

Simulation of a Urea Synthesis Reactor. 1. Thermodynamic Framework

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A thermodynamic model for the system $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O-urea}$ is developed as a supporting program of a urea synthesis reactor simulation module. The model covers a wide range of composition and temperature and can be used to predict the behavior of the system at and removed from urea synthesis conditions. Calculated equilibrium phase compositions and vapor pressures at different temperatures are in very good agreement with published experimental data. When used as thermodynamic support of the reactor simulation module, the proposed thermodynamic model yields good agreement with production-scale plant data. Calculated partial molal enthalpies for all components in the gas and liquid phases lead to a satisfactory prediction of local equilibrium temperatures. The solution algorithm for the nonlinear system of phase and chemical equilibrium equations is simple and robust. A multiple-step parameter estimation strategy is adopted to regress published experimental data.

Introduction

Urea (NH_2CONH_2) is produced commercially by reaction of ammonia (NH_3) and carbon dioxide (CO_2), under conditions depending on each particular plant technology. In most operating processes the synthesis reaction is carried out in the liquid phase, at pressures from 13 to 25 MPa and at temperatures between 170 and 200 °C. A complete survey of operating process technologies has been published by Chao (1967). Subsequently, different process have been described by Uchino (1986) and Stamicarbon Staff (1986).

The synthesis proceeds via formation of ammonium carbamate as intermediate, which then dehydrates to give urea. At pressures above its dissociation pressure the formation of ammonium carbamate is fast and complete.

The carbamate dehydration reaction is slower and does not proceed to completion. The equilibrium conversion usually reaches values greater than 80% on a CO_2 basis (Lemkowitz et al., 1972).

To overcome the limitation imposed by chemical equilibrium on the one-pass conversion to urea, several urea technologies include total or partial recycle of unreacted ammonium carbamate.

Unreacted CO_2 and NH_3 present in the reactor outlet stream are recovered in a sequence of medium- and low-pressure carbamate decomposers and gas separators. A fraction of the total CO_2 fed to the process is used in these gas separators as a stripping agent to aid the NH_3 and CO_2 separation from the product stream. Before it is recycled to the synthesis reactor, the stream of recovered gases is condensed and recompressed.

The rest of the fresh CO_2 , together with liquid NH_3 and the recycle stream, is fed to the tubular synthesis reactor. At the reactor inlet, global NH_3/CO_2 (L) and $\text{H}_2\text{O}/\text{CO}_2$

Table I. Typical Reaction Feed and Outlet Streams in a Total Recycle Urea Process

stream	NH_3 feed	CO_2 feed	carbamate recycle	outlet stream
mass flow (kg/h)	16 770	8 310	21 800	46 880
composition (wt %)				
NH_3	100	0	40.83	36.74
CO_2	0	100	36.19	11.24
H_2O	0	0	21.81	19.68
urea	0	0	1.17	32.34
temp (°C)	96.0	89.4	106.9	192.9

(W) mole ratios are kept close to 4.0 and 0.7, respectively. Typical inlet and outlet streams conditions are described in Table I.

Over the past 50 years a sustained effort has been put on the chemical and thermodynamic modeling of the system $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ at and far from urea formation conditions. In the pioneering work of Fréjacques (1948) a single reversible reaction for urea formation



was proposed. This oversimplified model overlooks the important fact that, at least, two independent reactions contribute significantly to the equilibrium composition: the carbamate formation reaction and the carbamate dehydration reaction.

In later work (Kawasumi, 1952, 1953a,b, 1954; Mavrovic, 1971) the reaction scheme



was proposed. This more realistic starting point leaves the way open for a more detailed treatment of chemical

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equilibrium. This possibility was lost because the thermodynamic model of chemical equilibrium built on this reaction scheme considered each mole of ammonium carbamate present at equilibrium as if it effectively were 1 mol of free CO₂ plus 2 mol of free NH₃. With this simplifying assumption, equilibrium composition can be determined with a single extent of reaction. However, the model is insufficient to describe simultaneous chemical and phase equilibrium at synthesis conditions, or chemical equilibrium in the liquid phase far from urea synthesis conditions.

Lemkowitz et al. (1973) considered eqs 2 and 3 as independent reactions, each one with its own extent of reaction. They solved chemical and gas-liquid equilibria using experimental values of the reaction equilibrium constants. Henry's constants of NH₃ and CO₂ were measured considering the reaction mixture as a solvent. Bubble points of liquid reaction mixtures and dew points of gas mixtures were predicted with the assumption of ideal behavior of gas and liquid phases.

Considering the severe conditions at which the synthesis reaction is conducted and that the liquid phase is an electrolytic solution, it can be concluded that this simplifying assumption limits the validity of the model when the system is removed from the conditions at which the empirical constants were determined.

There are abundant experimental data reported on the chemical equilibrium of the synthesis reaction in the liquid phase (Kawasumi, 1952, 1953a,b, 1954; Kotula, 1981; Inoue et al., 1972a,b). The conversion of CO₂ to urea has been measured for different initial values of the NH₃/CO₂ and H₂O/CO₂ mole ratios and for different temperatures in the range of interest for urea synthesis. On the basis of the reported data, Gorlovskii and Kucheryavii (1980) developed a useful correlation to predict the equilibrium conversion within a wide range of initial conditions.

The thermodynamic models for the system NH₃-CO₂-H₂O-urea reviewed so far in this section deal with chemical and phase equilibria.

