

# Praxis, Technik

## Constituent and Component Measurements and Calculations of the Vapour/Liquid Equilibrium of the Ternary System Carbon Dioxide-Ammonia-Water under Urea Synthesis Conditions



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### Abstract

A new calculation method is presented for the calculation of the constituent and component composition of the liquid and co-existing gaseous phase of the ternary system carbon dioxide-ammonia-water at thermodynamic equilibrium under urea synthesis conditions. Approximation equations for the equilibrium constants of the physical (heterogeneous) and chemical (homogeneous) equilibria are given. Calculations were performed within the temperature range of 160 to 180°C and within the pressure range of 70 to 145 bar at  $L = 2$  and  $-0.6 \leq W \leq 0$ . Comparisons of calculated and experimentally found data are presented and discussed as well as new transformation equations for the calculation of the component composition of the phases in question.

### Introduction

Knowledge of the constituent and component composition of the liquid and co-existing gaseous phase of the system carbon dioxide-ammonia-water at thermodynamic equilibrium at high temperature (160 to 220°C) and under high pressure (50 to 250 bar) is extremely important for the industrial synthesis of urea from ammonia and carbon dioxide. In spite of this importance only a few authors, namely *Bolotov* et al. [1-5], *Kawasumi* [6-10], *Rathgeb* [11], *Buck* et al. [12-15] and *Durisch* et al. [16-22] published experimental data concerning the composition and the equilibrium pressure of this two-phase system in the above-

mentioned temperature and pressure range. The most important reasons for this dearth of experimental data are the great experimental difficulties caused by the high temperature and pressure, the corrosiveness of the liquid phase and the tendency of the gas samples to solidify upon cooling. Another problem is the extremely difficult chemical analysis of the liquid and gaseous samples.

The calculation of the composition of the liquid and co-existing gaseous phase is strongly complicated by the occurrence of chemical (homogeneous) equilibria and by the occurrence of temperatures higher than the critical temperature of carbon dioxide and ammonia. The first reasonable attempt to perform such calculations was done by *Efremova* et al. [23]. However, according to their model, the liquid phase contains no molecular (free) carbon dioxide and the water concentration in the gaseous phase was neglected, since it amounts to only a few mole percent. These shortcomings were overcome by *Lemkowitz* et al. [24-27]. These authors postulate three physical equilibria between the liquid and co-existing gaseous phase and two chemical equilibria in the liquid phase. Their model, however, can neither calculate the biuret concentration in the liquid phase nor the urea and isocyanic acid concentrations in the gaseous phase. The purpose of this article is to describe a new thermodynamically consistent calculation method for the calculation of the constituent composition of the liquid

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and co-existing gaseous phase of the ternary system carbon dioxide-ammonia-water. This method includes biuret in the liquid phase as well as urea and isocyanic acid in the gaseous phase. The thermodynamic background of this calculation method is not dealt with here, the reader being referred to a recently published article of Durisch et al. [22]. The present article also presents the relations (transformation equations) between the actual constituent concentrations and the concentrations of the components carbon dioxide, ammonia and water.

### The vapour/liquid system

To describe the vapour/liquid system dealt with here a heat conducting (diathermic) cylinder which initially contains  $n_1$  moles of carbon dioxide,  $n_2$  moles of ammonia and  $n_3$  moles of water is considered. The cylinder is closed with a diathermic movable piston. Both cylinder and piston are in thermal contact with a heat reservoir. It is assumed that at certain initial values of the pressure and temperature in the cylinder, the above-mentioned three chemical substances form a gaseous mixture containing only these three substances. Now the temperature and pressure are changed so that this gaseous mixture partially condenses (liquefies). It is assumed that in the condensed liquid phase the substances ammonium carbamate ( $\text{NH}_4\text{CO}_2\text{NH}_2$ ), urea ( $\text{NH}_2\text{CONH}_2$ ) and biuret ( $\text{NH}_2\text{CONHCONH}_2$ ) are formed by chemical reactions. Furthermore it is assumed that a small amount of the urea formed in this liquid evaporates into the co-existing gaseous phase, where it partially dissociates to ammonia and isocyanic acid (HNCO). After a sufficiently long time the properties of the thus obtained vapour/liquid system no longer change with time: the system is then at thermodynamic equilibrium. A schematic representation of a section along the phase boundary surface is shown in Fig. 1.

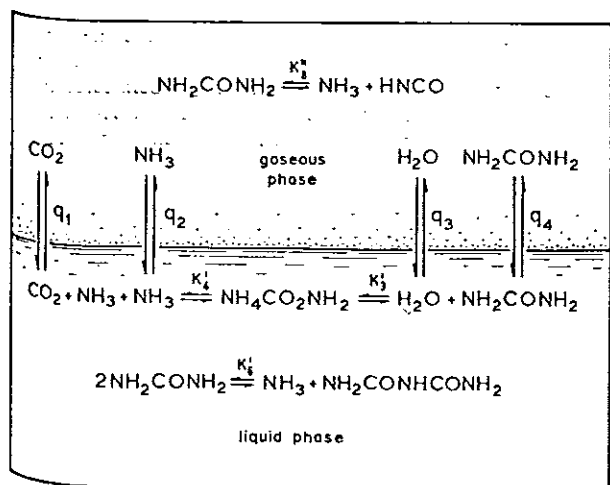


Fig. 1: Schematic representation of a section along the interface between the gaseous and liquid phase of the vapour/liquid system.

