	15.7	15.4	0.1004
	2.38	0.50	18.4	14.0	0.1013
	2.43	0.41	23.4	8.2	0.0993
	3.10	0.38	27.7	3.9	0.1023
	2.84	0	32.2	0	0.1010
90.1	0.31	0.185	0.815	34.7	0.1086
	1.25	0.51	7.12	28.3	0.1086
	2.20	0.68	15.1	20.5	0.1087
	3.08	0.76	23.9	13.6	0.1088
	3.27	0.71	26.7	10.7	0.1086
	3.57	0.69	29.6	8.5	0.1090
	3.70	0.45	35.1	3.2	0.1090
	3.55	0.30	36.2	1.73	0.1091
	3.50	0.21	37.7	0.77	0.1085
	3.45	0.15	37.1	0.53	0.1084
	3.40	0.11	37.2	0.33	0.1090
	3.32	0.06	37.5	0.13	0.1085
	3.34	0	39.4	0	0.1094

Table 4-4 Experimental measurements of the vapour-liquid equilibria.

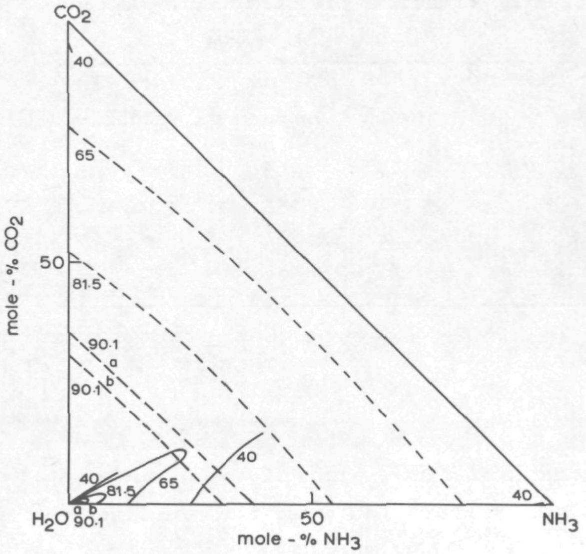


Fig. 4-4 Dew point and bubble point lines at 0.1 MPa and various temperatures. Dashed lines: dew points. Solid lines: boiling points. Temperatures in ^{o}C. a: 0.1009 MPa. b: 0.1088 MPa.

series (see Table 4-3). From Fig. 4-2e it is seen that the liquid area becomes very small with CO_2 concentrations well below 1 mole-%. The tongue-like shape of the liquid region becomes less pronounced. The two dew point lines are straight, indicating ideal behaviour of the vapour phase (Figs. 4-3d and 4-3e). The measurement of the vapour composition of the NH_3-H_2O system in the case of the higher pressure deviates substantially from the literature value, whereas the ternary measurements closely join this value. The reason for this phenomenon is not known.

A summary of the measurements is presented in Fig. 4-4 in which for clarity no separate points and no tie-lines are drawn.

4.4 Further discussion and conclusions

The precision of the measured vapour phase compositions is estimated as 1 - 2% relative for each of the three components. This estimation is based on the standard deviations calculated for every determination (8 - 10 measurements). As discussed in Section 4.2, the results of the binary measurements agree rather well with literature values. Therefore the accuracy of the vapour phase measurements is estimated to be of the same order of magnitude as the precision.

Temperature °C	Effect of pressure on composition mole-%/MPa		
	NH_3-H_2O		CO_2-H_2O
	Liquid	Vapour	Vapour
40	114	64	71
65	124	255	240
80	95	488	455
90	83	702	674

Table 4-5 Effect of pressure on equilibrium composition at constant temperature.

For the measurements at 40°C the values of the vapour's water content are about 1.7 and 0.5 mole-% lower than those from the literature for the NH_3-rich and CO_2-rich equilibria, respectively. The 65°C measurements also show a discrepancy of 1.1 - 1.6 mole-%, concerning the vapour phase water content. It is assumed that these differences also occur in the ternary compositions at 65°C.

The accuracy of the liquid phase measurements is estimated as 3-5% relative. The largest contribution to this error gives the titration error, over errors due to weighing and injecting samples.

In Figs. 4-2 and 4-3 some literature values from Table 2-3 are also shown. At the conditions of the measurements only a few literature values are available. It appears that the measurements of Schmidt (4) and Ginzburg (5) agree well with the present measurements; deviations occur concerning the water content of the vapour phase. Other investigators (6, 7, 8) have presented liquid phase compositions which closely agree with the measured boiling points. Otsuka's vapour phase compositions exhibit an anomalously high water content.

The expected behaviour of the system, as sketched on the basis of theoretical considerations in Chapter 2, was found. Agreement with the known binary systems is good, except for the vapour phase compositions at 40°C and, to a lesser extent, at 65°C. The pressure has an important influence on the measured equilibria, especially at higher temperatures and therefore accurate phase measurements require careful pressure control. In spite of doubts concerning the accuracy of the gas chromatographic analysis system good vapour phase results were obtained. To increase the accuracy of this analysis method further research is necessary (see Appendix A).

References

1. J.L. Clifford, E. Hunter, *J. Phys. Chem.* 37 (1933) 101.
2. J. Wucherer, *Z. ges. Kälte-Ind.*, 39 (1932) 97.
3. A. Guyer, T. Piechowicz, *Helv. Chim. Acta*, 27 (1944) 858.
4. D. Schmidt, *Enthalpie-Zusammensetzungs-Diagramme für Dreistoffsysteme am Beispiel des Systems* NH_3-CO_2-H_2O, PhD thesis, Technische Universität Braunschweig, West Germany, 1973.
5. D.M. Ginzburg, *J. Appl. Chem. U.S.S.R. (Engl. Transl.)*, 38 (1965) 2157.
6. E. Otsuka, S. Yoshimura, M. Yakabe, S. Inoue, *Kogyo Kagaku Zasshi*, 63 (1960) 1214; *Chem. Abstr.*, 56 (1962) 9501c.
7. R. Mezger, T. Payer, *Gas Wasserfach*, 68 (1925) 651.
8. L. Jäger, J. Nývlt, H. Kocová, J. Gottfried, *Chem. Prum.*, 15 (1965) 404; *Chem. Abstr.*, 63 (1965) 10718g.

5 MATHEMATICAL DESCRIPTION OF THE VAPOUR-LIQUID EQUILIBRIA OF THE NH_3-CO_2-H_2O SYSTEM

5.1 Introduction

A mathematical description of experimentally determined vapour-liquid equilibria is necessary if these equilibria are to be used in engineering calculations involving equipment for distillation and absorption. The so-called data-reduction of the experimental measurements gives a set of equations with which the vapour-liquid equilibrium at given conditions can be calculated. A good correlation will facilitate interpolation of the measurements and even allows for some extrapolation. Regression analysis may lead to an accurate representation of the measurements, but reliable extrapolations are not likely. Furthermore, such a correlation will not give any insight in the physico-chemical characteristics of the system under investigation. The use of a model based on the thermodynamics of fluid-phase equilibria is advantageous in the interpretation of the measurements, and extrapolations are likely to follow the real behaviour of the system.

The general equation for the vapour-liquid equilibrium of a component i, using as liquid standard state the hypothetical ideal solution of unit molality (1, 18), is:

$$\phi_i \, y_i \, P = \gamma_i \, m_i \, H_i \qquad (5\text{-}1)$$

It is seen from eq. 5-1 that calculation of the distribution of component i between liquid and vapour at a given temperature and pressure is possible when the deviations from ideal behaviour of both phases, represented by the fugacity coefficient ϕ_i and the activity coefficient γ_i, can be described. Fugacity coefficients can be calculated from equations of state or from corresponding state correlations. Satisfactory results can be obtained if the interaction parameters, occurring in the equations of state, are estimated from experimental measurements.

Assumptions concerning the molecular interactions occurring in the liquid phase, lead to models from which the dependence of the activity coefficients on the composition can be found. Various models have been proposed, resulting in well-known equations such as those of Van Laar, Wilson and the NRTL-equation (1). It should be noted, however, that these equations were developed for non-electrolyte systems. For solutions containing electrolytes the literature contains many less models, due to the complexity of the interactions in such a solution. The well-known Debye-Hückel theory holds only for very dilute solutions. For higher concentrations more or less empirical extensions have to be made, as is, for example, presented in Ref. 2.

The models which have been proposed for the NH_3-CO_2-H_2O system are reviewed in section 2. A model for the correlation of the measurements presented in Chapter 4, is presented in section 3. Section 4 gives a comparison between experimental and calculated values and finally section 5 presents a discussion and conclusions.

5.2 Review of literature

The first model to correlate vapour-liquid equilibria of the NH_3-CO_2-H_2O system was presented by Van Krevelen et al. (3). It is based on the various chemical equilibria occurring in the solution:

$$NH_3 + CO_2 + H_2O \rightleftarrows NH_4^+ + HCO_3^- \qquad (5\text{-}2)$$

$$NH_3 + HCO_3^- \rightleftarrows NH_2CO_2^- + H_2O \qquad (5\text{-}3)$$

$$NH_3 + HCO_3^- \rightleftarrows NH_4^+ + CO_3^{2-} \qquad (5\text{-}4)$$

The equilibrium constants of these equilibria can be found from experimental equilibrium measurements which give the partial pressures of NH_3 and CO_2 and the total concentration of NH_3 and CO_2 in the liquid phase at a given temperature. Because the number of unknowns (6 liquid concentrations) is one greater than the number of equations (two mass balances, one ion balance, two vapour-liquid equilibrium relations) it is necessary to provide additional data to solve the system of equations. Since the carbonate formation (eq. 5-4) has only minor influence on the vapour-liquid equilibrium, the literature value for the equilibrium constant is used, making calculation of the other two equilibrium constants possible. The concentration of free NH_3 is found from the partial pressure of NH_3, using Henry's law and taking into account the activity coefficient of free NH_3. The vapour-liquid equilibrium for NH_3 can be expressed by:

$$NH_{3_V} \rightleftarrows NH_{3_L} \qquad (5\text{-}5)$$

The vapour-liquid equilibrium for CO_2 is combined with eq. 5-2 to yield:

$$NH_{3_L} + CO_{2_V} + H_2O_L \rightleftarrows NH_4^+ + HCO_3^- \qquad (5\text{-}6)$$

Thus, *the concentration of free* CO_2 *in the solution is omitted*. This is not a serious omission because this concentration is very small compared to the other carbon containing constituents. Using their own measurements and those of Pexton and Badger (4), Van Krevelen et al. found that the equilibrium constant of eq. 5-6 varied linearly with the ionic strength, I, of the solution for I > 0.25 mol/l. The ionic strength is defined as

$$I_c = \tfrac{1}{2} \Sigma c_i z_i^2 \qquad (5\text{-}7)$$

The equilibrium constant of the carbamate formation reaction did not appear to be dependent on the ionic strength. For the experimental conditions (20-60°C and dilute solutions) a reasonable agreement (within 5-10% relative) between measured and calculated partial pressures was found at a given temperature and liquid composition.

Wicar (5) used the same model as discussed above to correlate vapour-liquid equilibria in the system NH_3-CO_2-H_2O-urea. The latter component does not take part in the equilibria (quaternary system). For a good correlation Henry's law for NH_3 had to be modified using an empirical expression:

$$p_{NH_3} = \frac{c_{NH_3}/H_c}{a + b\, c_{NH_3}/H_c} \qquad (5\text{-}8)$$

This is obviously necessary because nearly every measured vapour composition contained more than 95 weight-% NH_3. This implies a high concentration of free NH_3 in the solution, leading to strongly non-ideal behaviour.

The approach proposed by Van Krevelen et al. (3) was also used by Frohlich (6) to correlate equilibria in a more concentrated region for solutions containing ammonium nitrate. The thermodynamic equilibrium constants of eqs. 5-4 and 5-6 were obtained from standard free enthalpy and heat of formation data. The Henry coefficient of NH_3 and the equilibrium constant of the bicarbonate-carbamate equilibrium were obtained from measurements. The relation between the activity coefficients of the ions and the ionic strength is expressed by the Debye-Hückel equation or by an extended version of this equation (see section 5.3.1). For the activity coefficient of free NH_3 an empirical equation, suggested by Van Krevelen et al., was applied (20):

$$\log \gamma_{NH_3} = k_1\, m_{NH_3} + k_2\, I \tag{5-9}$$

The parameters were found from measurements of the system NH_3-H_2O-NH_4NO_3 and the system NH_3-H_2O. The correlation of equilibrium measurements, made at 90, 120 and 150°C, yielded the thermodynamic equilibrium constant of the bicarbonate-carbamate equilibrium and an empirical constant of the extended Debye-Hückel equation. However, Frohlich did not compare experimental and calculated equilibrium compositions, making assessment of the proposed assumptions difficult. A more detailed description of Frohlich's model is presented in section 5.3.1.

Koubsky and Hladky (7) assumed that the non-idealities of the system could be accounted for by expressing the Henry coefficients of NH_3 and CO_2 as functions of ionic strength and NH_3 concentration. The results of Refs. 3 and 6 were used for the correlation. The equilibrium constants were dependent only on temperature.

Contrary to the methods described thus far, Kucheryavyi and Zinovev (8) published a model based on regression analysis of experimental results covering a large range of temperatures and pressures. The only chemical reaction mentioned is the formation of ammonium carbamate. Henry coefficients for NH_3 and H_2O, the total pressure and the equilibrium constant are given as function of temperature and liquid composition. A serious restriction is that the model can only be applied for liquid NH_3/CO_2 ratios greater than 2, due to the omission of the ammonium bicarbonate equilibrium. Calculations with this model resulted in large deviations from experimental values, probably because the range of conditions covered is too large for an accurate description and because the model contains only one chemical reaction.

A method to calculate vapour-liquid equilibria for aqueous solutions of volatile weak electrolytes, such as NH_3, CO_2, H_2S, SO_2 and HCN, was presented by Edwards et al. (9). The method can be used for a temperature range of 0-100°C and a concentration range of 10^{-4}-1 or 2 moles/kg H_2O. The model is based on the dissociation equilibria of the various weak electrolytes such as:

$$NH_3 + H_2O \rightleftarrows NH_4^+ + OH^- \tag{5-10}$$

For the NH_3-CO_2-H_2O system a linear combination of the dissociation equilibria of NH_3, CO_2 (first and second dissociation) and H_2O gives eqs. 5-2 and 5-4. Only the formation of ammonium carbamate is presented as eq. 5-3 because this compound cannot be formed by dissociation reactions alone. The activity coefficients of the ions and molecules in the solution were expressed using the equation

$$\ln \gamma_i = -\frac{\alpha z_i^2 \sqrt{I}}{1 + \sqrt{I}} + 2 \sum_{k \neq w} \beta_{ik} m_k \qquad (5\text{-}11)$$

The first term of eq. 5-11 is the classical Debye-Hückel expression for the long-range Coulombic forces, whereas the second term takes into account the short-range interactions. The short-range interactions can be devided into the classes molecule-molecule, molecule-ion and ion-ion. The molecule-molecule interaction parameter is obtained from data reduction of vapour-liquid equilibria of the aqueous solution of the weak electrolyte, in which the substance exists largely in molecular form. The other interaction parameters are obtained from correlations with the partial molar entropy of the particular ion in the solution. Edwards et al. apply the second virial coefficient of the particular electrolyte, together with the Lewis fugacity rule, to calculate vapour phase fugacity coefficients. The application of this correction to ideal behaviour of the vapour phase seems exaggerated, in relation to the model's temperature range and the accuracy of the calculation of the liquid phase composition. Comparison of calculations with experimental results from Refs. 3, 4 and 10 shows a reasonable agreement (within 20%), taking into account that no ternary parameters are necessary in the calculations. The most important limitation is the low concentration range for which the model is applicable.

To extend the range of application of the model to higher concentrations (10-20 moles/kg H_2O) and higher temperatures (0-170°C). Edwards et al. (11) presented a complicated equation for the activity coefficients, based on Pitzer's theory of electrolytes (12)

$$\begin{aligned} \ln \gamma_i = {} & - A z_i^2 \left\{ \frac{\sqrt{I}}{1 + 1.2 \sqrt{I}} + \frac{2}{1.2} \ln (1 + 1.2 \sqrt{I}) \right\} + \\ & + 2 \sum_j mj \left\{ \beta_{ij}^{o} + \frac{\beta_{ij}^{1}}{2\,I} \left[1 - (1 + 2 \sqrt{I}) \exp (-2 \sqrt{I}) \right] \right\} + \\ & - \frac{z_i^2}{4\,I^2} \sum_j \sum_k m_j\, m_k\, \beta_{jk} \left\{ 1 - (1 + 2 \sqrt{I} + 2\,I) \exp (-2 \sqrt{I}) \right\} \qquad (5\text{-}12) \end{aligned}$$

The fugacity coefficients were obtained from an equation of state based on a perturbed hard sphere theory (13). The interaction parameters were obtained as in Ref. 9. Calculations concerning the NH_3-CO_2-H_2O system were compared with results of Otsuka et al. (14). The deviations between calculated and experimental vapour pressure and vapour compositions amount up to 20% relative. It can be concluded that application of the model in a more concentrated range can only be achieved by using very complicated equations for the activity coefficients.