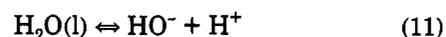
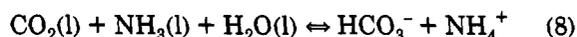
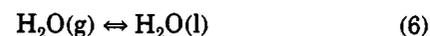
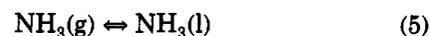
The rigorous simulation of critical equipment in urea synthesis processes also requires the accurate calculation of local temperatures. Therefore, the supporting thermodynamic model for the NH₃-CO₂-H₂O-urea mixture must be able to estimate partial molal enthalpies for all components in the gas and liquid phases.

In the particular case of modeling and simulation of the synthesis reactor, local reaction rates must be predicted. This puts on the supporting thermodynamic model the burden of predicting the local composition and temperature at any point in the reaction volume (Kummel et al., 1981; Kucheryavii and Gorbushenkov, 1970).

This paper is intended to develop a thermodynamic model capable of supporting a rigorous reactor simulation program (Irazoqui et al., 1993). The model parameters will be estimated by regression of published operating data from pilot-scale plants and from laboratory data found in the literature.

Reaction Scheme

The behavior of the system NH₃-CO₂-H₂O has been extensively studied under conditions removed from those at which urea is formed (Edwards et al., 1978; Pawlikowsky et al., 1982; Kawazuishi and Prausnitz, 1987; Göppert and Maurer, 1988). The chemical model on which this body of work is based does not include urea either as a reactant or as a product.



This system of reactions does not account for an alternative way to dissolve CO₂ different from the production of ionic species. Except for the negligible amount that remains unreacted, all of the CO₂ dissolved has been used to form HCO₃⁻, CO₃²⁻, and H₂NCOO⁻ anions.

This confers some lack of flexibility to the scheme, which for intermediate to high concentrations leads to overestimation of the ionic strength of the mixture.

Undissociated carbamic acid formed from dissolved CO₂ and NH₃ according to



may be present in the NH₃-CO₂-H₂O mixture under certain conditions (Hatch and Pigford, 1962; Buckingham et al., 1986).

Partial dissociation of ammonium carbamate can be included by considering the equilibrium



together with eq 7.

At high ammonia and carbon dioxide concentrations and for temperatures above 160 °C, the urea synthesis reaction



must also be taken into account.

Although the objective of this work is to develop a thermodynamic subprogram to assist an urea synthesis reactor simulator, all of the above chemical reactions must be taken into account in order to profit from experimental data taken under different conditions, even if they were measured outside the synthesis range.

In this way, no a priori restrictions on the degrees of freedom of the chemical system are imposed. The values of the parameters obtained by regression of the available experimental data will show which of the reactions in the scheme are relevant and which are not under urea synthesis conditions. However, chemical reactions with negligible equilibrium reaction extents will be disregarded in the final version of the phase and chemical equilibrium model to avoid unnecessary time-consuming iteration loops to be executed in each call to the thermodynamic supporting program.

Activity Coefficients

Most of the work published on the chemical and thermodynamic modeling of the system NH₃-CO₂-H₂O

deals with solutions from dilute to moderate concentrations of NH_3 and CO_2 in water. Under such circumstances it is natural to choose the pure liquid at the system temperature, T , and pressure, P , as the standard state for water and that of infinite dilution in pure water for CO_2 and nonvolatile species.

At synthesis conditions ammonia is fed to the reactor in great excess over its stoichiometric ratio to CO_2 . Urea and water, already present in the recycle stream, are produced in equal molar quantities by the urea synthesis reaction, representing together more than 50% of the outlet stream mass flow rate.

In this situation, it is convenient to choose the pure liquid at the system temperature, T , and pressure, P , as the standard state for ammonia, water, and urea and infinite dilution in pure water as the standard state for the remaining components in the mixture.

To estimate the activity coefficients in the mixture NH_3 - CO_2 - H_2O , Bernardis et al. (1989) used an extended UNIQUAC model (Sander et al., 1986a,b). In this paper, some of the most important binary interaction parameters are considered as functions of the temperature and of the ionic strength of the mixture. It is noticeable the strong dependence found for the binary interaction parameters on the ionic strength, which seems to be an indirect way to compensate for the inherent limitations of the adopted reaction scheme to interpret the chemical changes occurring in the medium far from synthesis conditions.

In this paper, the chemical reaction system discussed in the previous section is adopted. Activity coefficients are predicted by means of the UNIQUAC extended equation

$$\ln \gamma_i(T, \mathbf{x}) = \ln \gamma_i^C(\mathbf{x}) + \ln \gamma_i^R(T, \mathbf{x}) + \ln \gamma_i^{\text{DH}}(T, \mathbf{x}) \quad (15)$$

where the combinatorial, $\gamma_i^C(\mathbf{x})$, and the residual, $\gamma_i^R(T, \mathbf{x})$, contributions to activity coefficients are given by

$$\ln \gamma_i^C(\mathbf{x}) = \ln(\phi_i/x_i) + (z/2)q_i \ln(\theta_i/\phi_i) + l_i - (\phi_i/x_i) \sum_j x_j l_j \quad (16)$$

and

$$\ln \gamma_i^R(T, \mathbf{x}) = -q_i \left\{ \ln \left(\sum_j \theta_j \tau_{ij} \right) - 1 + \sum_j [\theta_j \tau_{ij} / (\sum_k \theta_k \tau_{kj})] \right\} \quad (17)$$

respectively. The Debye-Hückel contribution for nonionic species (Sander et al., 1986a), is

$$\ln \gamma_i^{\text{DH}}(T, \mathbf{x}) = (2A/b^3)M_i [1 + bI^{1/2} - 1/(1 + bI^{1/2}) - 2 \ln(1 + bI^{1/2})] \quad (18)$$

while in the case of ionic species is

$$\ln \gamma_i^{\text{DH}}(T, \mathbf{x}) = -z_i^2 A I^{1/2} / (1 + bI^{1/2}) \quad (19)$$

where

$$\theta_i = x_i q_i / \left(\sum_j x_j q_j \right) \quad (20)$$

$$\phi_i = x_i r_i / \left(\sum_j x_j r_j \right) \quad (21)$$

$$l_i = (z/2)(r_i - q_i) - (r_i - 1) \quad (22)$$

$$\tau_{ij} = \exp(-a_{ij}/T); \quad a_{ij} \neq a_{ji}; \quad a_{ii} = a_{jj} = 0 \quad (23)$$