According to Fig. 1 the two-phase system contains seven chemical substances (constituents), namely carbon dioxide, ammonia, water, urea, ammonium carbamate, biuret and isocyanic acid. The concentrations (mole fractions) of these constituents are denoted, respectively by  $x_1$  to  $x_7$  in the liquid phase and by  $y_1$  to  $y_7$  in the gaseous phase (this notation will be used in the next section). Note that the mole fraction  $x_7$  of isocyanic acid in the liquid phase and the mole fractions  $y_5$  and  $y_6$  of ammonium carbamate and biuret in the gaseous phase are assumed to be zero. For this reason only four and not seven physical (heterogeneous) equilibria occur. The equilibrium constants of these four physical equilibria (which will be discussed in the next section) are denoted by  $q_1$  to  $q_4$  (see Fig. 1). Concerning the chemical (homogeneous) equilibria, it is seen in Fig. 1 that three chemical equilibria occur in the liquid phase and one chemical equilibrium in the gaseous phase. The corresponding equilibrium constants of these equilibria are denoted by  $K'_3$ ,  $K'_4$ ,  $K'_6$  and  $K''_8$  (see Fig. 1). These constants will also be discussed in the next section.

Furthermore, in urea technology it is customary to characterize the composition of the above-mentioned initial mixture of carbon dioxide, ammonia and water by the molar ammonia to carbon dioxide ratio,  $L$ , i.e.,  $L = n_2/n_1$ , and the molar water to carbon dioxide ratio,  $W$ , i.e.,  $W = n_3/n_1$ . Note that if, in addition to carbon dioxide, ammonia and water, the initial mixture also contains  $n_4$  moles of urea and  $n_5$  moles of ammonium carbamate, then  $L$  and  $W$  are expressed as:  $L = (n_2 + 2n_4 + 2n_5)/(n_1 + n_4 + n_5)$  and  $W = (n_3 - n_4)/(n_1 + n_4 + n_5)$ . It then follows that if in the initial mixture the number of moles of urea,  $n_4$ , is greater than the number of moles of water,  $n_3$ , then  $W$  is negative.

### The equilibrium constants

The equilibrium constants  $q_1$  to  $q_4$  of the heterogeneous equilibria and the equilibrium constants  $K'_3$ ,  $K'_4$ ,  $K'_6$  and  $K''_8$  of the homogeneous equilibria (see Fig. 1) are defined in this work as follows:

- 1  $q_1 = y_3/x_1$  (1)
- 2  $q_2 = y_2/x_2$  (2)
- 3  $q_3 = y_3/x_3$  (3)
- 4  $q_4 = y_4/x_4$  (4)
- 5  $K'_3 = x_3x_4/x_6$  (5)
- 6  $K'_4 = x_4/(x_1x_2^2)$  (6)
- 7  $K'_6 = x_2x_4/x_4^2$  (7)
- 8  $K''_8 = y_2y_7/y_4$  (8)

Note that all these equilibrium constants are defined by means of mole fractions. Therefore, strictly speaking, each equilibrium constant  $q_1$  to  $q_4$  is a function of pressure, temperature and all mole fractions  $x_1$  to  $x_7$  and  $y_1$  to  $y_7$ , and the equilibrium constants  $K'_3$ ,  $K'_4$  and  $K'_6$  depend on pressure, temperature and all mole fractions  $x_1$  to  $x_7$ .  $K''_8$  depends on pressure, tempera-

$$x_7 = 0$$

$$y_5 = 0$$

$$y_6 = 0$$

- 1  $\text{CO}_2$
- 2  $\text{NH}_3$
- 3  $\text{H}_2\text{O}$
- 4 urea
- 5 Carbamate
- 6 Biuret
- 7 Isocyanic Acid

ture and all mole fractions  $y_1$  to  $y_7$ . On the basis of certain simplifying assumptions, which are formulated in [16], all the above-mentioned equilibrium constants depend only on pressure and temperature. For a real multi-component system, of course, all these equilibrium constants depend on pressure and temperature only, if all concentrations  $x_1$  to  $x_7$  and  $y_1$  to  $y_7$  are constant. However, if the equilibrium constants are only weakly dependent on the concentrations (at constant pressure and temperature), then the equilibrium constants can be approximated by a function dependent on pressure and temperature only, at least around a fixed concentration point ( $x_{10}, x_{70}, y_{10}, y_{70}$ ). How large the range around this point is, in which such an approximation is permissible, depends on the nature of the multi-component system under consideration and the maximum acceptable deviation between the approximated and the true value of the equilibrium constants. The statements presented here can only be checked by comparing approximated equilibrium constants with very accurately measured ones.

For the ternary system carbon dioxide-ammonia-water the approximation equations for the equilibrium constants  $q_1$  to  $K_6^*$  were found to be:

$$q_1 = p^{-1} \exp(43.32522 - 3803.22/T + 0.0019688 T - 4.61441 nT + 0.345778 p/T + 460.42 p/T^2) \quad (9)$$

$$q_2 = p^{-1} \exp(55.57294 - 5121.96/T + 0.0019980 T - 6.50331 nT - 0.924275 p/T + 544.84 p/T^2) \quad (10)$$

$$q_3 = p^{-1} \exp(60.17097 - 10114.7/T + 0.0005818 T - 5.75561 nT - 0.860317 p/T + 714.75 p/T^2) \quad (11)$$

$$q_4 = p^{-1} \exp(167.6540 - 15636.0/T + 0.0093358 T - 22.9241 nT - 0.607100 p/T + 1515.3 p/T^2) \quad (12)$$

$$K_3^* = \exp(12.600175 - 2685.24/T - 1.21791 nT - 0.05038 p/T) \quad (13)$$

$$K_4^* = \exp(-71.20722 + 12896.3/T + 7.75041 nT + 0.22960 p/T) \quad (14)$$

$$K_5^* = \exp(-8.187559 - 4152.00/T + 1.81201 nT + 0.00361 p/T) \quad (15)$$

$$K_6^* = p^{-1} \exp(-13.920512 - 5728.264/T - 0.00436085 T + 5.347861 nT - 0.654756 p/T + 811.161 p/T^2) \quad (16)$$