Beutier and Renon (15) incorporated ternary interactions in order to correlate equilibria of concentrated solutions. Two ternary interaction parameters have to be found from experimental measurements. The vapour phase is considered to be ideal for pressures below 0.2 MPa. To simplify the calculations various assumptions are made concerning the interactions, e.g. no binary and ternary interactions between molecules and no ternary moleculeion interactions occur. This approach still leads to very complicated equations for the activity coefficients. About the same accuracy is found as in the second article of Edwards et al. (11). High concentrations of free NH_3 are detrimental to a good description. According to the authors this problem can be solved by a better representation of the NH_3-H_2O system.

An approach completely different from those discussed so far is found in the works of Takahashi (16) and Yanagisawa et al. (17). In both references the Van Laar equation is used to correlate the vapour-liquid equilibria. Takahashi calculated Van Laar parameters using the binary systems NH_3-H_2O, NH_3-ammonium carbamate and ammonium carbamate-H_2O. Erroneously, the third system is presented as a binary system whereas it is part of the ternary system. For the NH_3-ammonium carbamate system no vapour-liquid equilibria are possible, except at urea synthesis conditions. In addition to these phase-theoretical objections the use of the Van Laar equation in itself, is subject to criticism. The equation is derived for non-electrolyte systems; therefore, its application here is merely a matter of curve fitting. The same remark holds for Ref. 17 in which the parameters are directly found from the ternary equilibria.

The following concluding remarks can be made concerning this literature review. Most references base the correlation on the chemical equilibria occurring in the solution. Differences occur in the description of the activity coefficients of the various species. Whereas Frohlich used a semi-empirical approach, Edwards et al. and Beutier and Renon derived their equations from a general ionic theory. For the description of concentrated solutions complicated equations are then necessary, leading to difficult methods for the solution of the equations. The regression analysis approach of Kucheryavyi and Zinovev has severe drawbacks concerning the limited concentration range (only NH_3-rich solutions) and the low accuracy. The use of the Van Laar equation to describe the phase equilibria in this system is in principle incorrect. The approach of Frohlich will be used for the development of a suitable model for the representation of the vapour-liquid equilibria presented in Chapter 4. Frohlich's model includes the chemical reactions occurring in the system and is therefore founded on a realistic physical-chemical basis. Furthermore, this model is simple and requires only a few parameters, obtainable from the measurements. Because the aim is to correlate the equilibria in the complete concentration range at a given temperature and pressure, it is likely that Frohlich's empirical approach has to be extended.

5.3 Proposal for a correlation

5.3.1 General outline

As starting point for the development of the correlation, the chemical and phase equilibria, presented in eqs. 5-3 to 5-6, are used. For every equilibrium an equilibrium constant is defined, relating activities and fugacities of the various constituents to each other. These so-called thermodynamic equilibrium constants are:

$$K_1^o = a_{NH_4} \, a_{HCO_3} \, / \, (f_{CO_2} \, a_{NH_3} \, a_{H_2O}) \qquad (5\text{-}13)$$

$$K_2^o = a_{NH_2CO_2} \, a_{H_2O} \, / \, (a_{NH_3} \, a_{HCO_3}) \qquad (5\text{-}14)$$

$$K_3^o = a_{NH_4} \, a_{CO_3} \, / \, (a_{NH_3} \, a_{HCO_3}) \qquad (5\text{-}15)$$

$$H^o = f_{NH_3} \, / \, a_{NH_3} \qquad (5\text{-}16)$$

$$p^o_{H_2O} = f_{H_2O} \, / \, a_{H_2O} \qquad (5\text{-}17)$$

Contrary to what is usually found, the activity of water is included in the various equilibrium constants. This is necessary because in concentrated solutions the activity of water is no longer constant. It should be noted that the activities of the solutes are expressed on a molality scale (moles/kg H_2O), whereas the water activity is expressed as mole fraction. This practice is usual for electrolytic solutions (18). The relation between activity and molality is given by the activity coefficient:

$$a_i = \gamma_i \, m_i \qquad (5\text{-}18)$$

By introduction of this equation into an expression for the thermodynamic equilibrium constant, a relation is found between the thermodynamic and the molality-based equilibrium constant. Taking, for example, eq. 5-15:

$$K_3^o = \gamma_{NH_4}\gamma_{CO_3} / (\gamma_{NH_3}\gamma_{HCO_3}) * m_{NH_4} \, m_{CO_3} / (m_{NH_3} \, m_{HCO_3}) = K_\gamma \, K_3 \qquad (5\text{-}19)$$

This equation also defines the relation between the molalities of the constituents in the equilibrium. Analogously, the following "constants" (which are dependent of temperature and composition) can be defined:

$$K_1 = m_{NH_4} \, m_{HCO_3} / m_{NH_3} \, p_{CO_2} \qquad (5\text{-}20)$$

$$K_2 = m_{NH_2CO_2} / m_{NH_4} \, m_{HCO_3} \qquad (5\text{-}21)$$

The eqs. 5-16 and 5-17 are transformed to:

$$p_{NH_3} = \gamma_{NH_3} \, m_{NH_3} \, H^o \qquad (5\text{-}22)$$

and

$$p_{H_2O} = \gamma_{H_2O} \, x_{H_2O} \, p^o_{H_2O} \qquad (5\text{-}23)$$

In addition to the equilibrium constants, two mass balances and the ion balance give relations between the concentrations:

$$m_{NH_3} + m_{NH_4} + m_{NH_2CO_2} = A \qquad (5\text{-}24)$$

$$m_{CO_2} + m_{HCO_3} + m_{CO_3} + m_{NH_2CO_2} = C \qquad (5\text{-}25)$$

$$m_H + m_{NH_4} = m_{NH_2CO_2} + m_{HCO_3} + m_{CO_3} + m_{OH} \qquad (5\text{-}26)$$

Because of their low values with respect to the other concentrations m_{CO_2}, m_H and m_{OH} will be neglected. The composition of a liquid phase in terms of constituents can be calculated from the component composition (A and C in eqs. 5-24 and 5-25, respectively) using the eqs. 5-19, 5-21, 5-24 to 5-26, provided that the activity coefficients can be calculated and the equilibrium constants are known. Then the partial pressures are found from eqs. 5-20, 5-22 and 5-23, again only if the activity coefficients and equilibrium constants are known. Furthermore, the fugacity coefficients should be known. It is assumed that at the low pressures studied, they are all unity. (Calculations of the pure component fugacity coefficients, based on the second virial coefficient, resulted in values greater than 0.99 for NH_3 and CO_2 and greater than 0.97 for H_2O, at the temperatures of interest and 0.1 MPa.)

It is clear that the correlation depends heavily on the ability to calculate the activity coefficients of the various species in the solution. Due to the various interactions of the ions in solution, it is extremely difficult to express the dependency of the activity coefficient on the composition. For very dilute solutions the inter-ionic attraction theory of Debye and Hückel leads to the well-known limiting law (19):

$$\log \gamma_i = - z_i^2 A \sqrt{I} \tag{5-27}$$

The constant A depends on the dielectric constant of water and the temperature and is tabulated in many textbooks (19). For a more concentrated solution (up to I = 0.1 mol/kg) the ion size, which was neglected in the derivation of eq. 5-27, has to be taken into consideration. This leads to

$$\log \gamma_i = - z_i^2 A \sqrt{I} \ / \ (1 + Ba_i \sqrt{I}) \tag{5-28}$$

Because the value of a_i cannot be accurately determined, the product Ba_i is considered to be an empirical parameter, usually with a value of 1.0 or 1.2. For more concentrated solutions eq. 5-28 can be extended with terms containing I, the first and second terms with powers of I of 1 and 1.5, respectively. Another approach is given by eq. 5-11, which describes the short-range interactions between the particular ion and all other particles in the solution. Eq. 5-28, enlarged by empirical terms in I, will be used to express the relation between the thermodynamic and concentration-based equilibrium constants of the equilibria presented in eqs. 5-6 and 5-3. Following Van Krevelen and Frohlich, the value of K_3 (eq. 5-19) has to be known in advance in order to calculate the other two constants. Therefore, eq. 5-28 as such is used for this equilibrium constant, cancelling out the activity coefficient of NH_3 and the empirical extension of eq. 5-28. The following equations are obtained:

$$\log K_1^o = \log m_{NH_4} m_{HCO_3} / m_{NH_3} p_{CO_2} x_{H_2O} - \log\gamma_{NH_3}\gamma_{H_2O} - 2A\sqrt{I}/(1 + \sqrt{I}) + + F_1(I) \qquad (5\text{-}29)$$

$$\log K_2^o = \log m_{NH_2CO_2} x_{H_2O} / m_{NH_3} m_{HCO_3} - \log \gamma_{NH_3}/\gamma_{H_2O} + F_2(I) \qquad (5\text{-}30)$$

$$\log K_3^o = \log m_{NH_4} m_{CO_3} / m_{NH_3} m_{HCO_3} - 4A\sqrt{I}/(1 + \sqrt{I}) \qquad (5\text{-}31)$$

The functions F_1 and F_2 can be determined from the equilibrium measurements at a given temperature, provided that the activity coefficients of free NH_3 and H_2O are known. The former has to be expressed as a function of the liquid phase composition. Both Van Krevelen et al. and Othmer and Frohlich (20) suggested a relation between γ_{NH_3}, m_{NH_3} and I (eq. 5-9). From equilibrium measurements of the NH_3-H_2O system, in which the ionic strength can be neglected, it was found that a linear relation between log γ_{NH_3} and m_{NH_3} (as assumed in eq. 5-9) is only a first approximation. Furthermore, the temperature dependency of the coefficient k_1 in eq. 5-9 as given by Othmer and Frohlich, is tenfold too small, resulting in values for γ_{NH_3} at higher temperatures which deviate greatly from those, calculated directly from equilibrium measurements. Therefore a new correlation was made to express the dependency of γ_{NH_3} on m_{NH_3} in the NH_3-H_2O system (section 5.3.2.2). The influence of salts on the activity of a neutral molecule (salting-in or salting-out effect) is also expressed approximately by eq. 5-9. From measurements of vapour-liquid equilibria of the NH_3-H_2O-NH_4NO_3 system, as presented in Ref. 6, it is seen that the linear relationship is inadequate for an accurate description. Using the newly developed correlation for γ_{NH_3} in a salt-free solution, the relation between γ_{NH_3} and ionic strength is found from results of Frohlich (16) and Schultz and Elmore (30) (section 5.3.2.2). For the application of this correlation to the NH_3-CO_2-H_2O system it has to be assumed that the effect of the ions present in the equilibrium solution, is equal to that of NH_4 and NO_3-ions, present in an NH_4NO_3 solution.

The activity coefficient of water can theoretically be found from the activity coefficient of all solutes using the Gibbs-Duhem equation. However, because the ionic activity coefficients are not calculated separately, this method cannot be used. Therefore, the activity coefficient of water, found from the partial pressure of H_2O, has to be correlated with the liquid composition, preferably with the ionic strength.

5.3.2 *Estimation of parameters*

5.3.2.1 *Thermodynamic equilibrium constants*

The thermodynamic equilibrium constants (as defined in eqs. 5-13 to 5-17) can be estimated by various methods. Frohlich used free energy and heat of formation data at 25°C to estimate K_1^o and K_3^o. H^o was found from experimentally determined vapour pressures of the NH_3-H_2O system by plotting the logarithm of the vapour pressure against the NH_3 mole fraction and determining the slope of the so obtained curve at $X_{NH_3} = 0$. Especially at higher temperatures this method is inaccurate due to the strong curvature of the lines. Because no thermochemical data were available concerning the carbamate ion, K_2^o was estimated from the ternary and quaternary measurements. Very large scatter in the determined values was found, making their accuracy doubtful. Edwards et al. (9) obtained Henry coefficients for NH_3 and CO_2 by data reduction of binary vapour-liquid equilibria from the literature. They also presented dissociation constants of NH_3 and CO_2 (first dissociation step) obtained from the literature. Together with the secondary dissociation constant of CO_2 and the dissociation constant of pure H_2O (15) these constants and Henry coefficients can be used to calculate K_1^o, K_3^o and H^o. Less is known about the equilibrium between bicarbonate and carbamate. Faurholt (21, 22) presented values for K_2^o at 0 and 18°C. The heat of reaction resulting from these values is -12.84 kJ/mole. From heat of solution data of ammonium carbamate as given by Claude (23), the heat of reaction for the equilibrium of eq. 5-3 is calculated as -13.05 kJ/mole. The K_2 values at an ionic strength of 0.5 molar, as presented by Christensson et al. (24) agree reasonably well with the values at zero ionic strength of Faurholt. Because of this good agreement and the lack of other data Faurholt's equilibrium constants will be extrapolated to the temperatures of interest to obtain values of K_2^o for the proposed model. The discrepancy of the values so-obtained with those of Frohlich is very large (see Fig. 5-1). Edwards et al. (9), referring to Faurholt, presented an equation for the temperature dependency of K_2^o, from which a heat of formation of -16.61 kJ/mole can be calculated. Furthermore, Faurholt's K_2^o-values cannot be calculated with the given equation. In a second article (11) Edwards et al. presented another equation, resulting in a larger heat of reaction (-24.10 kJ/mole) and again not leading to reliable values for K_2^o. In this second article new correlations are also presented for the other constants for an enlarged temperature range. Calculations show that the values of the first dissociation constant of CO_2 deviate substantially from those given in Ref. 9, which are based on literature values up to 65°C. The differences between values for the other constants are within 2%, except for K_2^O. The correlations presented in Ref. 11 will be used to calculate values for K_1^O, K_3^O and H^O.

The vapour pressure of H_2O is calculated using the Antoine equation, its coefficients were taken from Ref. 25.

The various equilibrium constants used in the model calculations are plotted as a function of temperature in Fig. 5-1, together with the values of Frohlich and those of Christensson et al. concerning K_2^O. It is seen that the deviations between the values of Frohlich and those of Edwards et al. concerning K_1^O and K_3^O increase with temperature, due to Frohlich's extrapolations from 25°C. The Henry coefficient for NH_3 also differs for both literature sources. The results of Christensson et al. at a ionic strength of I = 0.5 molar agree well with the extrapolated values of Faurholt, taking into account the effect of ionic strength.