Table II. Extended UNIQUAC Model: Pure Component Parameters

component (<i>i</i>)	r_i	q_i
H_2O (1)	0.92	1.40
NH_3 (2)	1.00	1.00
CO_2 (3)	1.32	1.12
NH_4^+ (4)	0.91	0.99
HCO_3^- (5)	1.54	1.44
H_2NCOO^- (6)	1.71	1.58
H_2NCOOH (7)	1.99	1.92
H_2NCONH_2 (8)	2.16	2.00

$$I = (1/2) \sum_j m_j z_j^2 \quad (24)$$

where m_i is the molality of the i ionic species referred to 1000 g of mixed solvent, M_i is the molecular weight of neutral species i , z_i is the charge number of a ionic species i ; b is the distance of closest approach between ions, z is the coordination number (usually $z = 10$), r_i and q_i are fixed UNIQUAC volume and surface pure component parameters (see Table II) and a_{ij} are adjustable binary interaction parameters. Following Sander et al. (1986a) $b = 1.5$ was chosen and the Debye-Hückel parameter A was taken as the one corresponding to pure water.

Activity coefficients based on the symmetric convention, $\gamma_i(T, \mathbf{x})$, can be related to those based on the unsymmetric convention,

$$\ln \gamma_i^\circ(T, \mathbf{x}) = \ln \gamma_i^{\circ,C}(\mathbf{x}) + \ln \gamma_i^{\circ,R}(T, \mathbf{x}) + \ln \gamma_i^{\circ,\text{DH}}(T, \mathbf{x}) \quad (25)$$

by means of

$$\ln \gamma_i^{\circ,C}(\mathbf{x}) = \ln \gamma_i^C(\mathbf{x}) - \ln \gamma_i^{\infty,C} \quad (26)$$

$$\ln \gamma_i^{\circ,R}(T, \mathbf{x}) = \ln \gamma_i^R(T, \mathbf{x}) - \ln \gamma_i^{\infty,R}(T) \quad (27)$$

$$\ln \gamma_i^{\circ,\text{DH}}(T, \mathbf{x}) = \ln \gamma_i^{\text{DH}}(T, \mathbf{x}) - \ln \gamma_i^{\infty,\text{DH}} \quad (28)$$

where

$$\ln \gamma_i^{\infty,C} = \ln(r_i/r_1) + (z/2)q_i \ln[q_i r_1 / (r_i q_1)] + l_i - r_i l_1 / q_1 \quad (29)$$

$$\ln \gamma_i^{\infty,R}(T) = -q_i (\ln \tau_{i1} - 1 + \tau_{i1}) \quad (30)$$

and

$$\ln \gamma_i^{\infty,\text{DH}} = 0 \quad (31)$$

give the limiting values of the configurational, residual, and Debye-Hückel contributions to the activity coefficient in the rational symmetric scale taken as $x_1 \rightarrow 1$ (pure water).

Following the same criterion of Sander et al. (1986b), the Debye-Hückel parameter A was taken as the one corresponding to pure water.

Mathematical Model

At global equilibrium, the following set of nonlinear, partial equilibrium conditions must be satisfied (subscript assignment to system components can be found in Table II).

Phase Equilibrium. At phase equilibrium, the following relationship must be satisfied for water ($i = 1$) and ammonia ($i = 2$)

$$x_i \gamma_i(T, \mathbf{x}) f_i^\circ(T, P=0) \exp(v_i P / RT) = P y_i \Phi_i(T, P, \mathbf{y}), \quad i = 1, 2 \quad (32)$$

while for carbon dioxide ($i = 3$) the phase equilibrium condition is

$$x_3 \gamma_3^\circ(T, \mathbf{x}) H_{3,1}(T, P_{v,1}(T)) \exp(v_3^\circ(P - P_{v,1}(T))/RT) = P y_3 \Phi_3(T, P, y) \quad (33)$$

where \mathbf{x} and y are arrays of the mole fractions in the liquid and gas phase, respectively.

The fugacity coefficient of component i in the gas mixture, $\Phi_i(T, P, y)$, is estimated using the equation of state proposed by Nakamura et al. (1976).

In eqs 15–33, $\gamma_i(T, \mathbf{x})$ is the activity coefficient of species i measured in the rational symmetric scale, while $\gamma_i^\circ(T, \mathbf{x})$ is the activity coefficient in the rational unsymmetric scale.

The temperature dependence of the pure liquid reference fugacity at zero pressure for ammonia ($i = 2$), f_2° , is modeled as

$$\ln f_2^\circ(T) = (A_1/T) + A_2 \ln T + A_3 T + A_4 \quad (34)$$

with f_2° in MPa and T in K.