For a detailed discussion of the calculation method and the estimation of the numerical values contained in the equations (9) to (16) the reader is referred to [16]. For the physical meaning of these numerical values the reader is also referred to [16]. It should be mentioned that some of these numerical values differ from those reported in [16]. This difference is due to a new fit of these values to the measurements presented by Durisch [16]. In this new fit the experimentally found azeotropic pressures of Lemkowitz [26] were no longer imposed as boundary condition, as was done in [16]. Furthermore, in this new fit the least squares fitting technique concerning the measured equilibrium constants was supplemented by direct comparison of measured and calculated concentrations. Note that the equations (9) to (16) are not dimensionally homogeneous; in using these equations the numerical values of the pressure  $p$  and the temperature  $T$ , which must be expressed in bar and  $K$  (Kelvin;  $(T)/K = (\vartheta)/^\circ C + 273.15$ ) respectively, have to be substituted in (9) to (16).

### The new calculation method

In a previous section a vapour/liquid system was described which initially consisted of a homogeneous mixture of carbon dioxide, ammonia and water. The composition of this initial mixture was characterized by the molar ratios  $L$  and  $W$ . At certain values of the pressure  $p$  and temperature  $T$  this mixture formed a vapour/liquid system, of which a section along the phase boundary surface is schematically shown in Fig. 1. The following question now arises: how can the concentrations (mole fractions  $x_1$  to  $y_7$ ) of all the constituents in the liquid and gaseous phase of the above-mentioned vapour/liquid system be calculated?

At thermodynamic equilibrium in the two-phase system, not only must the equilibrium conditions (1) to (8) be satisfied, but also the law of conservation of mass. On the basis of this law the following additional equation in the mole fractions and molar ratios  $L$  and  $W$  can be derived:

$$\frac{x_1 + x_4 + x_5 + 2x_6}{1 + x_4 + 2x_5 + 2x_6} \cdot \frac{1}{1 + L + W} = \frac{1}{1 + L + W} \cdot \frac{y_1 + y_4 + y_5}{1 + y_4} + \frac{x_2 + 2x_4 + 2x_5 + 3x_6}{1 + x_4 + 2x_5 + 2x_6} \cdot \frac{L}{1 + L + W} = \frac{L}{1 + L + W} \cdot \frac{y_2 + 2y_4 + y_5}{1 + y_4}$$

This equation results from the law of conservation of mass (formulated as element balances) by simple algebraic manipulations assuming that the mole fractions  $x_7$ ,  $y_6$  and  $y_8$  are zero and taking into account the following equations in the mole fractions:

$$x_1 + x_2 + x_3 + x_4 + x_5 + x_6 = 1 \quad (18)$$

$$y_1 + y_2 + y_3 + y_4 + y_5 = 1 \quad (19)$$

If now the equilibrium constants corresponding to equations (9) to (16) are introduced into equations (1) to (8), then, together with the equations (17) to (19), a new system of equations is obtained, which consists of eleven equations with fifteen unknowns. If the pressure  $p$ , the temperature  $T$  and the initial molar ratios  $L$  and  $W$  are given, this new system of equations can be solved for all mole fractions  $x_1$  to  $y_7$ . Unfortunately this system of equations is non-linear; i.e., more than one mathematical solution exists and the system can not be solved by elementary methods. To solve this system of equations, ordinary numerical methods were applied.

### The transformation equations

In spite of the existence of seven chemical substances (constituents) in the vapour/liquid system under discussion (see Fig. 1), it is nevertheless a ternary, i.e., a three component system. This is due to the fact that the four constituents urea, ammonium carbamate, biuret and isocyanic acid can be transformed into the three constituents carbon dioxide, ammonia and water via the four independent chemical reactions shown in

Fig. 1. Carbon dioxide, ammonia and water are therefore called the components of the system. For detailed information concerning the number of components in chemically reactive systems the reader is referred to Zemansky [28]. For comparisons of calculated and measured component concentrations, it is necessary to transform the calculated constituent concentrations of the liquid and gaseous phase respectively, into component concentrations. The mathematical relations between the actual constituent concentrations and the component concentrations are called transformation equations.

On the basis of the law of conservation of mass the component concentration (mole/mole) of carbon dioxide ( $X_1$ ), ammonia ( $X_2$ ) and water ( $X_3$ ) respectively, are expressed as follows.