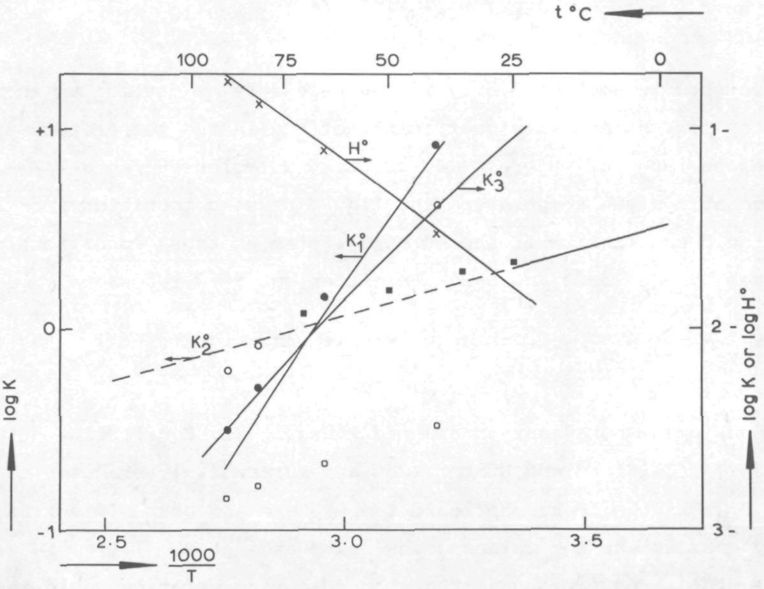


Fig. 5-1 Thermodynamic equilibrium constants and Henry coefficient for ammonia. Lines based on Ref. 11. Closed circles, open squares and open circles and crosses denote values from Ref. 6 for K_1^O, K_2^O, K_3^O *and* H^O*, respectively. Closed squares from Ref. 24.*

5.3.2.2 The activity coefficients

Eq. 5-28, eventually extended with empirical terms, is used to calculate the deviations of the concentration-based equilibrium constants from the thermodynamic ones (eqs. 5-29 to 5-31). The parameter B does not vary much with temperature, its value being about $0.33\ 10^{10}\ m^{-1}\ mol^{-0.5}\ kg^{0.5}$ (26). The value of 1 for the product Ba_i therefore implies a distance of closest approach of $3\ 10^{-10}$ m. The parameter A depends on the temperature, the dielectric constant of water and the density of water, according to

$$A = 1.8246\ 10^6\ (DT)^{-1.5}\ d_o^{\ 0.5} \qquad (5\text{-}32)$$

Using values of A given by Hamer (26) at temperatures from 20 to 100°C, the following equation was obtained by linear regression:

$$A = 0.4915 + 7.025\ 10^{-4}\ t + 2.664\ 10^{-6}\ t^2 + 7.489\ 10^{-9}\ t^3 \qquad (5\text{-}33)$$

As discussed in section 5.3.1, it was necessary to develop an accurate correlation for the activity coefficient of NH_3 in the temperature and concentration range of interest (40-120°C, 0-30 moles NH_3/kg H_2O). γ_{NH_3} can be calculated at a given temperature and liquid phase composition from the vapour-liquid equilibrium of the NH_3-H_2O system at those conditions, represented by eqs. 5-22 and 5-23. Rewritten eq. 5-22 reads:

$$\gamma_{NH_3} = y_{NH_3}\ P/H^o\ m_{NH_3}$$

Ideal vapour phase behaviour is assumed in eq. 5-22. Equilibrium data of Wucherer (27), Clifford and Hunter (28) and Perman (29) were used to correlate γ_{NH_3} and m_{NH_3} in the above mentioned temperature and composition range. For the Henry coefficient the values given by Edwards et al. (11) were used. A linear least squares fit showed that the following relation could represent the measurements:

$$\log \gamma_{NH_3} = a_1\ m_{NH_3} + a_2\ m_{NH_3}^{\ 2} \qquad (5\text{-}34)$$

$$a_1 = 0.01758 - 9.77\ 10^{-5}\ t$$
$$a_2 = -1.22\ 10^{-4} + 4.7\ 10^{-7}\ t$$

The regression can be qualified by a squared multiple regression coefficient of 0.9907 and a residual root mean square of 0.0072. Eq. 5-34 gives a temperature coefficient of a_1 tenfold that presented in Ref. 20. A comparison of literature results and eq. 5-34 at 90°C is made in Fig. 5-2, whereas Fig. 5-3 presents the predicted γ_{NH_3} at various temperatures.

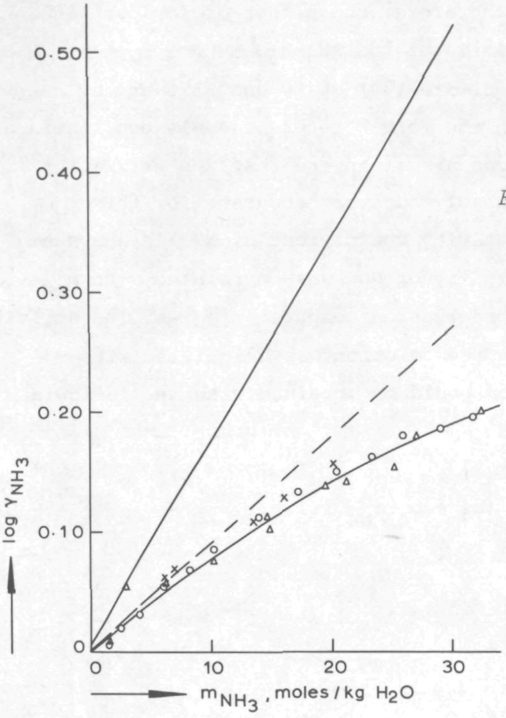


Fig. 5-2 Activity coefficient of NH_3 as function of concentration at 90°C in the NH_3-H_2O system. Triangles: Ref. 28, circles: Ref. 27, crosses: Ref. 6. Curved line: eq. 5-34. Straight lines: Ref. 20. The dashed line was obtained by applying a correction on the temperature dependence of k_1 (eq. 5-9).

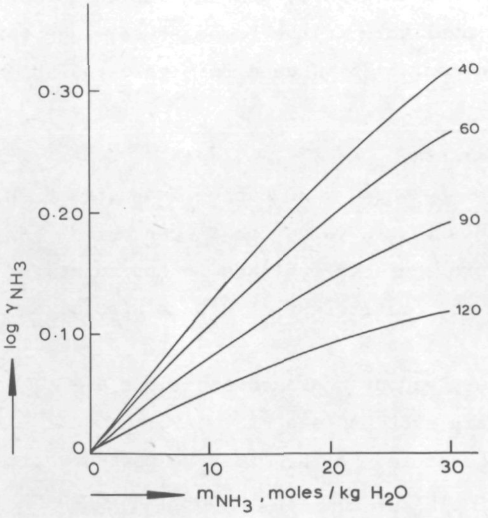


Fig. 5-3 Activity coefficients of NH_3 in the NH_3-H_2O system, as predicted by eq. 5-34. Numbers by the lines denote the temperature in °C.

The influence of ionic strength on the activity coefficient of free NH_3 is more difficult to represent. The ions which are largely responsible for the interaction in the NH_3-CO_2-H_2O system are NH_4^+, HCO_3^- and $NH_2CO_2^-$. It is, however, not possible to estimate their effect from measurements because in the system chemical reactions occur. Therefore, the effect of ionic strength is estimated from vapour-liquid equilibria of the NH_3-H_2O-NH_4NO_3 system. Measurements were made by Schultz and Elmore (30) at 10 and 35°C and by Frohlich (6) at 90, 120 and 150°C. In the former reference only equilibria with two different NH_4NO_3 concentrations are given, so that the estimation of the effect of ionic strength is probably not very accurate for this temperature range. The ratio of the activity coefficient of NH_3 in a system with and without NH_4NO_3 at a given molality of NH_3 was correlated with m_{NH_3}, I and the temperature, using a linear regression computer program. The activity coefficient of NH_3 ($\gamma^*_{NH_3}$) in the salt-free solution was calculated with eq. 5-34. A satisfactory representation could be obtained with the following expression:

$$\log \gamma_{NH_3}/\gamma^*_{NH_3} = (b_1 + b_2\, m_{NH_3})\, I + (b_3 + b_4\, m_{NH_3})\, I^2 \qquad (5\text{-}35)$$

$$b_1 = -0.0147 + 6.5\ 10^{-5}\ t$$
$$b_2 = -\ 7\ 10^{-4} - 5.61\ 10^{-6}\ t$$
$$b_3 = 1.9\ 10^{-4}$$
$$b_4 = 3.03\ 10^{-5}$$

The squared multiple correlation coefficient is 0.9695, and the residual root mean square 0.0155. Because no data are available in the temperature range for which the activity coefficient is needed, eq. 5-35 is used for its calculation.

5.3.2.3 Parameters from ternary measurements

The empirical functions F_1 and F_2 of eqs. 5-29 and 5-30 can be found from ternary equilibrium measurements, provided that a value for K_3 can be calculated (eq. 5-31). The calculation procedure is outlined in Appendix 3. As a result of the calculation the activity coefficient of H_2O is also given for the particular conditions.

Because at 40°C and 0.1 MPa the ternary vapour phase compositions are situated very close to those of the binary systems (see Fig. 4-3a) no calculations were performed at this temperature. At the other temperatures it appeared that the calculated results were very sensitive to the liquid phase

composition values used. Better results were obtained by smoothing of the boiling point curves. Liquid phase compositions were taken from the smoothed curves at the same NH_3-content as the original data points.
Calculations with experimental liquid phase compositions with a high ionic strength (at 65°C) or with a high NH_3/CO_2-ratio (at 90.1°C) sometimes resulted in an early termination because a negative carbamate concentration was calculated. This corresponds to an excessively large concentration of free NH_3, calculated from the vapour-liquid equilibrium of NH_3 (eq. 5-22). Obviously the reason for this phenomenon is the inaccuracy of the applied correlation to calculate γ_{NH_3} (eq. 5-35). The effect of the ionic strength on the activity coefficient is estimated from equilibrium measurements of the NH_3-H_2O-NH_4NO_3 system, based on the assumption that the ions present in the liquid phase of this system have the same influence on molecular NH_3 as the ions present in the NH_3-CO_2-H_2O liquid phase.

The results of the calculations are presented in Fig. 5-4. It is seen that at 65°C a clear linear relationship is found between the functions F_1 and F_2 and the ionic strength, as is expected from theory. At the other temperatures much scatter is found. Due to the fact that the solutions at these temperatures contain much less solutes than at 65°C, the ionic strength is also much less. Because the empirical extensions in the eqs. 5-29 and 5-30 are relatively unimportant at an ionic strength below 1 mole/kg, it can be expected that their estimation is inaccurate. However, a close inspection of the results revealed that calculations with measurements situated on the CO_2-rich part of the phase diagram yielded results which satisfactorily obeyed the expected linear relationship. This is because relatively high values for p_{CO_2} and m_{HCO_3} will produce more accurate values for F_1 and F_2. At 81.5°C only the experiments with a high CO_2-content were used. For 90.1°C ($P = 0.1088$ MPa) all measurements which gave convergence on calculation were situated on the CO_2-rich part of the phase diagram. On extrapolation to $I = 0$ the lines of Fig. 5-4 should give the values of log K_1^o or log K_2^o at the given temperatures. It is seen that this indeed happens for F_1 at 65°C and 90.1°C. At 81.5°C a much smaller value is found. The reason for this anomaly is not clear. The extrapolated lines of F_2 all produced values of K_2^o higher than those extrapolated from Faurholt's measurements (see section 5.3.2.1). Because the latter extrapolation is based on only two experimental values of unknown accuracy, deviations from values found by extrapolation to $I = 0$ may easily occur.

The slopes and the values of K_2^o from Fig. 5-4 are presented in Table 5-1. It is seen that at every temperature the effect of the ionic strength on the value of K_1 is positive, whereas the effect on the value of K_2 is negative.

Temperature	Slopes		K_2	γ_{H_2O}
	C_1	C_2	estimated	average
65	0.0566	-0.1580	2.59	0.892
81.5	0.292	-0.8416	7.58	0.967
90.1	0.420	-8.6478	66.43	1.010

Table 5-1 Parameters obtained from ternary measurements.

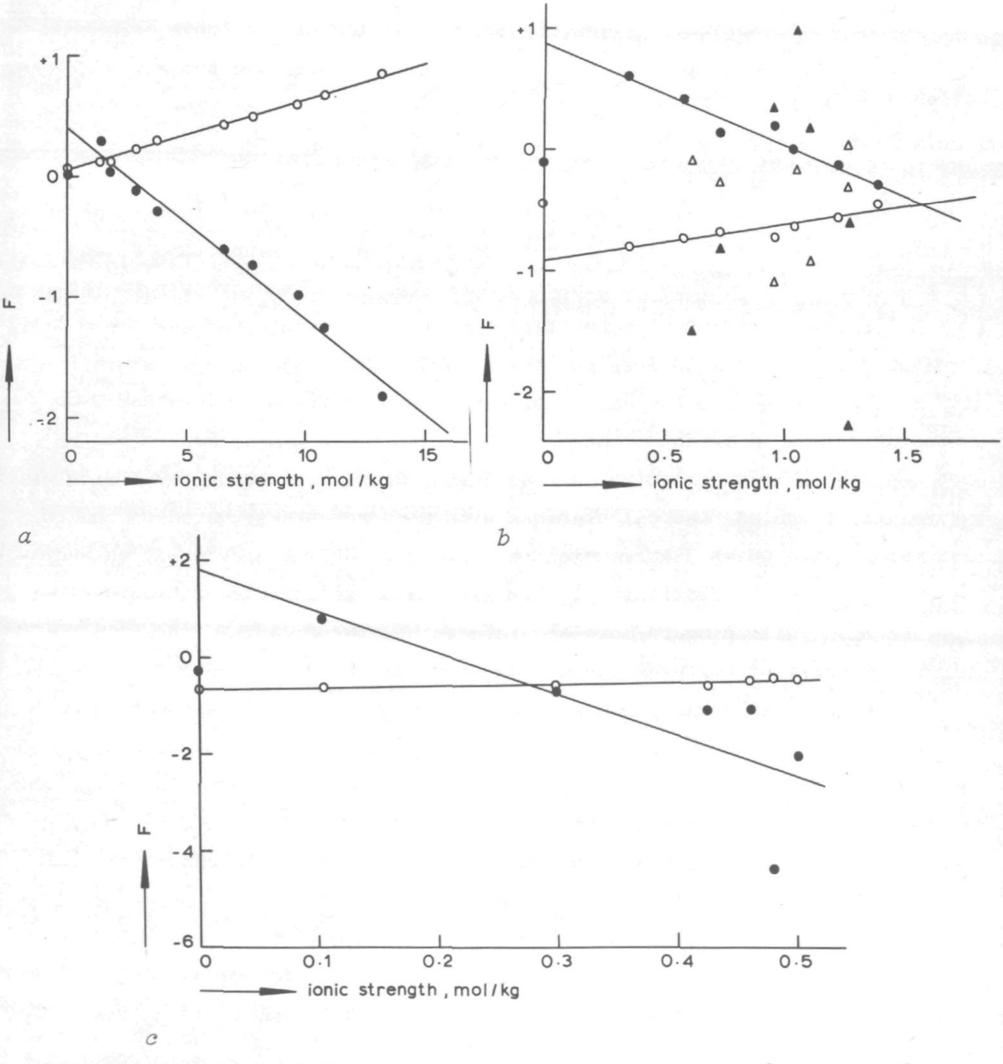


Fig. 5-4 Functions F_1 and F_2 at various temperatures. a: 65°C, b: 81.5°C, c: 90.1°C. Open symbols: F_1, closed symbols F_2. Triangles: results based on NH_3-rich equilibria. Points for $I = 0$ from Ref. 11 and Refs. 22 and 23.

The proportionality factors are strongly dependent on the temperature. It should be noted, however, that the range of the ionic strength at 81.5 and 90.1°C is too small to draw definite conclusions concerning this temperature dependence. For the same reason the accuracy of the values found for K_2^o is doubtful. It is seen from Table 5-1 that K_2^o increases with temperature, which is impossible for an exothermic reaction (see Section 5.3.2.1). To increase the accuracy it is necessary to perform measurements at higher pressures at these temperatures, at which higher ionic strengths occur.

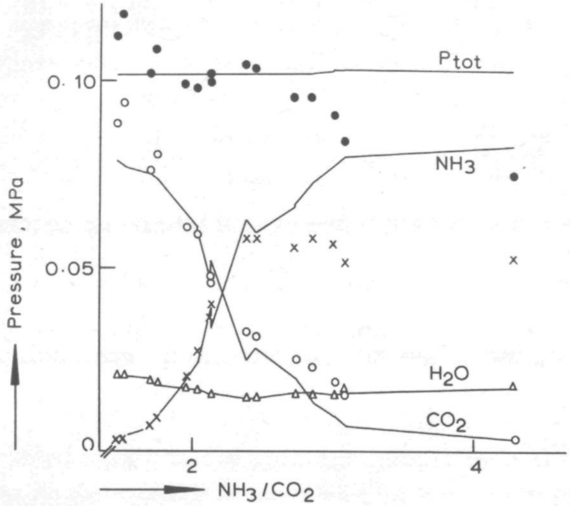
From the evaluation of the measurements values for γ_{H_2O} were also obtained. Due to the scatter in the results it was not possible to correlate the activity coefficient of water with the ionic strength. The average values are presented in Table 5-1. At 65°C unrealistically low values were found as caused by a too low vapour phase water content (see Section 4.3).