In the limit of x_1 approaching 1 (pure water), the relationship

$$\ln H_{3,1}(T) = \ln \gamma_3^\circ(T) + \ln f_3^\circ(T) \quad (35)$$

between Henry's constant of CO₂ ($i = 3$) in water, $H_{3,1}$; the hypothetical standard state fugacity, f_3° , and the limiting form of the activity coefficient in the rational symmetric scale, γ_3° , holds for this noncondensable solute.

The dependence of $\ln f_3^\circ$ on the system temperature can be modeled with an empirical expression with the same form as that chosen for $\ln f_2^\circ$ (eq 34). Besides,

$$\ln \gamma_3^\circ(T) = \ln \gamma_3^{C,\infty} + \ln \gamma_3^{R,\infty}(T) \quad (36)$$

which, from eqs 23, 29, and 30, can be shown to be of the form

$$\ln \gamma_i^\circ(T) = (a_{i1}/T) - q_i \tau_{i1} + C_i \quad (37)$$

where C_i is a constant that depends on component i .

The empirical function

$$\ln H_{3,1}(T) = (B_1/T) + B_2 \ln T + B_3 T + B_4 - q_3 \tau_{31} \quad (38)$$

chosen to model the temperature dependence of Henry's constant of CO₂ in water, $H_{3,1}$, is consistent with eqs 34, 35, and 37, as required.

Chemical Equilibrium. The functional form

$$\ln K_j(T) = (C_{1,j}/T) + C_{2,j} \ln T + C_{3,j} T + C_{4,j} \quad (39)$$

was adopted to describe the temperature dependence of the j reaction equilibrium constant.

The estimation of the parameters of the phase and chemical equilibrium model was done by a nonlinear regression of experimental data using the maximum likelihood principle (Anderson et al., 1978).

To lower the number of parameters to be regressed, exploratory runs of the parameter estimation program were made on the basis of the chemical reaction scheme described by eqs 7–13.

Provisional but still significant estimated values of the model parameters were used to assess the relative importance of the chemical reactions 7–14 in the whole range of experimental conditions. By solving the phase and chemical equilibrium, it was found that in the temperature, pressure, and composition range of the experimental data only eqs 7, 8, 12, and 14 have to be considered to account for the detailed equilibrium composition. The remaining chemical reactions showed values of their reaction extents too low to influence the phase and chemical equilibrium composition.

Therefore, the following set of nonlinear equations was chosen to describe the chemical equilibrium of the NH₃–

CO₂–H₂O–urea system over the temperature, pressure, and composition range of the experimental data

$$K_r(T) = K_{x,r}(\mathbf{x}) K_{\gamma,r}(T, \mathbf{x}); \quad r = 7, 8, 12, 14 \quad (40)$$

where

$$K_{x,7}(\mathbf{x}) = \frac{x_4 x_6}{(x_2)^2 x_3} \quad (41)$$

$$K_{\gamma,7}(T, \mathbf{x}) = \frac{\gamma_4^\circ(T, \mathbf{x}) \gamma_6^\circ(T, \mathbf{x})}{(\gamma_2(T, \mathbf{x}))^2 \gamma_3^\circ(T, \mathbf{x})} \quad (42)$$

$$K_{x,8}(\mathbf{x}) = \frac{x_4 x_5}{x_1 x_2 x_3} \quad (43)$$

$$K_{\gamma,8}(T, \mathbf{x}) = \frac{\gamma_4^\circ(T, \mathbf{x}) \gamma_5^\circ(T, \mathbf{x})}{\gamma_1(T, \mathbf{x}) \gamma_2(T, \mathbf{x}) \gamma_3^\circ(T, \mathbf{x})} \quad (44)$$

$$K_{x,12}(\mathbf{x}) = \frac{x_7}{x_2 x_3} \quad (45)$$

$$K_{\gamma,12}(T, \mathbf{x}) = \frac{\gamma_7^\circ(T, \mathbf{x})}{\gamma_2(T, \mathbf{x}) \gamma_3^\circ(T, \mathbf{x})} \quad (46)$$

and

$$K_{x,14}(\mathbf{x}) = \frac{x_1 x_8}{x_4 x_6} \quad (47)$$

$$K_{\gamma,14}(T, \mathbf{x}) = \frac{\gamma_1(T, \mathbf{x}) \gamma_8(T, \mathbf{x})}{\gamma_4^\circ(T, \mathbf{x}) \gamma_6^\circ(T, \mathbf{x})} \quad (48)$$

The electroneutrality condition is automatically satisfied when the extents of reactions 7, 8, 12, and 14 are used to compute the equilibrium composition of the reaction mixture.

Given the temperature of the system and the initial values of the NH₃/CO₂ and H₂O/CO₂ mole ratios, the set of nonlinear equations is solved by an iteration method, according to the following procedure:

(i) Initially each of the activity coefficients is set equal to 1.

(ii) The value of the extent of the urea synthesis reaction (eq 14) is guessed.

(iii) The system formed by eqs 32, 33, and 41–46 is solved to obtain the extent of the reactions 7, 8, and 12 in terms of the current value of the extent of reaction 14.

(iv) With the liquid composition resulting from step iii, activity coefficients are calculated and substituted in eqs 32, 33, and 41–46. Steps iii and iv are repeated until convergence on mole fractions is obtained.

(v) With the current values of the activity coefficients and of the extents of the reactions 7, 8, and 12, eqs 47 and 48 are solved to obtain the extent of reaction 14. This can be done by solving a quadratic equation and disregarding the unphysical root. The algorithm returns to step ii, repeating steps ii and iii until the convergence criterion imposed on the extent of reaction 14 is satisfied.