For the gaseous phase:

$$X_1^* = \frac{y_1 + y_4 + y_5 + 2y_6 + y_7}{1 + y_4 + 2y_5 + 2y_6} \quad (20)$$

$$X_2^* = \frac{y_2 + 2y_4 + 2y_5 + 3y_6 + y_7}{1 + y_4 + 2y_5 + 2y_6} \quad (21)$$

$$X_3^* = \frac{y_3 - y_4 - 2y_6 - y_7}{1 + y_4 + 2y_5 + 2y_6} \quad (17) \quad (22)$$

For the liquid phase:

$$X_1 = \frac{x_1 + x_4 + x_5 + 2x_6 + x_7}{1 + x_4 + 2x_5 + 2x_6} \quad (23)$$

$$X_2 = \frac{x_2 + 2x_4 + 2x_5 + 3x_6 + x_7}{1 + x_4 + 2x_5 + 2x_6} \quad (24)$$

$$X_3 = \frac{x_3 - x_4 - 2x_6 - x_7}{1 + x_4 + 2x_5 + 2x_6} \quad (25)$$

Note that in the equations (20) to (25) the relations (18) and (19) have been taken into account. Furthermore, it can easily be checked that the equation  $X_1 + X_2 + X_3 = 1$  holds for the liquid and gaseous phase, respectively. Equation (22) further shows that the more urea ( $y_4$ ) and isocyanic acid ( $y_7$ ) the gaseous phase contains, the smaller the component concentration of water in the gaseous phase,  $X_3^*$ , becomes.  $X_3^*$  can even become negative. It should be mentioned that the transformation equations (20) to (25) differ from those reported in [16]. This difference is caused by using ammonia,  $\text{NH}_3$ , instead of double ammonia,  $(2\text{NH}_3)$ , as the ammonia component.

#### Application

By means of the new calculation method presented in this article the constituent composition of the liquid and co-existing gaseous phase have been calculated as a function of the pressure  $p$ , the temperature  $T$  and the initial molar ratios  $L$  and  $W$ . From the calculated constituent composition of the liquid phase, ( $x_1, \dots, x_6$ ), the mass fractions of urea,  $w_4$ , and biuret,  $w_6$ , in the liquid phase were calculated according to the relation  $w_j = x_j M_j / \sum x_j M_j$ , in which  $M_j$  denotes the molecular

mass (g/mole) of the constituent  $j$ . The calculation of the two quantities,  $w_4$  and  $w_6$ , is important because these two quantities can be experimentally determined, and therefore direct comparison of calculated and experimentally found values is possible. From the calculated constituent composition of the gaseous phase, ( $y_1, \dots, y_7$ ), the component concentrations  $X_1^*$ ,  $X_2^*$  and  $X_3^*$  of the components carbon dioxide, ammonia and water in the gaseous phase were calculated according to the transformation equations (20) to (22). The calculation of these component concentrations is also important because they too can be experimentally determined (via the classical CHN-elementary analysis). From the calculated constituent composition of the liquid phase the urea-yield  $x$  according to  $x = x_4 / (x_1 + x_4 + x_5 + 2x_6)$  has also been calculated because this quantity is of particular importance to the industrial urea synthesis. Corresponding experimental yields could be deduced from the experimental data presented by Durisch [16]. The above-mentioned calculations were performed at the temperatures 160, 170 and 180°C, at  $L = 2$ , and within the ranges of  $-0.6 \leq W \leq 0$  and  $70 \text{ bar} \leq p \leq 145 \text{ bar}$ , as under these conditions most experimental data are found. The equilibrium pressures required for these calculations are taken from [17]. In the following graphs, examples of such calculations will be presented. In these graphs calculated values are compared with scarce data in literature. The concentrations represented in the following Fig. 2 to 7 are plotted as a function of the initial molar water to carbon dioxide ratio  $W$ , at various temperatures and at a constant initial molar ammonia to carbon dioxide ratio of  $L = 2$ .

#### Discussion

In Fig. 2 the urea concentration (mass fraction) in the liquid phase is presented as a function of the molar ratio  $W$ , at various temperatures. It is seen that the concentration of urea increases as the initial water to carbon dioxide ratio  $W$ , decreases, as is to be expected from the law of mass action for the dehydration of ammonium carbamate to urea and water. Through the experimentally found urea concentrations of Durisch (closed symbols) a family of smooth curves can be drawn, and the agreement between the experimental values of Durisch (closed symbols) and the calculated curves is excellent. Note that the calculation method presented in this article was originally developed to describe the  $\text{CO}_2/\text{NH}_3/\text{H}_2\text{O}$  vapour-liquid system, only within a limited concentration space. That the urea concentration in the liquid phase can be calculated even within the large range of 40 to 70 mass-% was not expected, but indicates the wide range of validity of the calculation method. The curvature of the calculated curves relative to the measured points (closed symbols) seems to be a little too strong. A possible reason for this fact might be that the equilibrium constant  $K_3'$