5.4 Equilibrium calculations

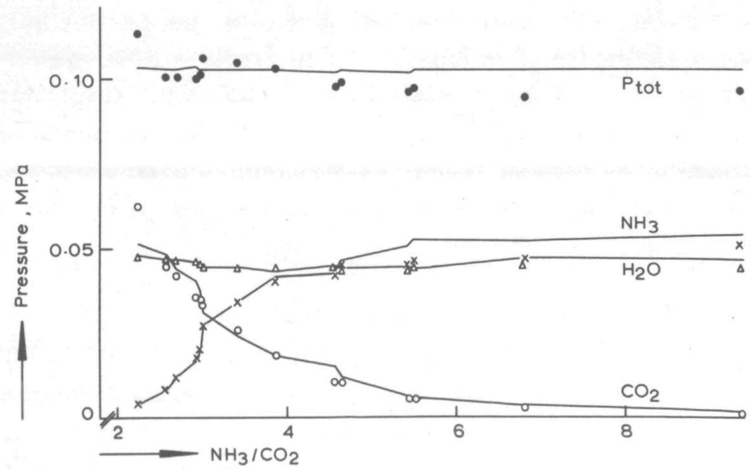
With the parameters, estimated in section 5.3, it is possible to calculate the vapour phase composition and the vapour pressure at a given temperature and liquid phase composition of the NH_3-CO_2-H_2O system. The calculation procedure is described in Appendix 3. The values of the parameters obtained from the ternary measurements were taken from Table 5-1. The results of a calculation are the partial pressures of NH_3, CO_2 and H_2O, from which the vapour phase composition and the total pressure are easily calculated. In comparing measured and calculated results it is preferable to use the partial pressures for comparison, because these quantities, contrary to molar percentages, are independent of one another. The results of calculations at 65, 81.5 and 90.1°C are presented in Fig. 5-5.

It is seen that the calculated partial pressures at 65°C agree well with the experiments, except for the ammonia-rich area. Probably this is due to the inaccuracy of the correlation of γ_{NH_3} with m_{NH_3} and I in this area of high ionic strength. At 81.5°C the good agreement between experimental and calculated values continues into the ammonia-rich area. The calculated total pressures deviate about 5% from the experimental values, again probably a result of too low values for γ_{NH_3}. Qualitatively the same behaviour is found at 90.1°C.

Calculations were also performed at 80°C with parameters obtained at 81.5°C. At this temperature no vapour phase compositions were determined. Because the parameter estimation at 81.5°C yielded doubtful values, the partial pressures at 80°C were also calculated with the values of C_1 and C_2 zero and


Ptot
NH3
H2O
CO2
0.10
0.05
0
2
4
Pressure , MPa
NH3/CO2

a


Ptot
NH3
H2O
CO2
0.10
0.05
0
2
4
6
8
Pressure , MPa
NH3/CO2

b

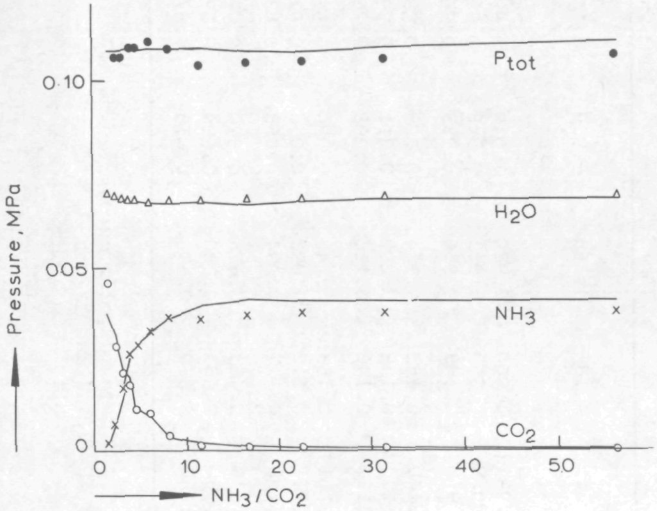


Fig. 5-5 *Comparison of measured and calculated partial pressures. a: 65°C, b: 81.5°C, c: 90.1°C (P = 0.1088 MPa). Lines are drawn by connecting the measured partial pressures. Symbols denote calculated results.*

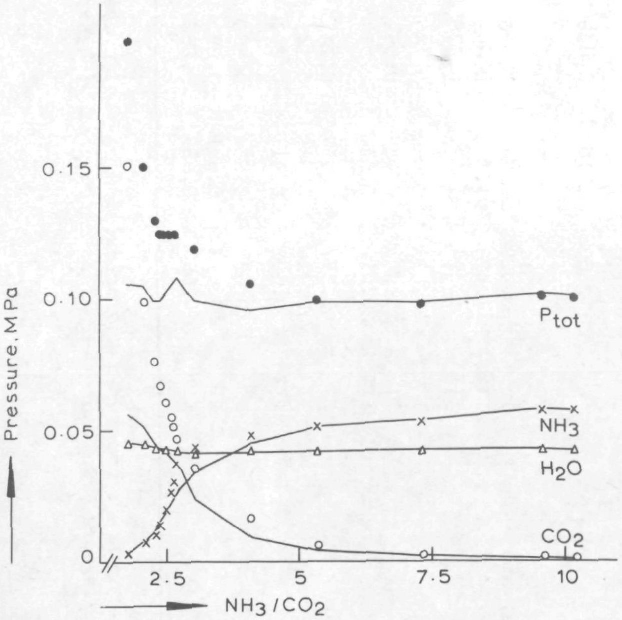


Fig. 5-6 *Calculated partial pressures at 80°C. Lines are drawn by connecting calculated partial pressures using K-values from Refs. 11, 21 and 22 and $C_1 = C_2 = 0$. Symbols represent calculations with parameters obtained at 81.5° (Table 5-1).*

			Liquid NH_3/CO_2 ratio								
			1.500	2.103	3.036	3.144	3.641	4.186	4.759	5.939	8.146
Total pressure, atm		I	0.989	0.997	0.996	0.997	0.991	1.000	0.980	1.019	0.997
		II	1.423	1.060	0.895	0.944	0.958	0.953	0.981	0.948	0.996
		III	1.394	1.137	0.935	0.967	0.958	0.943	0.956	0.939	0.989
	NH_3	I	0.033	0.057	0.069	0.091	0.140	0.155	0.184	0.229	0.280
		II	0.009	0.039	0.064	0.093	0.133	0.158	0.202	0.212	0.291
		III	0.012	0.040	0.067	0.088	0.122	0.146	0.186	0.205	0.286
Partial pressure, atm	CO_2	I	0.277	0.257	0.242	0.230	0.181	0.153	0.140	0.080	0.039
		II	0.720	0.330	0.141	0.164	0.141	0.112	0.098	0.056	0.030
		III	0.692	0.411	0.183	0.196	0.156	0.117	0.094	0.058	0.031
	H_2O	I	0.691	0.674	0.686	0.675	0.676	0.683	0.676	0.670	0.691
		II	0.694	0.691	0.690	0.687	0.684	0.683	0.680	0.680	0.676
		III	0.690	0.687	0.685	0.683	0.680	0.679	0.676	0.676	0.672

Table 5-2 *Comparison of measured and calculated partial pressures at 90.1°C. I: measured, II: calculated with parameters from Table 5-1, III: calculated with K-values from Refs. 11, 21 and 22 and* $C_1 = C_2 = 0$.

the values of K_1^o and K_2^o as obtained from Refs. 11 and 21, 22, respectively. It is seen from Fig. 5-6 that at low NH_3/CO_2 ratios the calculated CO_2 partial pressures differ for the two sets of parameters. The same comparison can be made at 90.1°C. At this temperature measured vapour phase compositions are also available. The results are presented in Table 5-2. From Fig. 5-6 and Table 5-2 it is seen that setting the parameters C_1 and C_2 equal to zero has only a minor influence on the calculated results at these temperatures. The reason for this is the low ionic strength of the solutions at these conditions making it unnecessary to provide for extensions in the Debye-Hückel equation.

5.5 Discussion and conclusions

It can be concluded that the proposed model can describe the vapour-liquid equilibria of the NH_3-CO_2-H_2O system reasonably well, because it is based on the physical and chemical equilibria actually occurring in the system. A highly accurate representation is, however, difficult because of the strong non-ideality of the liquid phase. It was necessary to introduce empirical parameters, estimated from the ternary measurements, to account for the influence of the various ions on each other. For reasons of simplicity the ionic strength was chosen to represent the total concentration of the ions. Because the number of different ions is limited, this approach as a first approximation can give good results. This can especially be seen from the evaluation results at 65°C, giving linear relationships between the deviation functions F_1 and F_2 and I. Because these functions were obtained from the measurements, it is no wonder that the calculated partial pressures agree with the measurements. Because of a low ionic strength, the functions F_1 and F_2 can be omitted in calculations at a total pressure up to 0.1 MPa at temperatures of 80°C and above. For an accurate estimation of F_1 and F_2 at these temperatures it is necessary to measure the vapour-liquid equilibria at pressures above 0.1 MPa, because then the ionic strength will become sufficiently large.

To increase the accuracy of the prediction of the ammonia partial pressure a better representation of the influence of the ionic strength on the activity coefficient of NH_3 is necessary. The present correlation predicts a too low value for γ_{NH_3}. In the evaluation of the measurements this may lead to the impossibility of obtaining ternary parameters, whereas in the equilibrium calculations the predicted partial pressures are too small.

Symbols used

α, A	Debye-Hückel parameter	$kg^{0.5}/mole^{0.5}$
a	activity	
a_i	distance of closest approach of ions	m
A	total molality NH_3	mole/kg H_2O
B	Debye-Hückel parameter	$kg^{0.5}/m\ mole^{0.5}$
β	interaction parameter	kg H_2O/mole
c	molarity	mole/liter
C	total molality CO_2	mole/kg H_2O
D	dielectric constant of H_2O	
d_o	density of H_2O	gr/ml
f	fugacity	
F	empirical function eqs. 5-29, 5-30	
H	Henry coefficient	MPa· kg H_2O/mole
H_c	Henry coefficient on molarity scale	MPa liter/mole
I	ionic strength	mole/kg H_2O
I_c	ionic strength on molarity scale	mole/liter
K	equilibrium constant	
m	molality	mole/kg H_2O
p	pressure	MPa
P	total pressure	MPa
t	temperature	°C
T	absolute temperature	K
y	mole fraction vapour phase	
z	valence	
γ	activity coefficient	
ϕ	fugacity coefficient	

References

1. J.M. Prausnitz, *Molecular thermodynamics of fluid-phase equilibria*, Prentice-Hall, Englewood Cliffs, New Jersey, 1969.
2. E. Hála, *Inst. Chem. Eng. Symp. Ser.* 32 3:8 (1969).
3. D.W. van Krevelen, P.J. Hoftijzer, F.J. Huntjens, *Recl. Trav. Chim. Pays-Bas* 68 (1949) 191.
4. S. Pexton, E.H.M. Badger, *J. Soc. Chem. Ind. London Trans. Commun.* 57 (1938) 106.
5. S. Wicar, *Br. Chem. Eng.* 8 (1963) 818.
6. G.J. Frohlich, *Vapor-liquid equilibria of aqueous systems containing ammonia and carbon dioxide*, PhD-thesis, Polytechnic Institute of Brooklyn, 1957.
7. P. Koubsky, V. Hladký, *Chem. Prum.* 25 (1975) 234; *Int. Chem. Eng.* 16 (1976) 392.
8. V.I. Kucheryavyi, G.N. Zinovev, *Khim. Prom-st*45 (1969) 354; *Chem. Abstr.* 71 (1969) 54192.
9. T.J. Edwards, J. Newman, J.M. Prausnitz, *AIChE J.* 21 (1975) 248.
10. E.H.M. Badger, D.S. Wilson, *J. Soc. Chem. Ind. London* 66 (1947) 84.
11. T.J. Edwards, G. Maurer, J. Newman, J.M. Prausnitz, *AIChE J.* 24 (1978) 966.
12. K.S. Pitzer, *J. Phys. Chem.* 77 (1973) 268.
13. R. Nakamura, G.J.F. Breedveld, J.M. Prausnitz, *Ind. Eng. Chem. Process Des. Dev.* 15 (1976) 557.
14. E. Otsuka, S. Yoshimura, M. Yakabe, S. Inoue, *Kogyo Kagaku Zasshi* 63 (1960) 1214; *Chem. Abstr.* 56 (1962) 9501c.
15. D. Beutier, H. Renon, *Ind. Eng. Chem. Process Des. Dev.* 17 (1978) 220.
16. T. Takahashi, *Kogyo Kagaku Zasshi* 65 (1962) 837; *Chem. Abstr.* 59 (1963) 2216h.
17. Y. Yanagisawa, Y. Harano, T. Imoto, *Nippon Kagaku Kaishi* (1973) (5) 917; *Chem. Abstr.* 79 (1973) 35558.
18. K. Denbigh, *The principles of chemical equilibrium*, Cambridge University Press, Cambridge, 1968, chapter 10.
19. H.S. Harned, B.B. Owen, *The physical chemistry of electrolytic solutions* Reinhold, New York, 1958.
20. D.F. Othmer, G.J. Frohlich, *Ind. Eng. Chem. Process Des. Dev.* 3 (1964) 270.
21. C. Faurholt, *Z. Anorg. Allg. Chem.* 120 (1921) 85.
22. C. Faurholt, *J. Chim. Phys. Phys-Chim. Biol.* 22 (1925) 1.
23. B. Claude, *Rev. Chim. Miner.* 2 (1965) 327.
24. F. Christensson, H.C.S. Koefoed, A.C. Petersen, K. Rasmussen, *Acta Chem. Scand. Ser. A* 32 (1978) 15.
25. M. Hirata, S. Ohe, K. Nagahama, *Computer aided data-book of vapour-liquid equilibria*, Elsevier, Amsterdam, 1975, p. 11.
26. W.J. Hamer, *Theoretical mean activity coefficients of strong electrolytes in aqueous solutions from 0 to 100^{o}C*, National Bureau of Standards, Washington, 1968, p. 3.
27. J. Wucherer, *Z. ges. Kälte-Ind.* 39 (1932) 97.
28. I.L. Clifford, E. Hunter, *J. Phys. Chem.* 37 (1933) 101.
29. E.P. Perman, *J. Chem. Soc. Trans.* 79 (1901) 718.
30. J.F. Schultz, G.V. Elmore, *Ind. Eng. Chem.* 38 (1946) 296.

6 PROCESSES RELATED TO THE NH_3-CO_2-H_2O SYSTEM

6.1 Introduction

In this chapter a brief discussion will be presented concerning the technological operations in which the vapour-liquid equilibria of the system NH_3-CO_2-H_2O play an important role. In particular the separation of NH_3 and CO_2 by distillation methods will be investigated. Due to the formation of chemical compounds in the liquid phase, the behaviour of the system when subject to distillation or rectification differs appreciably from systems in which no chemical reactions or azeotropy occur. Although not present at the conditions studied in this thesis, a binary minimum pressure azeotrope in the NH_3-CO_2 system characterizes the ternary system's behaviour on distillation. Therefore, a general description of the distillation behaviour of a ternary system with a binary minimum pressure azeotrope will be given. From this description interesting conclusions can be drawn concerning this behaviour.

In Chapter 1 the most important industrial processes which are related to the NH_3-CO_2-H_2O system were already mentioned: the synthesis of urea and of melamine. Especially the coupling of the two processes is an example of the application of phase equilibria for a chemical process. Because the linking together of process plants decreases flexibility and may lead to a lower on-stream factor for both units, attention will also be given to the complete separation of NH_3 and CO_2, produced in the melamine synthesis.

Whereas the connection of a urea plant with a melamine plant concerns only a recirculation stream, a more complete integration is possible in the combined synthesis of ammonia and urea. Although numerous patents and articles discuss the possibilities of such an integration, no integrated process has yet been built. A brief discussion concerning this integration will be given in section 6.4. In addition to the processes for production of NH_3, urea or melamine, the phase behaviour of the NH_3-CO_2-H_2O system is important in the cleaning of certain process effluents (sour water stripping). Here the removal of especially NH_3, up to concentrations in the ppm region, requires knowledge of the phase behaviour of the system. This application will be briefly discussed in section 6.4.

The assessment of the various processes in which vapour-liquid equilibria of the NH_3-CO_2-H_2O system are important is difficult. The process descriptions given in articles, are often superficial concerning the physico-chemical principles of the process. Patents always contain a comprehensive explanation of the invention, but the theoretical basis is often not mentioned or hardly discussed. Due to this lack of information, it is difficult to draw definite conclusions from the presented material.

6.2 Distillation and rectification in a ternary system with one binary azeotrope

It is a well-known fact that a binary mixture containing an azeotrope can not be separated into its components by distillation. Depending on the kind of azeotrope (positive or negative), on distillation the azeotropic composition is finally obtained in the residue or in the distillate. A ternary system in which one or even more binary azeotropes are present will also exhibit unusual behaviour upon distillation. This behaviour was already studied at the turn of the century (1). Reinders and De Minjer (2) investigated the distillation behaviour of ternary systems at constant pressure, which is nearly always the case in practice. Some conclusions, which were obtained by Schreinemakers (1), were again derived by Haase (3). This author did not use the Van der Waals equation of state, as Schreinemakers and others did, in the derivations.