Bubble pressure and bubble composition can be calculated by means of eqs 32 and 33. In the synthesis reactor the presence of a gas phase is undesirable. The calculation of the bubble pressure at every point in the reactor is necessary only to ensure that the reaction mixture is always subcooled at synthesis conditions.

The proposed calculation procedure is simple and robust. It has the additional advantage that it is able to cover

situations in which the synthesis reaction shows a measurable progress (as in the reactor) and also those in which it is negligible (as in the recycle stream). In the latter of the two situations, the extent of reaction 14 is set equal to zero and no iterative loop between steps ii and v is needed.

Enthalpy Calculations. Neglecting pressure corrections, the partial molal enthalpy for water ($i = 1$) and ammonia ($i = 2$) in the liquid phase (Prausnitz et al., 1980) can be approximated by

$$\bar{H}_i(T, \mathbf{x}) = H_i^\circ(T) - RT^2(\partial \ln \gamma_i / \partial T) \quad (49)$$

where

$$H_i^\circ(T) = H_i^*(T) - RT^2(\partial \ln f_i^\circ / \partial T) \quad (50)$$

In eqs 49 and 50, $H_i^\circ(T)$ is the molal enthalpy of the hypothetical liquid pure component at zero pressure and at the system temperature and $H_i^*(T)$ is the molal enthalpy of the ideal gas pure component at the same temperature.

For carbon dioxide ($i = 3$), the dilute solution in pure liquid water has been chosen as the reference state. The corresponding expression of the partial molal enthalpy in the liquid phase is

$$\bar{H}_3(T, \mathbf{x}) = \bar{H}_3^\circ(T) - RT^2(\partial \ln \gamma_3^\circ / \partial T) \quad (51)$$

where the molal enthalpy of CO_2 in its hypothetical liquid standard state at zero pressure and at the system temperature is given by

$$\bar{H}_3^\circ(T) = H_{3,1}^*(T) - RT^2(\partial \ln H_{3,1} / \partial T) \quad (52)$$

where $H_{3,1}$ is Henry's constant of CO_2 in water, given by eq 38.

The partial molal enthalpies of ionic and neutral reaction products can be calculated using the appropriate forms of the van't Hoff equation relating the standard molal enthalpies of the reaction products to those of the reactant species.

The dilute solution in pure liquid water has been chosen as the reference state for all reaction products. The corresponding expression of the partial molal enthalpy in the liquid phase is

$$\bar{H}_i(T, \mathbf{x}) = \bar{H}_i^\circ(T) - RT^2(\partial \ln \gamma_i^\circ / \partial T) \quad (53)$$

where $\bar{H}_i^\circ(T)$ is the molal enthalpy of the i product species in its hypothetical liquid standard state at zero pressure and at the system temperature.

Anions and cations belonging to the same electrolyte are not independent species since their concentrations have to satisfy the electroneutrality condition. For this reason it is convenient to work with partial molal enthalpies of each dissociated electrolyte instead of working with ionic partial molal enthalpies.

The partial molal enthalpies of dissociated ammonium ($i = 4$) bicarbonate ($i = 5$) and ammonium carbamate ($i = 6$) are given by

$$\bar{H}_{4,5}(T, \mathbf{x}) = \bar{H}_{4,5}^\circ(T) - RT^2[(\partial \ln \gamma_4^\circ / \partial T) + (\partial \ln \gamma_5^\circ / \partial T)] \quad (54)$$

and

$$\bar{H}_{4,6}(T, \mathbf{x}) = \bar{H}_{4,6}^\circ(T) - RT^2[(\partial \ln \gamma_4^\circ / \partial T) + (\partial \ln \gamma_6^\circ / \partial T)] \quad (55)$$

respectively, where

$$\bar{H}_{4,5}^\circ(T) = \bar{H}_4^\circ(T) + \bar{H}_5^\circ(T) \quad (56)$$

and

$$\bar{H}_{4,6}^\circ(T) = \bar{H}_4^\circ(T) + \bar{H}_6^\circ(T) \quad (57)$$

are the standard molal enthalpies of the electrolytes.

Rearranging the van't Hoff equation written for $K_7(T)$, $K_8(T)$, $K_{12}(T)$, and $K_{14}(T)$, the following expressions of the standard molal enthalpies of the product species are obtained:

$$\bar{H}_{4,6}^\circ(T) = 2H_2^\circ(T) + \bar{H}_3^\circ(T) + RT^2(\partial \ln K_7(T) / \partial T) \quad (58)$$

$$\bar{H}_{4,5}^\circ(T) = H_1^\circ(T) + H_2^\circ(T) + \bar{H}_3^\circ(T) + RT^2(\partial \ln K_7(T) / \partial T) \quad (59)$$

$$\bar{H}_7^\circ(T) = H_2^\circ(T) + \bar{H}_3^\circ(T) + RT^2(\partial \ln K_{12}(T) / \partial T) \quad (60)$$

$$\bar{H}_8^\circ(T) = H_1^\circ(T) + 2H_2^\circ(T) + \bar{H}_3^\circ(T) + RT^2(\partial \ln K_{14}(T) / \partial T) \quad (61)$$

Finally, the molal enthalpy of the liquid mixture is given by

$$H(T, \mathbf{x}) = \sum_j x_j \bar{H}_j(T, \mathbf{x}) \quad (62)$$

where x_j is the mole fraction of species j in the mixture.