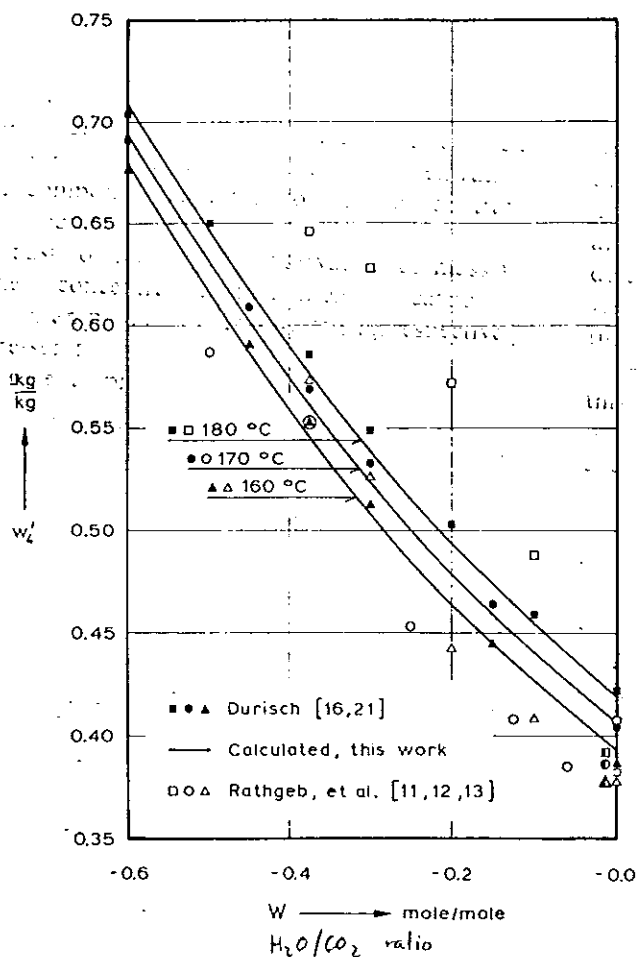


Fig. 2: The urea concentration  $w'_6$  (mass fraction) in the liquid phase at various temperatures and varying  $W$ , at  $L=2$ . Closed and open symbols represent experimentally determined values. The drawn lines are calculated according to this work. The half closed triangle represents an interpolated value of *Kawasumi's* [7] measurements at 160°C,  $L=2$  and  $W=0$ . The half closed circle (170°C) and square (180°C) represent extrapolations of *Kawasumi's* [7] measurements at  $L=2$  and  $W=0$ .

of the urea formation from ammonium carbamate is assumed to be independent of the urea concentration in the liquid phase. The urea concentrations of *Kawasumi* (half closed symbols) are systematically a few percent (absolute) lower than the calculated and measured values of *Durisch*. It is possible that *Kawasumi's* values may be somewhat too low, since in order to determine the urea concentration, *Kawasumi* concentrated his samples at 70°C, and at this temperature some of the urea was probably hydrolysed. The scatter of *Rathgeb's* experimentally determined urea concentrations (open symbols) is rather large, and the agreement between *Rathgeb's* concentrations and the concentrations of *Durisch* (closed symbols) is poor. Possible reasons for this scatter and disagreement may be hydrolysis of urea during *Rathgeb's* sampling procedure (hot water in sampler), analysis errors (too little xanthinol excess) and non-equilibrium state at the time

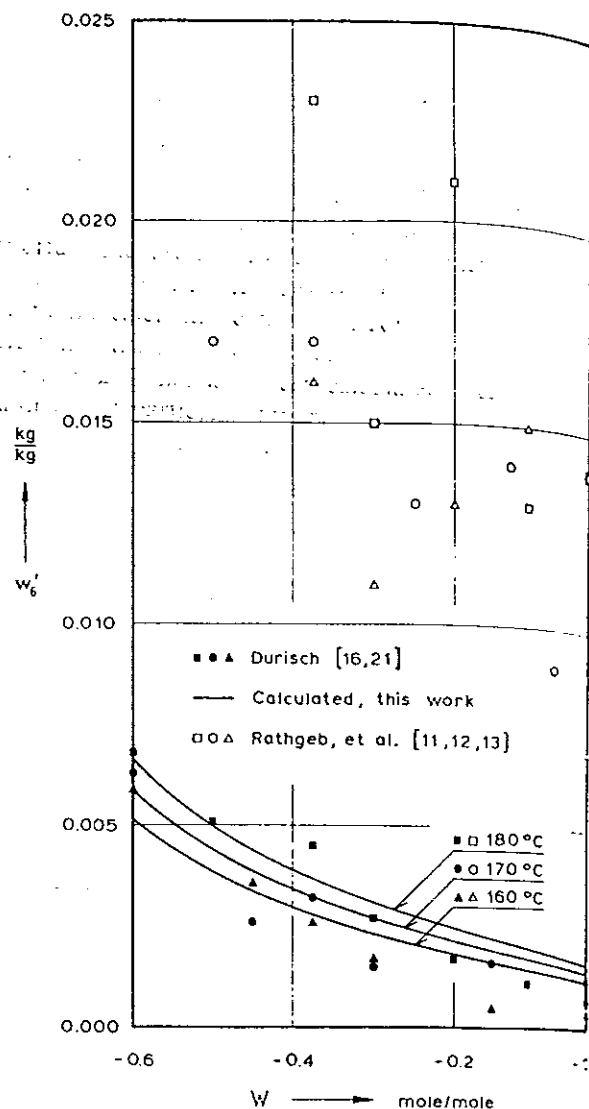


Fig. 3: The biuret concentration  $w'_6$  (mass fraction) in the liquid phase at various temperatures and varying  $W$ , at  $L=2$ . The symbols and lines have the same meaning as in Fig. 2.

of sampling [21]. Especially peculiar is the convex curvature of the suggested curve through *Rathgeb's* points at 180°C (open squares) relative to the concave curvature found by *Durisch*. Because of this anomalous behaviour and because of the large scatter of *Rathgeb's* measurements, his data were not used in the least squares fit for the calculation of the numerical values in equations (9) to (16).