Especially the work of Reinders and De Minjer (2) will be used to give insight in the distillation behaviour of the NH_3-CO_2-H_2O system. This system belongs to the ternary systems A-B-C, with a maximum temperature azeotrope (at constant pressure) in the binary system BC and with the following sequence of boiling points at a given constant pressure:

$$t_B \text{ and } t_C < t_{AZ} < t_A$$

It is assumed that no critical behaviour is found at the conditions under consideration. For two temperatures the vapour-liquid equilibria are sketched in Fig. 6-1. To investigate the distillation behaviour assume that liquid L_1 is the mixture to be distilled. On distilling this mixture a small amount of vapour (composition V_1) will be distilled off. Therefore the liquid composition changes to L_2, situated on the extended tie-line L_1V_1. Because the more volatile components are removed from L_1, L_2 has a higher boiling point. On continued distillation the liquid composition will at first shift in the

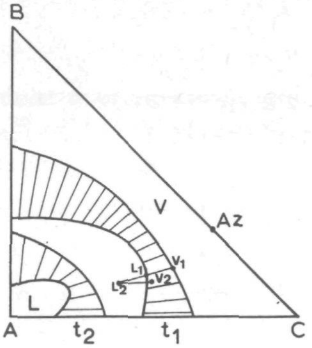


Fig. 6-1 *Isobaric vapour-liquid equilibria of the system ABC at two temperatures. $t_1 < t_2$. Az: binary maximum temperature azeotrope. For further explanation see text.*

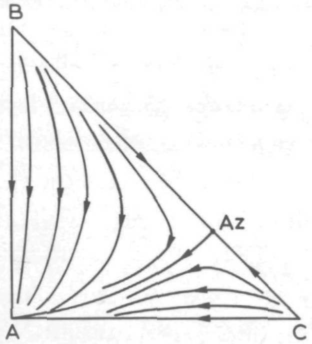


Fig. 6-2 *Distillation lines of system ABC at constant pressure.*

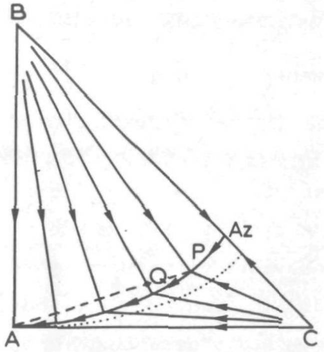


Fig. 6-3 *Ideal rectification lines of system ABC at constant pressure. Dotted line: rectification boundary line at higher pressure. For further explanation see text.*

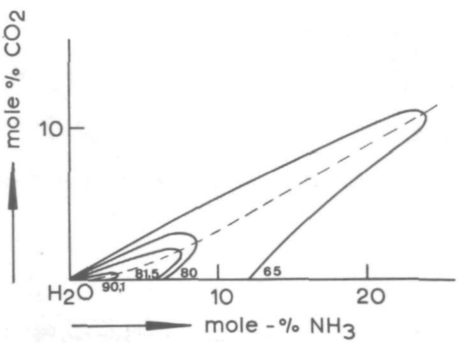


Fig. 6-4 *Boiling point lines and estimated boundary line of the system NH_3-CO_2-H_2O at 0.1 MPa. Figures at isotherms denote temperature in °C.*

direction of the tie-line L_2V_2. The line of the so obtained liquid compositions is called the distillation line. In every point of such a line a tie-line can be drawn tangent to the line. For the case considered here the distillation lines are presented in Fig. 6-2. It is seen that the lines can be divided into two bundles separated by the line Az-A, the boundary line. More interesting than simple distillation is the rectification or the fractional distillation. With this method the vapour formed is partially condensed with enrichment of the more volatile components. This process is repeated throughout the still. In an ideal rectification process a pure component will eventually be distilled off (in the case no azeotropy occurs). Analogous to the distillation lines, rectification lines can be constructed. In the ideal case they are straight. For the present case, in which a binary azeotrope is present, the rectification lines are shown in Fig. 6-3. Again a boundary line is found. Reinders and De Minjer (2) have pointed out that this rectification boundary line cannot be straight if the distillation boundary line is also not straight. Both lines may coincide, or otherwise the rectification boundary line lies on the concave side of the other line.

By erecting a temperature axis perpendicular to the composition triangle at a constant pressure the temperature can be considered to be the third variable. All liquid compositions then form an isobaric boiling point surface. The boundary line is situated on the ridge of this surface. This type of liquid surface is also mentioned by Kaasenbrood (4) for the quasi-ternary system NH_3-CO_2-(urea : H_2O = 1 : 1) and by Lemkowitz (20) for the NH_3-CO_2-H_2O system at chemical equilibrium (urea present). Chermin (23) presented a general discussion of this type of vapour-liquid equilibria, including also quaternary systems.

It is seen from Fig. 6-3 that on rectification of a certain liquid mixture firstly B or C is the distillate, depending on the situation of the original mixture in the triangle relative to the boundary line. The composition of the residue will approach the boundary line and then will follow this boundary line towards A, thereby producing vapours with compositions between Az and C. It can be concluded that in this system it is not possible to separate a ternary mixture into its components by isobaric rectification. Only one of the two more volatile components can be obtained in pure state. To obtain the other volatile component the boundary line has to be overstepped. One way to do this is to make use of the pressure dependence of the position of the boundary line in the triangle, which is related to the pressure dependence of the azeotropic composition. A liquid composition situated at the boundary line at pressure p_1 will lie alongside the boundary line at pressure p_2. With a well chosen pressure change the boundary line is therefore transgressed. This method is discussed further in section 6.3.3 for the NH_3-CO_2-H_2O system. The second method makes use of the curvature of the boundary line. When point P in Fig. 6-3 is reached from the area rich in C, addition of a certain amount of A will give a mixture on the other side of the boundary line (Q), yielding B on rectification. For a further discussion see section 6.3.3.

The above mentioned general behaviour also holds for the system NH_3-CO_2-H_2O at 0.1 MPa. Although the vapour-liquid equilibria at temperatures below 65^oC end in equilibria involving solids (see Chapter 2) and the NH_3-CO_2 system does not exhibit azeotropy at 0.1 MPa, the behaviour of the system is qualitatively similar to that sketched in Figs. 6-2 and 6-3. The position of the boundary line can be estimated from the equilibrium measurements presented in Fig. 4-4 by connecting those liquid compositions with a minimum water content on a given isotherm (see Fig. 6-4). As is seen from Fig. 6-4 the boundary line ends on the NH_3-H_2O side or is tangent to this side. According to Haase (3) the general behaviour of a boundary line when approaching the least volatile component corner point is such that the line will be tangent to the binary side which does not contain the component with the greatest volatility. This is indeed the case with the present system, in which CO_2 is the most volatile component.

6.3 The coupling of a urea plant with a melamine plant

6.3.1 Introduction

Melamine is nowadays produced from urea, according to the reaction

$$6H_2NCONH_2 \rightarrow C_3N_6H_6 + 6NH_3 + 3CO_2 \qquad (6\text{-}1)$$

An intermediate step in this reaction is the formation of isocyanic acid and ammonia from urea. According to Ref. 5 the isocyanic acid reacts with cyanic acid (formed according to the cyanic acid-isocyanic acid equilibrium) to cyanamide (NH_2CN) with formation of CO_2, in the presence of a catalyst containing hydroxyl groups. The cyanamide formed trimerizes to melamine. This mechanism holds for the low-pressure process (0.1-1 MPa). Because the high pressure process (liquid phase reaction without catalyst) has only a market share of about 25% (6), attention will only be given here to the low-pressure process.

In the low-pressure process molten urea is fed to the reactor, in which the catalyst is fluidized with ammonia. The reactor temperature is about 400°C. After reaction melamine has to be separated from the reaction mixture and be further purified. The resulting gas mixture can be used for urea synthesis or for other purposes (i.e. nitrogenous fertilizers). Often NH_3 is separated for recycle as fluidization gas. The low-pressure processes developed by BASF (7) and DSM (8) are commercially successful. They have significant differences concerning the fluidization gas and the way melamine is separated. Whereas DSM uses pure NH_3, BASF prefers an NH_3/CO_2 mixture for fluidization, without loss in conversion due to consecutive reactions, which are possible when CO_2 is present. The second difference concerns the separation section. DSM uses an aqueous carbamate solution to cool the hot gas mixture coming from the reactor and to dissolve the produced melamine. It is removed and purified by crystallization and centrifuging, leading to a large separation and purification section. Part of the NH_3 present in the resultant gas mixture can be recycled to the reactor after separation by rectification. Because water is introduced in the process, the resultant gas mixture will contain water. Upon recirculation to the urea plant this water will have a detrimental effect on the urea conversion. Therefore, in the coupling with the urea process the water content of the recycle stream has to be decreased (see section 6.3.2). A simplified flow sheet of the DSM melamine process is presented in Fig. 6-5.

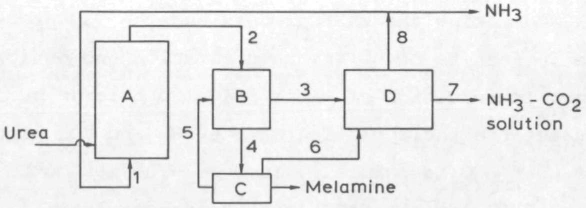


Fig. 6-5 Simplified flowsheet of the DSM melamine process. A: melamine reactor. B: separator. C: melamine purification section. D: coupling section. 1: NH_3 *fluidization gas. 2: reactor effluent. 3:* NH_3*-*CO_2*-*H_2O *vapour mixture. 4: melamine solution (saturated with* NH_3 *and* CO_2*). 5: mother liquor to melamine separation. 6: ammonia liquor from crystallizers. 7: carbamate solution to urea synthesis. 8: recovered* NH_3*.*

In the BASF process cooling of the reactor gas takes place by mixing this gas with a cold recycle NH_3/CO_2 mixture, upon which melamine is separated by desublimation. No water is introduced and there is no need for a large melamine purification unit, because the crystals obtained already have a high purity. Without further treatment the resultant gases can be recycled to the melamine reactor. It is, however, not clear from Ref. 7 in what way the off-gases are recycled to the urea reactor. In BASF patents various proposals were made, such as cooling with NH_3 to crystallize ammonium carbamate (9) and contacting the gases with liquid ammonia, leading to a suspension of ammonium carbamate in liquid NH_3 (10). Absorption in water is also mentioned. To obtain a concentrated solution a two-step absorption is proposed, the second step operating at a higher pressure (11). A BASF method to separate NH_3 and CO_2 will be discussed in section 6.3.3.

The OSW melamine process (5), which is not commercially operated, is comparable with the DSM process. The reaction section is divided into two parts. In the first reactor urea is decomposed into ammonia and isocyanic acid. In the second reactor conversion to melamine takes place in the presence of a catalyst. The separation of melamine from the off-gases takes place by quenching them with water saturated with NH_3, CO_2 and melamine. NH_3 is recovered from the residual gas mixture by rectification and is dried with liquid NH_3, after which it can be recycled to the first reactor. The resulting solution of NH_3 and CO_2 can be used for various purposes, such as production of ammonium sulfate, ammonium nitrate or urea. In the latter case concentration of the solution is necessary (see section 6.3.2).

In conclusion it can be said that the processes developed by OSW and DSM do not differ very much. Comparing the BASF process and the DSM process, the important difference is seen to occur in the separation and purification of the produced melamine. Introduction of water leads to a large purification section, but facilitates the recirculation of the NH_3 and CO_2 produced to the urea plant, provided that H_2O is partially removed. The method used for the recirculation of NH_3 and CO_2 in the BASF process is not clear; it is probable that difficulties arise in a slurry recirculation method without water.

6.3.2 Coupling methods

It is advantageous to reconvert the large amount of NH_3 and CO_2 produced in the melamine synthesis to urea. Since a urea plant always precedes the melamine plant the easiest recirculation method would be to compress the gases as such from recirculation stage to urea reactor pressure. Because of the large pressure difference involved and possible corrosion problems (20) this compression would be very expensive. Furthermore, the large quantity of water in the gas (except for the BASF process) may lead to condensation on interstage cooling (21). The high water content will also decrease urea conversion if it is not lowered prior to feeding the recycle stream to the urea reactor. Because of these reasons methods were developed to recycle NH_3 and CO_2 in solution form with a reduced water content.

DSM (8) concentrates the dilute carbamate solution obtained after NH_3 recovery by steam stripping and condensation at a higher pressure level (2 MPa). The flow sheet is presented in Fig. 6-6. The gases coming from the

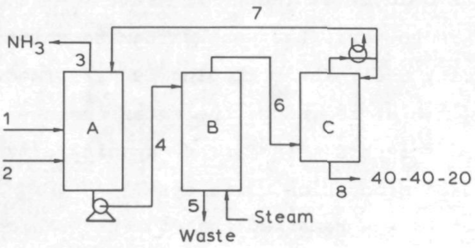


Fig. 6-6 DSM coupling system (simplified).
A: ammonia tower. B: desorber. C: wash tower.
1: vapours from melamine separator. 2: ammonia solution from melamine crystallization section. 3: recovered NH_3 to reactor. 4: dilute carbamate solution to desorber. 5: waste. 6: desorber vapours to wash tower. 7: NH_3 recovered in wash tower. 8: concentrated solution to urea synthesis unit.

melamine separator are fed to an ammonia tower, in which CO_2 and H_2O are absorbed in a liquid stream coming from the crystallization section. Water-free NH_3 is obtained at the top of the column by introduction of liquid NH_3 from the wash tower. At the bottom a dilute ammonium carbamate solution is obtained. This solution is pumped to the steam distillation column, operating at about 2 MPa, in which all the NH_3 and CO_2 are evaporated. The vapours coming from the distillation column are condensed in the wash tower, under recovery of NH_3. This NH_3 is recycled to the NH_3 tower. The resultant solution contains 40 weight-% NH_3 and 40 weight-% CO_2 (mole percentages of 54 and 21, respectively) and is pumped to the stripper of the DSM stripping process. Thus, the melamine effluent gases are partially separated in pure ammonia and a concentrated carbamate solution. Disadvantages of the method are the introduction of water in the recycle stream to the urea reactor and the high energy requirements in the coupling step. Therefore, DSM has patented some methods to improve the coupling of the two processes. If the separation of melamine from the reactor effluent takes place with an ammonium carbamate solution of a high concentration (1 to 5 kg carbamate per 1 kg melamine to be separated) the cooling of the gas is accomplished by dissociation of the carbamate, instead of the evaporation of water. This results in a low water content of the obtained gas. According to the patent (12), on condensation of these gases under recovery of NH_3, the concentrated 40-40-20 solution is directly formed. Therefore, this method results in lower investment and utilities costs. To effectively utilize of the heat of condensation of the gas mixture the pressure should be at least 0.5 MPa.

Another proposal (13) is to strip the weak carbamate solution obtained from the ammonia tower (Fig. 6-6). The stripping is performed with CO_2 at urea synthesis pressure (15 MPa) to reduce the water content of the stripped gas. Because CO_2 is needed for this method, the capacity of the melamine unit can only be half of the urea production capacity.

In the previous section it was remarked that for the OSW melamine process recirculation of the produced NH_3 and CO_2 to a urea plant also implies concentration of the dilute ammonium carbamate solution obtained. For this aim in Ref. 5 a process of the German firm Uhde is mentioned. Inspection of the flow sheet reveals, however, that the proposed method is virtually the same as the DSM process. It is believed that Uhde is simply a licensee for this DSM process.

The processes so far discussed in this section have only the objective to recirculate NH_3 and CO_2, produced in melamine synthesis, back to the urea synthesis unit. Because the compositions of the melamine reactor effluent gases are ammonia-rich, it is also possible to separate NH_3 for recycle to the melamine synthesis unit itself. The strong coupling of the two processes by this recirculation decreases flexibility in operation. If the urea plant has a shut-down, the melamine plant has to be shut down too, because the recirculation stream cannot be processed. As already mentioned, the fact that the recirculation flow contains water is a serious drawback for the optimal operation of the urea plant. Complete separation of the recycle stream into its components NH_3, CO_2 and H_2O will prevent all these problems from occurring.