Parameter Estimation Strategy

The model adopted to fit the chemical and phase equilibrium behavior of the $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ -urea system contains a total of 80 adjustable parameters. Among these are the A_i constants of eq 34, with $i = 1, \dots, 4$; the B_i constants of eq 38, with $i = 1, \dots, 4$, and the C_{ij} constants of eq 39, with $i = 7, 8, 12, 14$ and $j = 1, \dots, 4$. These equations give the pure liquid reference fugacity of NH_3 at zero pressure, the Henry's constant of CO_2 in water, and the chemical equilibrium constants of reactions 7, 8, 12, and 14, respectively, as functions of temperature.

The remaining 56 adjustable parameters are UNIQUAC interaction parameters a_{ij} , with $i, j = 1, \dots, 8$, which are necessary to model the temperature dependence of the activity coefficients of the components in the mixture and to calculate their molal partial excess enthalpy.

The UNIQUAC interaction parameter a_{31} also appears in the empirical function chosen to model the temperature dependence of Henry's constant of CO_2 in H_2O (eq 38) through the function

$$\tau_{31} = \exp(-a_{31}/T)$$

To calculate the reactor temperature profile, the temperature corresponding to each local enthalpy and composition has to be computed. The accuracy of the prediction of temperatures from molal enthalpy values at given compositions largely depends on the accuracy of the coefficients listed above.

This is why plant measurements of the adiabatic mixing temperature of the reactor feed streams have been included as experimental points to estimate the model parameters, in addition to liquid-vapor and chemical equilibrium data.

These additional experimental measurements are needed because of the proven fact that "...correct predictions of the vapor phase compositions and pressures by a solution model do not guarantee that the description of the liquid phase is correct" (Pelkie et al., 1992).

A slightly modified version of the parameter estimation program published by Prausnitz et al. (1980), which is based on the method of Anderson et al. (1978), has been adopted in this work.

Before starting the parameter estimation process, a set of initial parameter estimates was generated. To this purpose it was recognized that different subsets among the model parameters can be related to different features of the system behavior.

In particular, the characteristic minimum shown by the isothermal bubble pressure of $\text{NH}_3\text{-CO}_2$ and $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ mixtures as a function of the CO_2/NH_3 ratio at, and outside, urea synthesis conditions, is ascribed to chemical reactions (Pelkie et al., 1992; Bernardis et al., 1989; Lemkowitz et al., 1973).

The C_{ij} parameters included in the correlation of the chemical equilibrium constants with temperature are reasonably expected to have an important impact on the prediction of the system behavior if the CO_2/NH_3 ratio is taken within the range in which the pressure minimum occurs as a consequence of the chemical reactions in the liquid phase.

Also, at low concentrations of NH_3 and CO_2 in H_2O the Debye-Hückel contribution to the activity coefficients will tend to dominate over the configurational and residual ones, thus attenuating the impact of the UNIQUAC interaction parameters a_{ij} on the phase and chemical equilibrium description.

Therefore, to obtain initial values of the parameters C_{1j} , C_{2j} , C_{3j} , and C_{4j} , for $j = 7, 8, \text{ and } 12$, the parameter estimation program was ran on a subset of experimental points of low concentration of NH_3 and CO_2 in H_2O , and with CO_2/NH_3 ratio about the pressure minimum. These points have been chosen among the extensive experimental data published by Göppert and Maurer (1988). In these initialization runs the UNIQUAC interaction parameters a_{ij} were taken equal to 0, while the A_i and B_i parameters of eqs 34 and 38 were obtained from published data by Gillespie et al. (1987) and by Edwards et al. (1978), respectively.

The low CO_2/NH_3 branch of the isothermal bubble pressure curve of the $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ system can be interpreted assuming that its asymptotic behavior is dominated by the $\text{NH}_3\text{-H}_2\text{O}$ binary interactions and by the chemical reactions present. On this basis, experimental points in the low CO_2/NH_3 region were selected from the data published by Göppert and Maurer (1988) to generate initial estimates of the a_{12} and a_{21} binary interaction parameters. The parameter estimation program was run on this subset of experimental points, using the initial values of the parameters C_{1j} , C_{2j} , C_{3j} , and C_{4j} , for $j = 7, 8, \text{ and } 12$, obtained before and taking the remaining a_{ij} parameters equal to 0.

Assuming that the asymptotic behavior of the $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ system at large CO_2/NH_3 ratios is dominated by the $\text{CO}_2\text{-H}_2\text{O}$ binary interactions in addition to the chemical reactions present, initial a_{13} and a_{31} values were estimated. For this, the parameter estimation program was run on a subset of experimental points in the large CO_2/NH_3 region selected from the same source as the others. The initial estimates of the a_{12} and a_{21} binary interaction parameters obtained before were used, as well as those of the parameters C_{1j} , C_{2j} , C_{3j} , and C_{4j} , for $j = 7, 8, \text{ and } 12$. The remaining a_{ij} parameters were taken equal to 0.

After the initialization procedure has been accomplished, the parameter estimation process for the $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$

system outside urea synthesis conditions begins, taking the initial estimates of the model parameters as the starting point.

In all the regressions made so far in this procedure, the urea synthesis reaction has been excluded from the chemical model and the interaction coefficients $a_{i,8}$ and $a_{8,j}$ were both taken equal to 0. This was done because the liquid-vapor equilibrium data used for the $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ system were reported at conditions outside those of urea synthesis.

In the following step the synthesis reaction was taken into account, as well as the interaction between urea and the other components in the mixture. The parameter estimation process was renewed on a set of 48 vapor-liquid and chemical equilibrium data for the $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ -urea system at synthesis conditions (Inoue et al., 1972).

To keep the number of adjustable parameters well below the number of experimental points, some of the a_{ij} interaction parameters in the $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ -urea system were given the same value as that already estimated for the $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ system on the basis of the experimental data by Göppert and Maurer (1988).