In Fig. 3 the biuret concentration in the liquid phase is presented as a function of  $W$  at various temperatures. As expected from the formation of biuret from urea, the concentration of biuret increases with decreasing  $W$ , since the urea concentration rises under these circumstances. Agreement between the calculated curves and the measured points of *Durisch* (closed symbols) is only fair due to the scatter of these points. The results of *Rathgeb* compare very poorly with the calculated and measured data of *Durisch*, but the extreme scatter

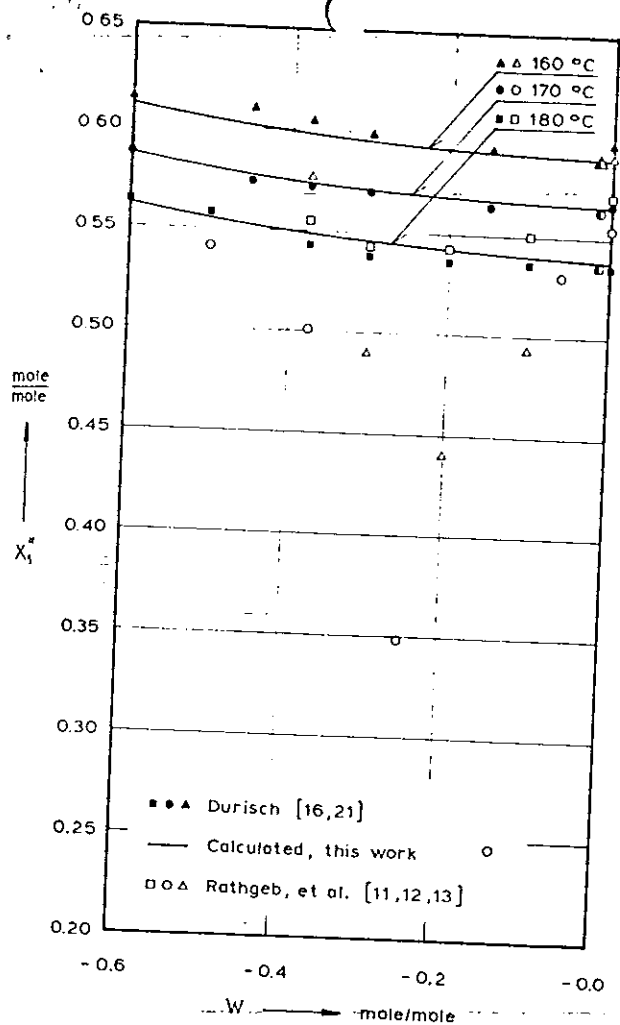


Fig. 4: The carbon dioxide concentration  $X_1''$  (mole fraction of the component, not constituent  $\text{CO}_2$ ) in the gaseous phase at various temperatures and varying  $W$ , at  $L=2$ . The symbols and lines have the same meaning as in Fig. 2.

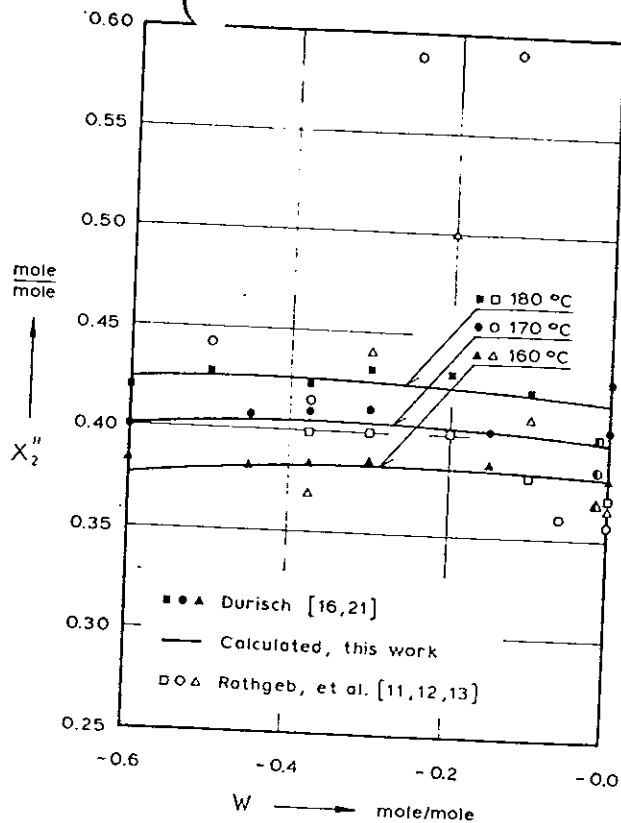


Fig. 5: The ammonia concentration  $X_2''$  (mole fraction of the component, not constituent  $\text{NH}_3$ ) in the gaseous phase at various temperatures and varying  $W$ , at  $L=2$ . The symbols and lines have the same meaning as in Fig. 2.

of Rathgeb's data (open symbols) renders them of very questionable value (although they do roughly exhibit the same trend already mentioned). In Fig. 4, 5 and 6 the concentrations of the components carbon dioxide, ammonia and water in the gaseous phase are graphically represented. For the carbon dioxide concentration (Fig. 4) agreement between Kawasumi's concentrations and the measured and calculated concentrations of Durisch is excellent, as is also the agreement between the calculated curves and the measurements of Durisch. It should be mentioned that Kawasumi's data were not used in calculating the numerical values in equations (9) to (16). Rathgeb's carbon dioxide concentrations (Fig. 4, open symbols) exhibit pronounced scatter, except for 180 °C, at which agreement with Kawasumi's and Durisch's data is quite reasonable. For the ammonia concentration (Fig. 5) a small systematic difference is found between Kawasumi's and Durisch's data. Again, agreement between the calculated lines and measured values of Durisch is quite good. And again Rathgeb's data exhibit considerable scatter, particularly at 170 °C (Fig. 5, open circles). In Fig. 6 the water concentrations of Kawasumi are systematically slightly higher than the experimental values of Durisch. Lemkowitz et al. [26] suggested that Kawasumi's water concentrations might be slightly too high due to possible analysis errors. The agreement between the calculated curves and the measurements of Durisch (Fig. 6, closed symbols) is rather good. The water concentrations of Rathgeb (Fig. 6, open symbols) exhibit extreme scatter. Rathgeb's water concentration in general seem to be systematically about 100 to 300% (relative) too high. In Fig. 7 the urea-yield (carbon dioxide conversion) is represented as a function of  $W$  at various temperatures. It is seen that the conversion increases with decreasing  $W$ , as is to be expected from the mass action law. The conversion also increases with temperature at constant  $W$ . The agreement between the experimental values of Durisch (closed symbols) and the calculated curves is excellent. The values of Kawasumi (half closed symbols) are systematically a few percent (absolute) lower than the calculated and measured values of Durisch. As already mentioned, the reason for this fact might be the hydrolysis of urea during Kawasumi's concentration of liquid samples. The large scatter of Rathgeb's experimental values (open symbols) and the peculiar course of his measurements at 180 °C correspond more or less to the behaviour shown in Fig. 2. For that