6.3.3 *Complete separation of NH_3 and CO_2*

As is discussed in section 6.2 it is not possible to separate a mixture of NH_3, CO_2 and H_2O into its components by simple ideal rectification. Depending on the mixture's composition, either NH_3 or CO_2 can be obtained in the pure state. Using selective absorption it is possible to obtain the other volatile component. This method is complicated, however, because the absorbent has to be regenerated and the process is quite energy consuming.

In the literature three methods are proposed for the complete separation of an NH_3-CO_2-H_2O mixture, two of which are based on rectification. The principles underlying the rectification methods were already mentioned in section 3.2.

A separation at two pressure levels, proposed by OSW, is discussed in Ref. 14. At low pressure (0.1 MPa) NH_3 is separated from the initial mixture, which is the effluent of the melamine separation section. This separation is performed by washing the gases with a dilute NH_3-CO_2-solution, obtained elsewhere in the separation process. The resulting solution (situated on the boundary line at this pressure) is compressed (to pressures of 0.5-3 MPa) and is subjected to a second rectification process, in which CO_2 is the top product. A part of the bottoms product is completely freed from NH_3 and CO_2 in a small desorber. A flow sheet is presented in Fig. 6-7. The first column (A) is composed of a CO_2 scrubber (upper part) and a NH_3-stripper (lower part). In the scrubber CO_2 is absorbed in a recycle solution, containing NH_3 and some CO_2. The NH_3 stripper removes excess NH_3 from the effluent of the CO_2 scrubber by contacting it with gases obtained from the desorption column. The NH_3 stripper's effluent is pumped to the second column, which is also divided into two parts. In the upper part (B) CO_2 is separated as top product. To keep the CO_2 NH_3-free, some water is fed to this CO_2 stripper. In the lower part of the column (C) a part of the resulting solution (after pressure reduction) is freed from NH_3 and CO_2; the waste water obtained can be used, for example, in in the melamine purification unit. The other part of the CO_2 stripper's effluent is used as absorbent in the CO_2 absorber. The necessary overstepping of the boundary line is achieved in this process by compressing the liquid to be rectified again (see Fig. 6-3). On pressure increase the boundary line will be displaced in the direction of the less volatile solute, which is NH_3 in the present case. The pressure ratio of the two rectification units has to be found by optimization. A small ratio leads to large recycle flows, because the difference in boundary line compositions will be small. A high ratio will lead to higher investment costs. Based on data presented in Ref. 14, Fig. 6-8

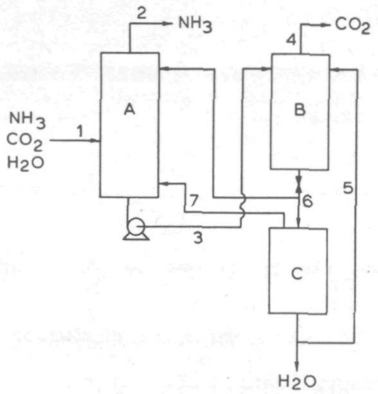
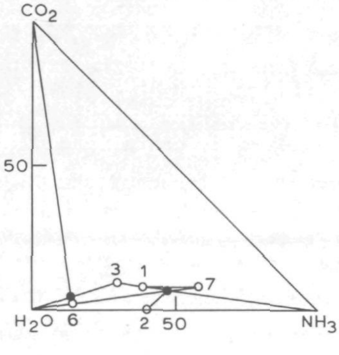


Fig. 6-7 Simplified flowsheet of OSW separation method.
A: CO_2 scrubber and NH_3 stripper. B: CO_2 stripper. C: NH_3-CO_2 stripper.
1: vapours from melamine separator. 2: recovered NH_3. 3: NH_3-CO_2 solution compressed to B. 4: recovered CO_2. 5: H_2O fed to CO_2 stripper. 6: NH_3-CO_2 solution to A and C. 7: NH_3-CO_2-H_2O vapour to NH_3 stripper.



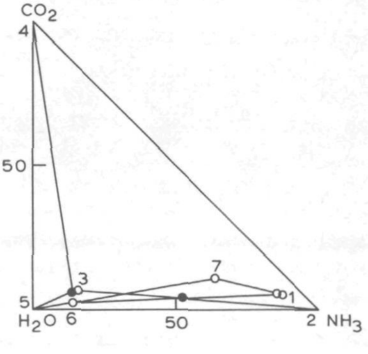


Fig. 6-8 Composition diagram for OSW separation method. Numbers refer to streams in Fig. 6-7. Closed circles denote sum points.

Fig. 6-9 Composition diagram for DSM separation method. 1: solution from melamine separation. 2: ammonia solution from inert scrubber. 3: NH_3-CO_2 solution from NH_3 rectification column to CO_2 rectification column. 6: liquid effluent of CO_2 rectifier to NH_3-CO_2 desorber. 7: vapour from desorber to NH_3 rectifier.

gives a simplified composition diagram with which the separation method can be illustrated.

Recently DSM published a patent application (15) for a new separation method with which it is not necessary to operate at two pressure levels. The principle of the method is the addition of water to the liquid positioned at the boundary line. Due to the curvature of this line the diluted solution will lie on the concave side of the boundary line (see Fig. 6-3). From Fig. 6-4 it is seen that the boundary line of the NH_3-CO_2-H_2O system at 0.1 MPa indeed exhibits curvature. The degree of curvature and the amount of water added will determine the efficiency of the operation. If the distance of the composition point of the diluted solution to the boundary line is small, only little CO_2 can be separated before the liquid composition again reaches the boundary line. This will lead to a large recirculation flow in the separation section. A phase diagram, based on data presented in Ref. 15, is given in Fig. 6-9. It is seen that the distance from the diluted liquid to the boundary line is rather small, compared to the OSW process (Fig. 6-8).

The flowsheet of the DSM process is much like that presented in Fig. 6-7. Differences are that a pump and a pressure-reducing device can be omitted and that stream 6 is completely fed to desorber C. Stream 2 is condensed and partially refluxed in the CO_2 scrubber. The amount of water recycled to the CO_2-stripper is much larger than in the OSW process. It is not easy to determine which of the two processes discussed will give lower separation costs. Concerning the equipment, both processes are practically identical. Because the DSM process is operated preferably at pressures higher than the melamine synthesis pressure, the pump is installed in the feeding line, instead of in the line connecting the two rectification units (Fig. 6-7). The advantage of the higher pressure level is that the NH_3 produced can easily be liquified. Based on the data presented in Fig. 6-9 there is some doubt concerning the effect of the water addition on the transgression of the boundary line. The change in pressure probably has a much larger effect. Due to lack of data this point cannot yet be clarified.

Completely different from the two processes mentioned above is the separation method proposed by BASF (16). The basis of the method is the difference in absorption kinetics of NH_3 and CO_2 in a carbamate solution. According to Ref. 16 NH_3 dissolves much faster than CO_2 at short contact times (less than 0.1 sec), leading to enrichment of the vapour phase with CO_2.

In two absorption steps (liquid jets) pure CO_2 can be obtained. By rectification of the ammonia-rich absorption solution NH_3 is separated. The bottom product of the rectification column is used as absorption solution in the second absorption unit. The CO_2 obtained is freed from traces of NH_3 by scrubbing with H_2O. A simplified flow sheet is presented in Fig. 6-10.

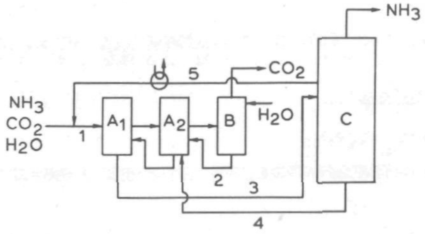


Fig. 6-10 Simplified flowsheet of BASF separation method.
A_1 and A_2: CO_2 absorbers. B: CO_2 scrubber. C: NH_3 rectification column.
1: NH_3-CO_2-H_2O vapour. 2: dilute NH_3-CO_2 solution. 3: NH_3-rich solution to NH_3 recovery. 4: NH_3-CO_2 solution. 5: concentrated carbamate solution which is combined with 1 after evaporation.

Little is known concerning the kinetics of simultaneous absorption of NH_3 and CO_2 in aqueous solution. Dissolution of CO_2 may proceed slower than that of NH_3 because the latter compound dissolves well and reacts to ammonium ions only by proton transfer. Because of the low (physical) solubility of CO_2, absorption can only be sufficiently large if chemical reactions occur. In this case reaction with H_2O and NH_3 is necessary to produce bicarbonate, the occurrence of this reaction possibly resulting in a lower absorption rate relative to NH_3.

The BASF process uses simple equipment. Furthermore there is only one rectification column, so that energy consumption is probably less than that of the DSM and OSW processes.

In this section three processes for the separation of NH_3 and CO_2 were discussed. It appeared that each of the three companies having a low-pressure melamine process developed their own method for a complete separation of NH_3 and CO_2 to overcome the disadvantages of the recirculation methods discussed in section 6.3.2. Mutual dependence of the urea process and the melamine process is reduced and the problem of introducing extra water into the urea reactor is prevented.

Although an economic evaluation of the complete separation versus the recirculation cannot be made in this thesis, for the above-mentioned reasons the complete separation of NH_3 and CO_2 produced in the synthesis of melamine, would seem preferable.

6.4 Other processes

In this section two processes related to the NH_3-CO_2-H_2O system will be briefly discussed.

Due to environmental regulations process effluents containing NH_3, H_2S, etc. should have very low concentrations of solutes. In the case of urea plants it is also economically advantageous to recover the NH_3 and urea present in effluents produced in the evaporation or crystallization section (17). Therefore, treatment of urea plant effluents usually takes place by hydrolysis and steam-stripping (17, 18). According to Ref. 17 the process condensate is fed to a desorber operating at 0.4 MPa. In the desorber part of the NH_3 is removed by introducing steam, containing NH_3 and CO_2, from the stripper (see Fig. 6-11).

Fig. 6-11 Steam stripping of urea process condensate.
A: desorber. B: hydrolyzer. C: stripper.
1: NH_3-CO_2-H_2O vapour to low-pressure condensor. 2: compressed desorber effluent to hydrolyzer. 3: steam containing NH_3 and CO_2 to desorber.

The urea present in the desorbed solution is converted to NH_3 and CO_2 in the hydrolyzer, operating at 1.1 MPa and 175°C. The hydrolysis reaction proceeds slowly, even at this temperature, the residence time being about 1 hour. The pressure of the hydrolysed solution is reduced to 0.4 MPa and the solution is stripped with steam. The effluent now contains about 60 ppm NH_3 and 45 ppm urea. In Ref. 18 a process is presented which reduces the NH_3 and urea content to less than 10 ppm each. Stripper and hydrolyzer are combined in one vessel and operate at about 1 MPa, using a steam-CO_2 mixture for the stripping action. Introduction of CO_2 will improve the removal of NH_3.

To calculate the equipment dimensions knowledge of the phase behaviour of the system is necessary. Darton et al. (19) discussed the calculation procedure, based on a model description of the phase behaviour. Unfortunately, no details concerning the model were given. Determination of the vapour-liquid equilibria at these low concentration conditions is difficult, compared to the conditions studied in this thesis. Sensitive analysis methods are necessary to determine the phase compositions. Therefore, at these conditions the vapour-liquid equilibria are most easily found using a model, based on measurements at higher concentrations. This implies extrapolation to a dilute region, in which the system behaves more ideally (e.g., the activity coefficients approach unity) compared to other conditions.

The second process to be mentioned here is the integrated ammonia-urea process. Because often a large part of the NH_3 produced is used as a feedstock for a urea plant, it can be useful to investigate whether both processes can be combined into one single unit. In the sixties most urea process development companies published proposals for such integrated processes. Possible integration points are: removal of CO_2 from the NH_3 synthesis gas, removal of NH_3 from the NH_3 reactor effluent and the compression of CO_2 to the urea synthesis pressure.

DSM patented a number of ideas (27, 28) concerning the integration of an ammonia process with the DSM stripping process. According to Ref. 27 the raw synthesis gas (before being subjected to the CO shift) is used as the stripping agent. The stripper gaseous effluent is introduced into the urea reactor, in which part of the stripped NH_3 and CO_2 is absorbed and converted to urea. In the upper part of the reactor the remaining NH_3 and CO_2 are absorbed in a recycled carbamate solution, followed by an absorption in water. Introduction of the synthesis gas in the urea reactor implies a larger reactor because of the large gas volume which includes much inerts. The combination of absorber and reactor into one piece of equipment may also lead to design problems. After CO conversion the synthesis gas is fed to an absorber in which CO_2 removal takes place. The CO_2 is absorbed by an aqueous stream containing NH_3, CO_2 and/or urea. Liquid NH_3 is also introduced to absorb the CO_2. The NH_3 present in the NH_3 synthesis effluent is separated partially by cooling and partially by absorption in the liquid effluent from the CO_2 absorber. The resulting solution is introduced into the urea reactor.

The process is very complicated and contains several process steps whose operation is doubtful. It is more advantageous to apply the synthesis gas after CO conversion for stripping. Thus, removal of the CO_2 produced takes place together with recycle of stripper gas. It can be concluded that only the stripped NH_3 and CO_2 enter the reactor in gaseous form. The main part of the reactants is introduced as aqueous solution, leading to a low conversion. Even water is introduced in the combined absorber/reactor. Another proposal for the removal of CO_2 from the synthesis gas and of NH_3 from the NH_3 synthesis effluent is made in Ref. 28. A urea melt is used as absorbent instead of an aqueous solution. The absorbed gases are desorbed at a somewhat higher temperature level prior to introducing them into the reactor. The advantages are a reduction of the amount of water introduced into the reactor and a reduction in the biuret content of the urea melt. The latter advantage is caused by reaction of the dissolved NH_3 with the biuret to urea.

In contrast to SNAM, which operated at 80 t/day integrated ammonia-urea pilot-plant for more than 5 years (25), DSM has apparently not worked continuously on the development of the integrated process. The patents discussed seem preliminary and some of the proposals seem doubtful.

Apparently SNAM was the only firm which has remained active in the development of the integrated process (see Ref. 24 for a description of the original SNAM integrated process). However, pilot-plant development of the process has not yet led to commercial plants. Negotiations with the government of the USSR concerning the fist integrated NH_3-urea plant are still going on (22). Compared to the original process description (24), the present version of the SNAM integrated process (25) contains an important modification (see Fig. 6-12 for the relevant part of the flowsheet). The separation of NH_3 from the NH_3-reactor effluent (*3*) remains unchanged: this proceeds by absorption in water, leading to a solution of 80 w% NH_3 in H_2O (*6*). The wet gas (*5*) is dehydrated by injection of liquid NH_3, obtained by cooling the reactor effluent. The removal of CO_2 from the raw synthesis gas mixture is no longer performed by absorption in the above-mentioned ammonia solution. As a new feature this CO_2 removal is integrated with the removal of unconverted reactants from the urea synthesis reactor effluent. This effluent

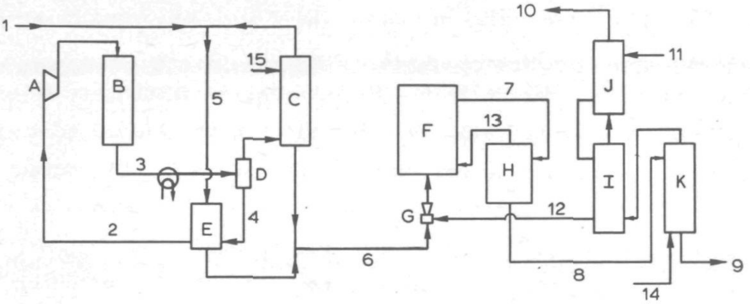


Fig. 6-12 SNAM ammonia-urea integrated process.
A: recycle compressor. B: NH_3 reactor. C: NH_3 absorption column D: gas-liquid separator. E: dehydration section. F: urea reactor. G: ejector. H: decomposer. I: CO_2 absorber. J: NH_3 absorber. K: stripper.
1: synthesis gas from methanator. 2: dried synthesis gas. 3: NH_3 reactor effluent. 4: liquid NH_3 to dehydration section. 5: wet synthesis gas. 6: NH_3 solution to urea reactor. 7: urea reactor effluent. 8: decomposer effluent to stripper. 9: stripper effluent to low pressure recovery. 10: synthesis gas to methanator. 11: dilute carbamate solution from low pressure recovery. 12: carbamate solution to urea reactor. 13. NH_3-rich vapours to urea reactor. 14: synthesis gas from CO-shift. 15: H_2O for NH_3 absorption.