At synthesis conditions, the liquid phase at chemical equilibrium can be thought of as a solution of ammonium salts in a mixed solvent formed by excess NH_3 , H_2O , and urea. Among the solutes, ammonium carbamate is the predominant species and the amount of free CO_2 in the liquid phase is negligible. The equilibrium concentrations of ammonium bicarbonate and carbamic acid are also very small compared to that of ammonium carbamate.

Under these circumstances the a_{ij} parameters in the $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ -urea system corresponding to binary interactions between solutes were assigned the same value they had in the $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ system. The same criterion was adopted for the interactions between carbamic acid and bicarbonate ions with each of the components of the mixed solvent.

The only a_{ij} parameters adjusted in this final step were those corresponding to interactions between the components of the mixed solvent (i.e., NH_3 , H_2O , and urea) and to interactions between each one of them with CO_2 and ammonium and carbamate ions.

The list of the parameters adjusted in this final step is completed with the binary interaction parameters $a_{i,8}$ and $a_{8,j}$, $i, j = 1, \dots, 7$, and the parameters $C_{1,14}$, $C_{2,14}$, $C_{3,14}$, and $C_{4,14}$, related to the temperature dependence of the synthesis reaction equilibrium constant. The multi-objective function to be minimized included the error between predicted and measured vapor equilibrium pressure over the reaction mixture at urea synthesis conditions, the error between predicted and measured conversion of initial CO_2 to urea, and the error between predicted and measured adiabatic mixing temperature of the reactor feed streams.

The proposed phase and chemical equilibrium model with the final set of adjusted parameters loaded was able to accurately reproduce the behavior of the $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ -urea system within the range of temperature and composition defined by the synthesis reactor inlet and outlet streams.

Analysis of Results

There is some disagreement in the equilibrium conversion of CO_2 to urea reported by different authors (Inoue et al., 1972; Kawasumi, 1952a,b, 1953, 1954; Kotula, 1981). Therefore, different parameter sets can be obtained depending on the set of experimental data used. However, the equilibrium conversion values predicted can be checked

Table III. Equilibrium Constants, Ammonia Fugacity, and Carbon Dioxide Henry's Constant Parameters

function	parameters			
	$10^{-3}A_1$	$10A_2$	10^3A_3	A_4
$\ln f_2^\circ$ (MPa)	-2.5141	2.8417	-2.5759	14.6460
function	parameters			
	$10^{-3}B_1$	$10B_2$	10^3B_3	B_4
$\ln H_{3,1}$ (MPa)	-2.6560	-3.5050	6.3216	18.1575
function	parameters			
	$10^{-3}C_{1,i}$	$10^2C_{2,i}$	$10^3C_{3,i}$	$C_{4,i}$
$\ln K_i$				
$i = 7$	9.9068	7.4296	-5.3985	-20.2220
$i = 8$	8.8226	0.8404	1.8736	-21.6135
$i = 12$	8.1358	0.0283	-0.1005	-21.5090
$i = 14$	-1.7352	-4.7506	9.3576	5.6601

Table IV. Extended UNIQUAC Model: Binary Interaction Parameters

i	j							
	1	2	3	4	5	6	7	8
1		-626.3	-401.5	355.6	-18.2	0.9	-118.0	-110.0
2	847.3		-291.4	-190.7	-41.9	335.0	-1366.7	357.1
3	2623.7	-610.0		836.1	825.3	-204.8	958.6	670.5
4	-272.8	-12.4	-653.6		-907.8	1476.5	-656.9	272.8
5	-2.6	844.7	-637.1	284.9		1158.4	82.9	-0.9
6	-96.6	-62.3	-302.6	-337.2	-632.5		157.5	221.6
7	-158.7	95.6	89.1	568.6	201.1	98.0		142.3
8	91.7	-532.5	269.0	-162.2	2.3	-166.2	-33.2	

Table V. Influence of Temperature and W on Equilibrium Conversion for $L = 4$; Comparison with Experimental Data

W	t (°C)	CO ₂ to urea equilb conv	
		exptl ^a	this model
0.0	180	79.2	80.2
	190	80.0	80.1
	200	79.6	79.9
	210	77.9	79.5
0.5	180	71.5	72.5
	190	72.3	72.4
	200	71.9	72.1
	210	70.2	71.5
1.0	180	63.8	65.6
	190	64.6	65.5
	200	64.1	65.2
	210	62.5	64.6

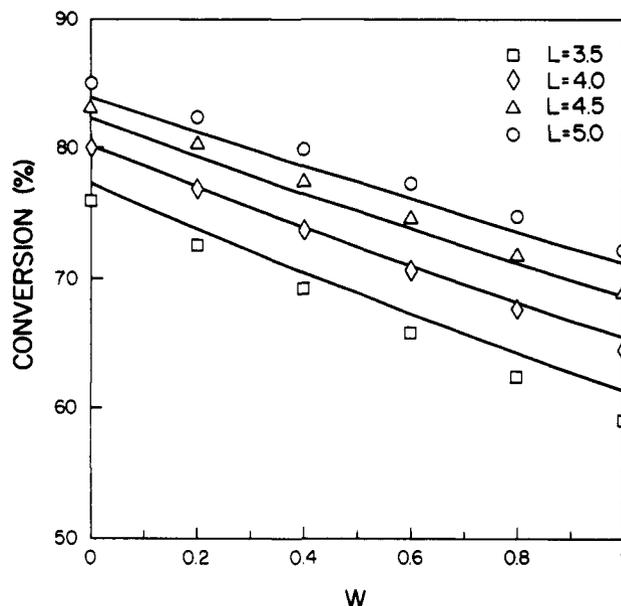
^a Calculated with the correlation of Gorlovskii and Kucheryavii (1980) which fits experimental results from several sources.

against those calculated by means of the correlation of Gorlovskii and Kucheryavii (1980), which is based on a large number of experimental data from many independent authors.