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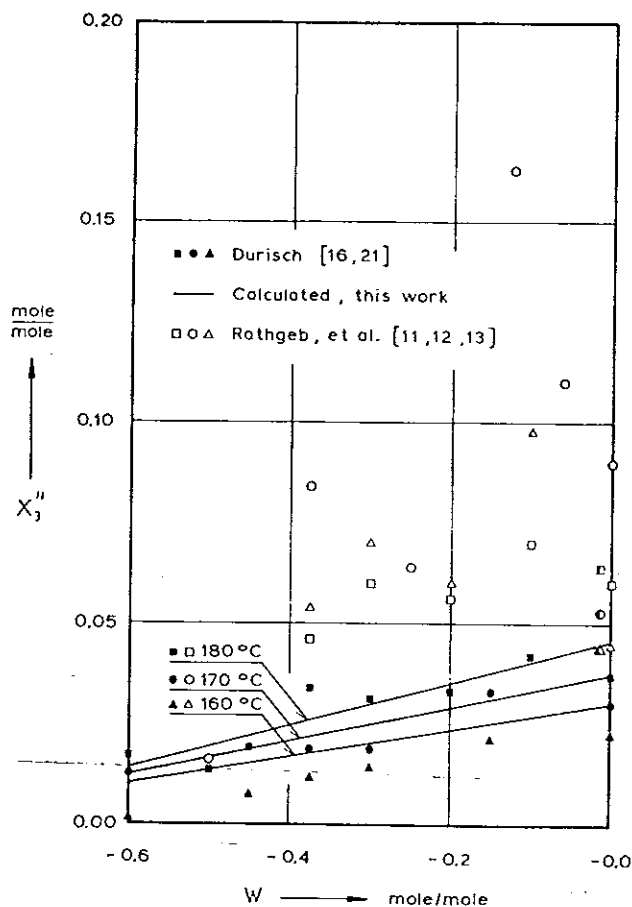


Fig. 6: The water concentration  $X_3''$  (mole fraction of the component, not constituent  $H_2O$ ) in the gaseous phase at various temperatures and varying  $W$ , at  $L=2$ . The symbols and lines have the same meaning as in Fig. 2.

behaviour, possible reasons were already mentioned. Note that at a temperature of  $180^\circ C$  and a  $W$  of  $-0.375$  a conversion of about 72% is found according to the experimental and calculated data of *Durisch*. This conversion value is considerably lower than the value of 90.4% experimentally found by *Rathgeb* and the value of 93% given in the patent [12] for the same temperature and molar ratio  $W$ .

### Conclusions

The presented comparisons of measured and calculated data (Fig. 2 to 7) show that the calculation method described in this article is reliable within the ranges of  $160^\circ C \leq \vartheta \leq 180^\circ C$ ,  $70 \text{ bar} \leq p \leq 145 \text{ bar}$  and  $-0.6 \leq W \leq 0$ , at  $L=2$ . As the calculation method is based on physical-thermodynamic (not statistical-mathematical) principles, extrapolations within reasonable limits are certainly admissible. With the possibility of extrapolation present, the calculation method most probably provides a useful tool for the economic improvement of existing urea plants as well as for the development of new less energy intensive routes for

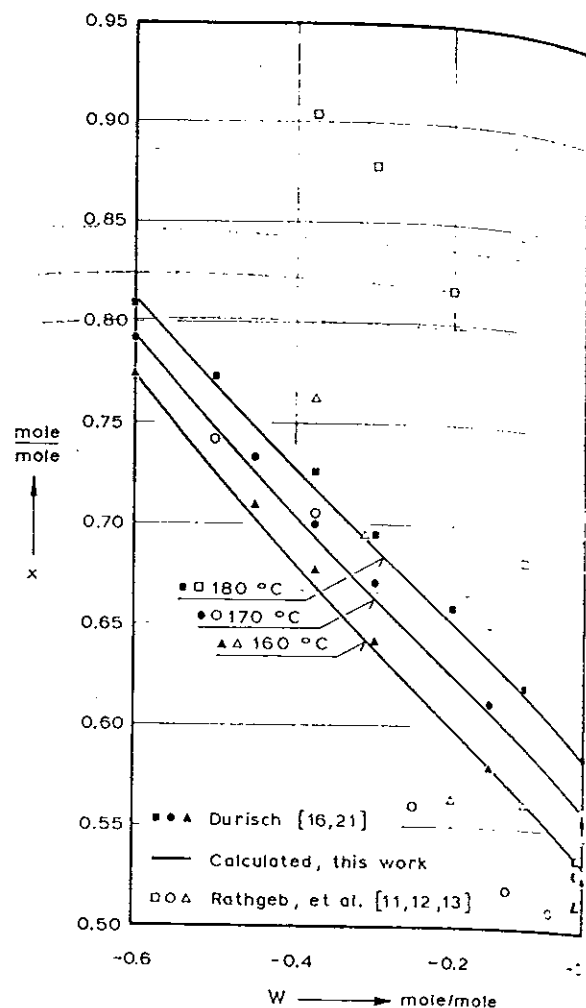


Fig. 7: The urea-yield (carbon dioxide conversion)  $x$  in the liquid phase at various temperatures and varying  $W$ , at  $L=2$ . The symbols and lines have the same meaning as in Fig. 2.