(*7*) is firstly sent to a decomposer (H) in which "self-stripping" of the solution takes place by simple heat exchange. The decomposer liquid effluent (*8*) is fed to the stripper (K) where it is contacted with the raw synthesis gas (*14*). In this stripper stripping occurs with a CO_2-N_2-H_2 mixture. Separation of the NH_3 and CO_2 from the stripper gas is accomplished in a CO_2 absorber (I) and an NH_3 absorber (J) using a recycle carbamate solution (*11*) from the urea purification section. The resultant concentrated carbamate solution (*12*) is fed to the urea reactor (F) via an ejector (G) using the NH_3 solution (*6*) from the NH_3 synthesis section as driving fluid. The absorbers gaseous effluent (*10*) is sent to a methanator and subsequently to the NH_3 synthesis loop. Vapour-liquid equilibria are especially important in the design of the NH_3 separator, the stripper and the two absorbers. For the NH_3 absorption in the NH_3 synthesis section the vapour-liquid equilibria of the NH_3-N_2-H_2-H_2O system at high pressure (20 MPa) are needed. SNAM investigated these equilibria and their description because the separation method can also be used in a single NH_3 plant (26). A disadvantage of the method is the fact that a deep dehydration of the resulting gas is necessary before passing it to the NH_3 reactor.

The integration of CO_2 removal with stripping of the urea reactor effluent seems favourable. A better stripping action is expected than in the original process, in which NH_3 was the stripping agent. It should be noted that the stripping with a CO_2-N_2-H_2 mixture resembles much the DSM CO_2-stripping process and the integrated process proposed in Ref. 27. The combined CO_2 (from CO shift and urea synthesis) is separated and recirculated to the urea reactor in one absorber. In this absorber and the NH_3 absorber coupled with it, the vapour-liquid equilibria of the NH_3-CO_2-N_2-H_2-H_2O system play an important role. It can be assumed that N_2 and H_2 will act as inerts, leading only to a pressure effect on the equilibrium. Because CO_2 removal is no longer performed with the NH_3 solution, obtained from the NH_3 synthesis unit, it can be questioned whether this separation method is worthwhile. All of the water introduced in this separation step is fed directly to the urea reactor, leading to a high H_2O/CO_2 ratio. In order to reach high conversion levels a high NH_3/CO_2 ratio (about 7) is necessary. A convential NH_3 separation by refrigeration produces pure liquid NH_3 as urea reactor feed, leading to a much lower H_2O/CO_2 ratio.

According to Ref. 25 a saving of 17% on raw material and utilities costs and of 15% on investments can be reached with the SNAM integrated NH_3-urea process, compared to the single processes. However, there are several questions which remain unanswered. If part of the NH_3 produced is needed for other purposes the process has to be enlarged with a conventional CO_2 removal unit and a distillation unit to recover the NH_3 not needed in urea production. This decreases the level of integration and the savings on production and investment costs. A conventional CO_2 removal unit is also necessary if feedstocks other than methane are fed to the reforming unit.

More important than the above-mentioned design features is the actual operation of the integrated plant. The process is very complicated, and the strong integration may well lead to difficult process control. Therefore, frequent plant shut-downs, leading to large production losses, may occur.

The above-mentioned discussion may give some explanation for the delay in construction of an integrated process.

References

1. F.A.H. Schreinemakers, *Z. Phys. Chem. Stoechiom. Verwandschaftsl.* 36 (1901) 413.
2. W. Reinders, C.H. de Minjer, *Recl. Trav. Chim. Pays-Bas* 59 (1940) 207.
3. R. Haase, *Z. Naturforsch. Teil A* 4 (1949) 342.
4. P.J.C. Kaasenbrood, *Chem. React. Eng., Proc. Eur. Symp.* 4th, 1968, Pergamon Press, (1971) p. 317.
5. A. Schmidt, *Hydrocarbon Process.* 45 (11) (1966) 146.
6. L.N. Altshuler, V.I. Zagranichnyi, V.M. Karlik, *Sov. Chem. Ind. (Engl. Transl.)* 8 (1976) 968.
7. M. Schwarzmann, *Hydrocarbon Process.* 48 (9) (1969) 184.
8. P. Ellwood, *Chem. Eng. (N.Y.)* 75 (11) (1968) 124.
9. BASF, *Ger. Offen. 1670286*, Nov. 10, 1967.
10. BASF, *Ger. Offen. 1939570*, July 31, 1969.
11. BASF, *Ger. Offen. 1770969*, July 24, 1968.
12. DSM, *Ger. Offen. 2116200*, April 3, 1970.
13. DSM, *Neth. Appl. 6801577*, Febr. 2, 1968.
14. A. Schmidt, *Chem. Ing. Tech.* 42 (1970) 521.
15. A.J. Biermans (Stamicarbon), *Ger. Offen. 2748639*, October 29, 1977.
16. W. Berkel, H. Gettert (BASF), *Ger. Offen. 2317603*, April 7, 1973.
17. E. Dooyeweerd, *Environ. Symp. Proc.* (1976) 103.
18. E.R. Hoffmann, R.K. Fidler, *Hydrocarbon Process.* 55 (8) (1976) 111.
19. R.C. Darton, P.F.A. van Grinsven, M.M. Simon, *Chem. Eng. (London)* (339) (1978) 923.
20. S.M. Lemkowitz, *Phase and corrosion studies of the* NH_3-CO_2-H_2O *system at the conditions of the hot gas recirculation process for the synthesis of urea*, PhD thesis, Delft University of Technology, The Netherlands, 1975.
21. S.M. Lemkowitz, J.C. van Erp, P.J. van den Berg, *Delft Prog. Rep.* 3 (1978) 83.
22. V. Lagana, U. Zardi, *Proc. Fert. Soc.* 167 (1977) Suppl. p. 7.
23. H.A.G. Chermin, *Internal Report DSM*, Sept. 22, 1976.
24. G. Pagani, U. Zardi, A. Bonetti, *Inst. Chem. Eng. Symp. Ser.* 44 (5) (1976) 107.
25. V. Lagana, U. Zardi, *Proc. Fert. Soc.* 167 (1977).
26. G. Guerreri, J.M. Prausnitz, *Process Technol. Int.* 18 (1973) 209.
27. P.J.C. Kaasenbrood, G.J.J.M. Taks (Stamicarbon) *US Patent 3607939*, Sept. 21, 1971.
28. Stamicarbon, *Neth. Appl. 153857*, July 15, 1977.

APPENDIX 1 THE GAS-CHROMATOGRAPHIC ANALYSIS OF H_2O WITH POROUS POLYMERS

The use of porous polymers in gas chromatography is widespread nowadays (1). Especially the separation of mixtures of small molecules, which may be polar, has become possible by the introduction of porous polymers. The analysis of water using porous polymer columns is discussed in Ref. 2.

In Chapter 3 it was shown that for H_2O a straight calibration line, passing through the origin was obtained by analysis of water-alcohol azeotropes (Fig. 3-6). In an investigation of the high-pressure vapour-liquid equilibria of the H_2O-CO_2 system (not reported in this thesis) the analysis of both phases took place with a method identical to that described in section 3.3. Because of the very low H_2O content of the equilibrium vapour phase (about 1 mole-% at 75°C and 15 MPa) it was necessary to provide for an accurate calibration line for H_2O in the region of 0-10 mole-% H_2O. The calibration was performed by analyzing water-ethanol mixtures of known composition. The determination of a mixture's composition took place using a Karl Fischer titration. A straight calibration line was found, but this line did not pass through the origin. Therefore, another method to obtain a calibration line was tried. A new water saturator was developed, which did not suffer from the large spread in results, reported by Lemkowitz (3). The saturator was a 0.30 m long straight double-walled cooler in which the thermostating liquid flowed countercurrently to the gas flow. At low saturation temperatures a cotton wick was inserted in the saturator for a better saturation. Before the gas (nitrogen) entered the saturator it was presaturated in another saturator, operating at a higher temperature. The lines from saturator to sample value were kept at 200°C to reduce adsorption on the walls. With this method an accurate calibration line passing through the origin could be obtained. The thus obtained calibration line was parallel to the line obtained using water-ethanol mixtures and differed from it by a constant value, being 0.5 mole-% richer in water. The cause of this discrepancy could be an inaccurate Karl Fischer titration or the introduction of H_2O in the liquid mixture after this titration. Therefore, a mixture containing an excess amount of Karl Fischer reagent (in which no water could be present) was injected. A water peak, equivalent to 0.5 mole-% H_2O, was found. These experiments lead to the conclusion that ethanol injected onto the column, displaces H_2O, which is adsorbed on the column material. Because the surface of the system's lines is small compared to the surface of the porous polymer it is not likely that water adsorbed on these lines plays an important role in this displacement phenomenon.

Further evidence was given by a GC-MS experiment. One µl ethanol was injected to a glass column filled with Porapak Q. This injection was preceded by two injections of 3 µl denterated water. The mass spectrometer was operated at a mass/charge ratio of 20. Two peaks were found, at the retention times of (deuterated) water and ethanol, respectively. An explanation of the appearance of two water peaks may be the following. In the first part of the column water desorbed from the column by exchange with ethanol will be separated from the ethanol by the normal chromatographic process, leading to a sharp water peak, which elutes prior to the ethanol. Due to a change of retention time caused by the presence of ethanol, a certain amount of water remains present in the ethanol peak and is not separated from this peak.

The quantitative analysis of water has been studied by various authors. Hollis and Hayes (2) presented a water calibration line by analysing water-ethylene dichloride mixtures in the range of 0-160 ppm H_2O. The line intersects the concentration axis at -70 ppm, showing the same behaviour as discussed above for the water-ethanol mixtures. No explanation is given. In a study of H_2O adsorption on porous polymer beads, Gough and Simpson (4) determined the moisture content of ethanol, distilled from magnesium ethoxide. Porapak QS and a gas density detector were used. A value of 0.19% was found. This value is unrealistically large considering the drying method applied. It was found that the amount of water adsorbed on the column after injection was in the order of 0.3% of the amount injected.

The adsorption mechanism of H_2O on porous polymers is not completely clear. Based on measured heats of adsorption it is assumed that there are two interaction mechanisms: adsorbent-adsorbate (low heat of adsorption, high degree of coverage) and adsorbate-adsorbate (high heat of adsorption, low degree of coverage) (5, 6). Gassiot-Matas and Monrabal-Bas (6) mentioned the possibility of the mútual interaction of ethanol and water on Porapak Q; they found that addition of water influenced the retention time of ethanol. From the above-mentioned literature it would appear that an interaction phenomenon between water and other polar compounds has been found to occur but as yet is poorly understood, and is sometimes not even recognized as such.

The interaction effect can be generalized to combinations of other polar compounds. The separation of NH_3 and H_2O in the vapour phase analysis discussed in Chapter 3 may also be effected by this interaction. To investigate this possibility another GC-MS experiment was performed. Dry NH_3 was injected into a Porapak Q column. The mass/charge ratios 17.00274 (OH^+) and 17.02655 (NH_3^+) were scanned by the mass spectrometer. Within the tail of the NH_3 peak a flat water peak was detected. This points to an exchange of adsorbed H_2O with NH_3. Because the retention time increases in the order NH_3-H_2O-ethanol in this case the water cannot separate from the NH_3 peak and forms a tail on this peak. A solution for this problem can probably be obtained by introducing a constant amount of NH_3 into the carrier gas, assuming that this action will not lead to a poor CO_2 separation.

References

1. O.L. Hollis, *J. Chromatogr. Sci.* 11 (1973) 335.
2. O.L. Hollis, W.V. Hayes, *J. Gas Chromatogr.* 4 (1966) 235.
3. S.M. Lemkowitz, *Phase and corrosion studies of the NH_3-CO_2-H_2O system at the conditions of the hot gas recirculation process for the synthesis of urea*, PhD thesis, Delft University of Technology, The Netherlands, 1975.
4. T.A. Gough, C.F. Simpson, *J. Chromatogr.* 68 (1972) 31.
5. V. Patzelova, J. Volkova, *J. Chromatogr.* 65 (1972) 255.
6. M. Gassiot-Matas, B. Monrabal-Bas, *Chromatographia*, 3 (1970) 547.

APPENDIX 2 LIQUID PHASE ANALYSIS WITH GAS CHROMATOGRAPHY

A gas-chromatographic determination of NH_3 and CO_2 present in the equilibrium liquid phase of the NH_3-CO_2-H_2O system may present several advantages over the analysis methods discussed in section 3.4. The method is simple and requires only injection of the sample as a manual action. Furthermore, no auxiliary solutions are necessary and the treatment of the analysis results is easier.

Therefore, the determination of liquid phase NH_3 and CO_2, using the apparatus presented in section 3.3.2 was investigated. Experiments were made with a diluted sample obtained from an equilibrium measurement at 90.1°C. Samples were introduced into the system using a syringe and an injection port fitted with a septum.

Because the composition range (high water content, low amounts of NH_3 and CO_2) is entirely different for liquid and vapour phase, attention has to be given to the calibration. Firstly, the calibration lines obtained in vapour phase analysis were used. 0.7 µl aliquots of the sample (equivalent to a 100% H_2O vapour sample) were injected. The average result of three determinations is compared with the composition found by titration in Table A2-1. It is seen that negative deviations occur, especially for CO_2. It is likely that noise and integration errors have a significant influence at these low concentrations.

Since this calibration method yielded unsatisfactory results another calibration method was tried. Ammonium carbamate solutions of known composition were analysed, giving calibration lines for NH_3 and CO_2 simultaneously. The advantage of this method was that larger injection volumes could be applied because it was not necessary to determine the H_2O peak area. However, for an accurate analysis separate determinations for each component are necessary. Because the NH_3/CO_2 ratio of the sample generally does not equal 2, well-chosen injection volumes must, for each component, give compositions lying within the region in which calibrations were made. Whereas for CO_2 an accurate calibration line was found (straight, passing through the origin), the NH_3 calibration line was curved. Below 0.2 mol NH_3 integration failed because the integrator interpreted the flat tailing peak as base line noise. The results obtained by the second calibration method are also presented in

Table A2-1. Whereas there is an increase in the accuracy of the CO_2 determination, the NH_3 determination remains inaccurate. Therefore, it was decided to use the gas-chromatographic analysis only for the vapour phase analysis.

Method	Injected volume	Composition			
	µl	NH_3		CO_2	
		mole-%	s	mole-%	s
Vapour calibration	0.7	3.11	7	0.013	10
Liquid calibration	5	3.55	4	0.018	7
Titration	100	3.38	2	0.021	2

Table A2-1. Comparison of various methods for liquid phase analysis. The averages of three determinations are given. s denotes the standard deviation as percentage of the mean.

Appendix 3 CALCULATION PROCEDURES

A 3.1 Parameter estimation

From a given experimental vapour-liquid equilibrium measurement (temperature, pressure and phase compositions (in terms of components) are known) numerical values for the functions $F_1(I)$ and $F_2(I)$ (eqs. 5-29 and 5-30) can be calculated using the parameters as given in the sections 5.3.2.1 and 5.3.2.2. Using the relations between partial pressure and liquid phase molality, together with mass balances, the constituent concentrations can be calculated. Eqs. 5-29 and 5-30 then give the desired values. γ_{H_2O} is also calculated, once the constituent concentration is known.

Because the system of equations to be solved is rather simple, no numerical techniques are necessary in the calculation procedure. Two iterative loops to calculate I and m_{NH_3} are sufficient. A simplified flow diagram is given in Fig. A3-1.

The calculation procedure will be explained in some detail. The ionic strength, based on molality as the concentration unit, is defined as follows:

$$I = \tfrac{1}{2} \Sigma\, m_i\, z_i^2 \tag{A3-1}$$

Together with eqs. 5-25 and 5-26 this leads to

$$I = C + 2m_{CO_3} \tag{A3-2}$$

An initial estimate for I is made by taking m_{CO_3} zero. The molality of free NH_3 is estimated from the NH_3 partial pressure, taking γ_{NH_3} unity:

$$m_{NH_3} = p_{NH_3}/H^o \tag{A3-3}$$

With a known value for m_{NH_3} the other concentrations can be found from mass and ionic balances and the bicarbonate-carbonate equilibrium constant K_3 (eq. 5-19). Combining the mass and ionic balances results in the following two expressions:

$$m_{HCO_3} = m_{NH_3} - A + 2C \tag{A3-4}$$

$$m_{NH_4} = m_{CO_3} + C \tag{A3-5}$$

A better guess of m_{CO_3} (and thus of I) can now be obtained by substituting eqs. A3-4 and A3-5 into eq. 5-19 and solving for m_{CO_3}:

$$m_{CO_3} = -0.5C + \sqrt{0.25C^2 + K_3\, m_{NH_3}\, (m_{NH_3} - A + 2C)} \tag{A3-6}$$

Substituting the value so obtained for m_{CO_3} in eq. A3-2 yields a better estimate for I. With the estimates for I and m_{NH_3} γ_{NH_3} can be calculated with eq. 5-35, after which the above-mentioned procedure is repeated, until the change in the values of I and m_{NH_3} is within 0.1%.

The value of $m_{NH_2CO_2}$ is found from the carbon balance, whereas γ_{H_2O} is calculated using eq. 5-23. The mole fraction of H_2O is found by summing up all molalities (including the molality of H_2O: 1000/18 mole/kg); the H_2O molality is divided by this sum. In modified form this gives:

$$x_{H_2O} = 1/(1 + 0.018\ (A + C - m_{NH_2CO_2}) \tag{A3-7}$$

The functions F_1 and F_2 at the calculated ionic strength can now be obtained from eqs. 5-29 and 5-30.

A3.2 Equilibrium calculations

With the model as outlined in section 5.3 it is possible to calculate the vapour pressure and vapour composition for a given liquid composition at a given temperature. Mass balances, the ionic balance and two equilibrium constants (for the bicarbonate-carbamate and the bicarbonate-carbonate equilibrium) are used to calculate the constituent concentrations. Partial pressures are then obtained from eqs. 5-20, 5-22 and 5-23. A simplified flow diagram is presented in Fig. A3-2.

Only one iteration loop is necessary to obtain accurate values for m_{NH_3} and I. A first estimate for I is the total molality of CO_2. A very rough first estimate for m_{NH_3} can be obtained by assuming that only ammonium bicarbonate is formed. Then the free NH_3 molality is:

$$m_{NH_3} = A - C \tag{A3-8}$$

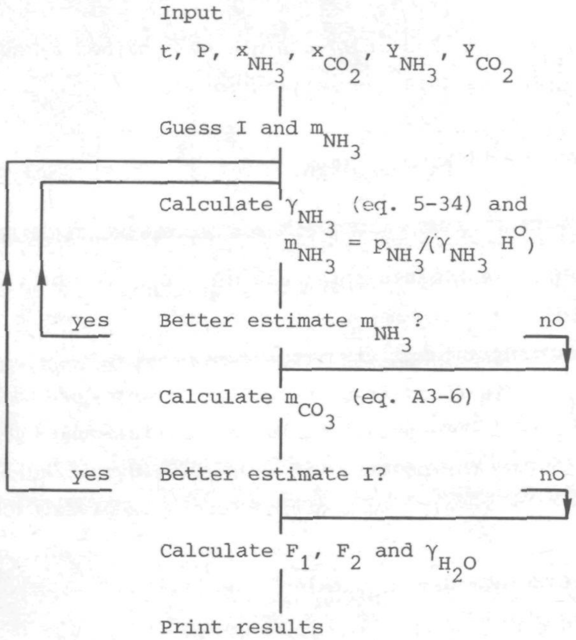


Fig. A3-1. Flow diagram for the calculation of parameters from measurements

Subsequently values for K_3, γ_{H_2O} and γ_{NH_3} are calculated. Together with a value for x_{H_2O}, these two activity coefficients are used to calculate K_2 (eqs. 5-21 and 5-30). The five equations (two mass balances, an ionic balance, and K_2 and K_3) containing the five constituent concentrations can be reduced to two equations, containing m_{NH_3} and m_{NH_4} as unknowns:

$$A - m_{NH_3} - m_{NH_4} - K_2/K_3\, m_{NH_4} (m_{NH_4} - C) = 0 \qquad \text{(A3-9)}$$

$$A - m_{NH_4} - m_{NH_3} - K_2\, m_{NH_3} (m_{NH_3} - A + 2C) = 0 \qquad \text{(A3-10)}$$

These two equations can easily be solved for m_{NH_3} and m_{NH_4} with Newton's method. A better estimate for I can then be obtained using eqs. A3-5 and A3-2. When the calculated value of I is accurate within 0.1% the partial pressures are calculated using eqs. 5-20, 5-22 and 5-23.

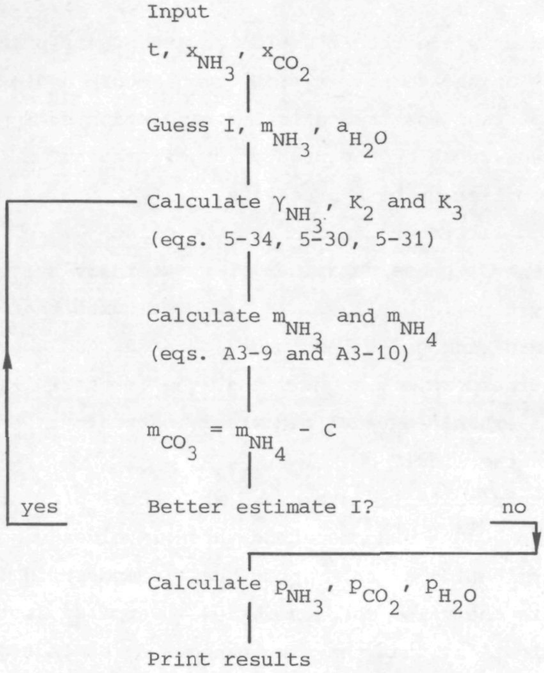


Fig. A3-2 Flow diagram of the calculation of the vapour-liquid equilibrium

SUMMARY

The subject of this thesis is the determination and the description of the vapour-liquid equilibria of the ternary system ammonia-carbon dioxide-water. These equilibria are important for the design of separation equipment of various chemical processes, such as the production of urea and melamine, and in particular for the coupling of both processes.

Using the results of a literature search and the principles of descriptive phase equilibria, the general phase behaviour of the ternary system and the three binary boundary systems is outlined. It can be assumed that at a pressure of 0.1 MPa equilibria involving solids no longer occur at and above a temperature of 65°C. Furthermore, it appears that the isothermal-isobaric vapour-liquid equilibria exhibit unusual behaviour, caused by the occurrence of chemical reactions in the liquid phase.

The equilibria are experimentally determined at a total pressure of 0.1 MPa and temperatures of 40 to 90°C, using a method which involves vapour recirculation. The determination of the vapour phase composition is performed using gas-chromatographic analysis. Chromosorb 104 is applied as the column material. There are indications that the simultaneous determination of ammonia and water using Chromosorb 104 may give a systematic error. This deviation is probably caused by displacement of water adsorbed at the column material by ammonia.

The concentrations of ammonia and carbon dioxide in the liquid phase are determined using titrimetric methods, after separation of the particular component from the sample. Ammonia is absorbed in a boric acid solution after expelling it from a boiling alkaline solution. The titration takes place potentiometrically using hydrochloric acid. Carbon dioxide is liberated by injecting a sample in concentrated sulfuric acid. Absorption and titration are performed in a mixture of dimethylformamide, mono-ethanolamine and thymol blue. Titration takes place colorimetrically using tetra-n-butylammonium-hydroxide.

The shape of the equilibrium curves, which were first qualitatively estimated, has been confirmed experimentally. The measured equilibria agree well with literature values of the equilibria of the binary ammonia-water and carbon dioxide-water systems. The estimated error of the measured compositions amounts to 1-2% for the vapour phase and 3-5% for the liquid phase. At higher temperatures the pressure has a significant influence on the equilibrium composition.

A mathematical model is proposed for the description of the measured equilibria. The chemical equilibria occurring in the liquid (formation of ammonium bicarbonate, carbamate and carbonate), together with the vapour-liquid equilibria of the constituents ammonia, carbon dioxide and water, form the basis of the model. The ionic activity coefficients are described with the Debye-Hückel equation. This equation is extended with a term which is linear in ionic strength for the determination of the equilibrium constants of the bicarbonate and carbamate formation. The necessary two parameters can be obtained from the measured equilibria. The dependency of the free ammonia activity coefficient from the ammonia concentration and the ionic strength has been found from published measurements of the vapour-liquid equilibria of the ammonia-water system and the ammonia-ammonium nitrate-water system. It is assumed in the model that the vapour phase behaves ideally.

The vapour composition and the total pressure can be calculated for a given temperature and liquid composition using the thus developed model. The deviations between measured and calculated partial pressures are within 5%, except for the ammonia partial pressure at ammonia-rich compositions. The large deviations which occur at ammonia-rich compositions are caused by an inaccurate description of the influence of ionic strength on the ammonia activity coefficient. Furthermore, it appears that it is not possible to accurately determine the empirical parameters at 80 and 90°C using the measurements. At these temperatures and a pressure of 0.1 MPa the ionic strength of the measured liquid phases is not large enough for an accurate determination of the parameters. For this aim it is necessary to perform measurements at higher pressure.

Finally processes for which the vapour-liquid equilibria of the ammonia-carbon dioxide-water system are important are discussed. In particular the coupling of a urea and a melamine process is discussed. From a general consideration of a ternary system with one binary azeotrope it appears that separation of the three components is only possible by ideal rectification if special measures are made to transgress the boundary line.

SAMENVATTING

Dit proefschrift heeft als onderwerp de bepaling en de beschrijving van vloeistof-dampevenwichten van het ternaire systeem ammoniak-kooldioxide-water. Deze evenwichten zijn van belang voor het ontwerpen van scheidingsapparatuur voor verschillende chemische processen, zoals de produktie van ureum en van melamine, en in het bijzonder voor de koppeling van beide processen.

Door middel van literatuuronderzoek wordt een algemeen beeld geschetst van het fasengedrag van het ternaire systeem en de drie binaire randsystemen. Er kan worden aangenomen dat bij een druk van 0.1 MPa bij temperaturen vanaf $65^{o}C$ evenwichten waaraan vaste stoffen deelnemen niet meer optreden. Verder blijkt dat de vloeistof-dampevenwichten bij constante temperatuur en druk een ongewoon gedrag vertonen ten gevolge van chemische reacties in de vloeistoffase.

De evenwichten zijn experimenteel bepaald bij een totaaldruk van 0.1 MPa en temperaturen van 40 tot $90^{o}C$ volgens een methode waarbij recirculatie van de damp plaatsvindt. De bepaling van de dampsamenstelling heeft plaatsgevonden met gaschromatografische analyse, waarbij Chromosorb 104 als kolommateriaal gebruikt is. Er zijn aanwijzingen gevonden dat de bepaling van ammoniak en water met dit kolommateriaal een systematische afwijking kan geven. Waarschijnlijk wordt dit veroorzaakt door verdringingsverschijnselen van geadsorbeerd ammoniak en water.

De hoeveelheid ammoniak en kooldioxide in de vloeistoffase is bepaald met titrimetrische methodes, na afscheiding van de desbetreffende component uit het monster. Ammoniak is na uitkoken van een alkalische oplossing geabsorbeerd in een boorzuuroplossing en potentiometrisch getitreerd met zoutzuur. Kooldioxide is vrijgemaakt door inspuiten van een hoeveelheid monster in geconcentreerd zwavelzuur. Absorptie en titratie zijn uitgevoerd in een mengsel van dimethylformamide, monoethanolamine en thymolblauw. Er is kolorimetrisch getitreerd met tetra-n-butylammoniumhydroxide.

De kwalitatief geschetste vorm van de evenwichtslijnen is experimenteel gevonden. De gemeten evenwichten sluiten goed aan bij uit de literatuur bekende evenwichten van de binaire systemen ammoniak-water en kooldioxide-water. De geschatte mogelijke fout in de bepaalde samenstellingen bedraagt 1-2% voor de dampfase en 3-5% voor de vloeistoffase. Bij hogere temperaturen heeft de druk een belangrijke invloed op de evenwichtsligging.

Ter beschrijving van de gemeten evenwichten wordt een rekenmodel voorgesteld. De chemische evenwichten in de vloeistof (vorming van ammoniumbicarbonaat, -carbamaat en -carbonaat), tesamen met de vloeistof-dampevenwichten van ammo-

niak, kooldioxide en water, vormen de basis van het model. De activiteitscoëfficiënten van de ionen worden beschreven met de Debye-Hückelvergelijking. Deze vergelijking wordt uitgebreid met een term welke een lineaire functie is van de ionensterkte bij de bepaling van de evenwichtsconstantes van de vorming van bicarbonaat en carbamaat. De hierbij benodigde twee parameters kunnen worden verkregen uit de gemeten evenwichten. De afhankelijkheid van de activiteitscoëfficiënt van het vrije ammoniak van de ammoniakconcentratie en de ionensterkte is bepaald uit gepubliceerde metingen van de vloeistof-dampevenwichten van het ammoniak-watersysteem en het ammoniak-ammoniumnitraat-watersysteem. De dampfase is ideaal verondersteld in het model.

Met het zo ontwikkelde model kan, uitgaande van een bepaalde temperatuur en vloeistofsamenstelling, de dampsamenstelling en de totaaldruk worden berekend. De afwijkingen tussen gemeten en berekende partiaalspanningen liggen binnen 5%, met uitzondering van de ammoniak partiaalspanning bij ammoniakrijke samenstellingen. De gevonden grote verschillen bij ammoniakrijke samenstellingen worden veroorzaakt door een onnauwkeurige beschrijving van de invloed van de ionensterkte op de activiteitscoëfficiënt van ammoniak. Voorts blijkt het niet goed mogelijk nauwkeurig de empirische parameters bij 80 en 90°C vast te leggen met behulp van de metingen. Bij deze temperaturen en een druk van 0.1 MPa is de ionensterkte van de gemeten vloeistoffasen te gering om een nauwkeurige bepaling van de parameters mogelijk te maken. Metingen bij hogere druk zijn hiervoor noodzakelijk.

Tenslotte wordt ingegaan op processen waarbij vloeistof-dampevenwichten van het systeem ammoniak-kooldioxide-water van belang zijn, in het bijzonder op de koppeling van ureum- en melamineproces. Uit een algemene beschouwing van een ternair systeem met een binaire azeotroop blijkt, dat scheiding van de drie componenten door ideale rectificatie alleen mogelijk is wanneer speciale maatregelen worden genomen om de grenslijn te overschrijden.

STELLINGEN

1. De definitie van azeotropie zoals gegeven door Wade en Merriman verdient de voorkeur boven de gangbare definitie, zeker in het geval van systemen waarin een chemische reactie optreedt.

   J. Wade, R.W. Merriman, *J. Chem. Soc.*, 99 997 (1911).

2. Het is niet mogelijk om door eenvoudige ideale rectificatie ammoniak en kooldioxide in waterige oplossing volledig van elkaar te scheiden.

   Dit proefschrift, Chapter 6.

3. Het belang van goede analysemethodes bij chemisch onderzoek kan moeilijk overschat worden.

4. Het mechanisme van de absorptie van nitreuzen in salpeterzuur dient nader onderzocht te worden.

   P.J. Hoftijzer, F.J.G. Kwanten, "*Absorption of nitrous gases*", in G. Nonhebel, *Gas purification processes for air pollution control*, Newnes-Butterworths, London, 1972, p. 164.

5. Bij de gaschromatografische analyse van water met poreuze polymeren is het wenselijk aandacht te besteden aan mogelijke systematische afwijkingen ten gevolge van wateradsorptie.

   T.A. Gough, C.F. Simpson, *J. Chromatogr.*, 68 (1972) 31.

6. Het volledig integreren van de ammoniak- en de ureumsynthese zal in de praktijk onvoldoende rendementsvoordeel bieden.

7. De complexiteit van de beschrijving van vloeistof-dampevenwichten volgens "molecular thermodynamics" neemt voortdurend toe. Vanuit het standpunt van de chemisch technoloog is dit te betreuren.

8. Het ontstaan van files in woon-werkverkeer kan alleen doeltreffend voorkomen worden door spreiding van vaste werktijden.

9. Na een langdurige bloeiperiode heeft de bestudering van de klassieke fasenleer aan belang ingeboet. Dit is een reden te meer om in de opleiding tot scheikundig ingenieur de toegepaste thermodynamica te stimuleren.

10. Het kunnen terugzien op een gereformeerde jeugd biedt schrijvers een grotere kans op succes.

11. De kerk heeft alleen kans op voortbestaan als er op plaatselijk niveau schaalverkleining plaatsvindt.

12. Het zendschema van Hilversum IV bevordert de culturele armoede.

Stellingen behorende bij het proefschrift 'VAPOUR-LIQUID EQUILIBRIA OF THE AMMONIA-CARBON DIOXIDE-WATER SYSTEM' van P. Verbrugge

Delft *28 augustus 1979*