the industrial synthesis of urea from ammonia and carbon dioxide. The calculation method presented here can be improved by deriving and applying more flexible functions (dependent not only on pressure and temperature, but also on concentrations) for the approximation of the equilibrium constants. Eventually more chemical and physical equilibria also have to be taken into account. From the measurements and calculations presented in this article it can be concluded that *Rathgeb's* [11] experimentally determined water concentrations in the gaseous phase are most probably about 100 to 300% (relative) too high. It can also be concluded that *Rathgeb's* [11] carbon dioxide conversion of 90.4% at  $180^\circ C$  and  $W = -0.375$  is most probably about 25% (relative) too high. For the urea synthesis process described in [12, 14] and [15] (applying *Rathgeb's* data) low water concentrations in the gaseous phase and low conversions are disadvantageous. From the calculations presented in this work, however, it is to be expected that the water concentration in the

gaseous phase and the conversion increase with temperature at constant  $L$  and  $H$ , so that the above-mentioned disadvantages may be somewhat compensated.

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#### Zusammenfassung und Schlussfolgerungen

Die Verfasser präsentieren eine neue Methode zur Berechnung der Konstituenten- und Komponenten-Zusammensetzung der flüssigen und koexistierenden gasförmigen Phase des ternären Systems Kohlendioxid/Ammoniak/Wasser unter Harnstoffsynthese-Bedingungen. Bei dieser Methode spielen Gleichgewichtskonstanten physikalischer und chemischer Gleichgewichte eine wichtige Rolle. Mittels Näherungsgleichungen für diese Gleichgewichtskonstanten führten die Verfasser Berechnungen durch im Temperaturbereich von 160 bis 180°C und im Druckbereich von 70 bis 145 bar bei konstantem  $\text{NH}_3 : \text{CO}_2$ -Verhältnis und variablem  $\text{H}_2\text{O} : \text{CO}_2$ -Verhältnis. Vergleiche von berechneten und gemessenen Daten zeigen, dass die vorgeschlagene Berechnungsmethode im untersuchten Bereich recht befriedigende Ergebnisse liefert und dass Extrapolationen – in Anbetracht der physikalisch-thermodynamischen Prinzipien worauf die Methode basiert – innerhalb vernünftiger Grenzen zulässig sind. Die mitgeteilte relativ einfache Berechnungsmethode kann sich deshalb als nützliches Werkzeug erweisen, sowohl zur wirtschaftlichen Verbesserung existierender als auch zur Entwicklung neuer weniger energieintensiven Verfahren zur industriellen Synthese des Harnstoffs aus Kohlendioxid und Ammoniak. Die oben erwähnten Vergleiche zeigen auch, dass ältere Messergebnisse von *Kawasumi* [6–10] recht gut übereinstimmen mit den hier berechneten Daten (*Kawasumis* Messergebnisse wurden nicht berücksichtigt beim Ermitteln der Parameter in den oben erwähnten Näherungsgleichungen), dass jedoch neuere Messungen von *Rathgeb* [11] im allgemeinen beträchtlich abweichen von den hier berechneten Daten. Es scheint, dass *Rathgeb* [11] experimentell ermittelten Wasserkonzentrationen in der gasförmigen Phase ca. 100 bis 300% (relativ) zu hoch sind. Ebenfalls zu hoch zu sein (ca. 25% relativ) scheinen die von *Rathgeb* [11] bei tiefen  $\text{H}_2\text{O} : \text{CO}_2$ -Verhältnissen gemessenen Harnstoffausbeuten in der flüssigen Phase bei 180°C (180°C stellt in etwa die untere Grenze dar der heute üblichen Harnstoffsynthese-Temperaturen). Für das von *Buck* und *Rathgeb* in Patentschriften [12, 14 und 15] beschriebene Verfahren zur Gewinnung von Harnstoff bzw. Verfahren zur Tiefhaltung des Wassergehalts in einem Harnstoffreaktor, Verfahren, zu dem Auslegung *Rathgeb*s Messergebnisse [11] herangezogen wurden, sind niedrige Wasserkonzentrationen in der gasförmigen Phase und tiefe Harnstoffausbeuten in der flüssigen Phase bzw. tiefe Wasserkonzentrationen in der gasförmigen Phase nachteilig. Gemäss den in der vorliegenden Arbeit mitgeteilten Ergebnissen ist zu erwarten, dass die Wasserkonzentration in der gasförmigen Phase und gleichzeitig die Harnstoffausbeute in der flüssigen Phase zunehmen, falls die Temperatur (und damit der Druck) erhöht wird bei konstantem  $\text{NH}_3 : \text{CO}_2$ - und  $\text{H}_2\text{O} : \text{CO}_2$ -Verhältnis. Hohe Wasserkonzentrationen in der gasförmigen Phase und gleichzeitig hohe Harnstoffausbeuten in der flüssigen Phase wären für das oben erwähnte Verfahren zur Gewinnung von Harnstoff [12] vorteilhaft.

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