Fortunately, abundant plant reactor data obtained under different operating conditions provide an irreplaceable tool for checking both the model performance and the parameter quality. Agreement between plant data and simulation results is an indication of the good performance of the thermodynamic model.

Tables III and IV show the model parameters obtained with the procedure explained above. The equilibrium data from Inoue et al. (1972) were used to correlate the urea synthesis reaction equilibrium constant with the system temperature.

Values of the adiabatic mixing temperature of the reactor feed streams from plant measurements and the temperatures of all inlet and outlet streams of known composition were included as part of the experimental data on which the parameter regression was based. This allowed an

**Figure 1. Influence of H₂O/CO₂ load ratio (W) on equilibrium conversion at $t = 190$ °C and different NH₃/CO₂ ratios (L). (□, ◇, △, ○) Gorlovskii and Kucheryavii (1980); (—) this model.****Table VI. Influence of Ratios L and W on Equilibrium Conversion at $t = 190$ °C; Comparison with Experimental Data**

L	W	CO ₂ to urea equilb conv	
		exptl ^a	this model
3.5	0.0	75.9	77.3
	0.2	72.5	73.8
	0.4	69.2	70.4
	0.6	65.8	67.3
4.0	0.8	62.4	64.3
	1.0	59.1	61.5
	0.0	80.0	80.2
	0.2	76.9	77.0
4.5	0.4	73.8	73.9
	0.6	70.7	71.0
	0.8	67.7	68.2
	1.0	64.6	65.6
5.0	0.0	83.1	82.3
	0.2	80.3	79.3
	0.4	77.5	76.5
	0.6	74.6	73.8
	0.8	71.8	71.2
	1.0	69.0	68.8
	0.0	84.9	83.9
	0.2	82.4	81.2
	0.4	79.9	78.6
	0.6	77.3	76.1
	0.8	74.8	73.6
	1.0	72.2	71.3

^a Calculated with the correlation of Gorlovskii and Kucheryavii (1980) which fits experimental results from several sources.

accurate prediction of the temperature profile along the synthesis reactor.

Figure 1 illustrates the model performance at predicting equilibrium conversions. It must be noticed that agreement is better for initial NH₃/CO₂ ratios closer to actual reactor operating conditions, because of the abundance of published experimental data in this region.

Tables V and VI summarize the model sensitivity to changes in the most important operating and control variables: temperature, NH₃/CO₂ load ratio (L), and H₂O/CO₂ load ratio (W). It can be noticed that the differences between predicted and measured equilibrium conversions are within experimental error.

Calculated bubble pressures against mole percent of ammonia for an NH₃-CO₂ initial mixture are shown in

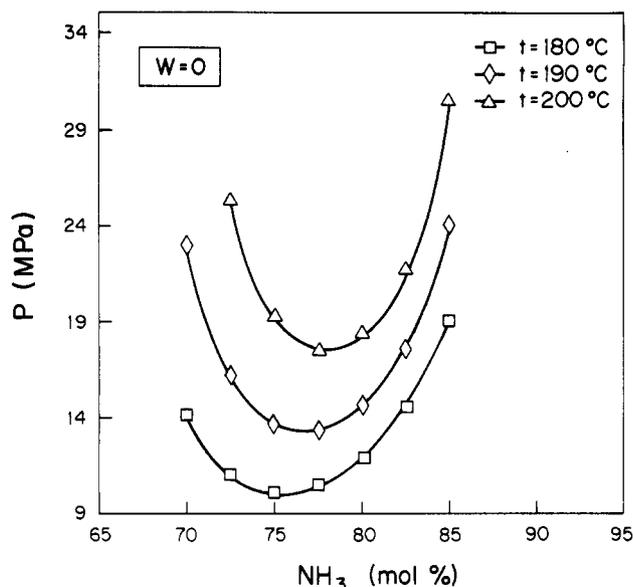


Figure 2. Vapor pressure of $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ system.

Figure 2. Agreement with data reported by Lemkowitz (1973) is excellent, reproducing the pressure minimum at its exact position for each temperature. This is a remarkable result if we consider the fact that experimental points with zero initial $\text{H}_2\text{O}/\text{CO}_2$ ratio were scarce.

Conclusions

Although the model proposed is intended to support an urea reactor simulator, it was also tested at predicting the behavior of the systems $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ and $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O-urea}$ over a wide range of composition and temperature. In all cases the model was able to predict vapor pressures and CO_2 to urea conversions satisfactorily.

When used as the thermodynamic support of an urea reactor simulation program (Irazaqui et al., 1993), results were in excellent agreement with observed plant data. The observed reactor sensibility to changes in NH_3/CO_2 and $\text{H}_2\text{O}/\text{CO}_2$ load ratios were correctly reproduced.

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Nomenclature

A = Debye-Hückel parameter
 A_j = j th parameter in the correlation of pure liquid reference fugacity of ammonia with temperature
 a_{ij} = UNIQUAC binary interaction parameters between components i and j
 B_j = j th parameter in the correlation of Henry's constant of carbon dioxide in water with temperature
 b = distance of closest approach between ions
 C_{kj} = k th parameter in the correlation of the equilibrium constant of chemical reaction j with temperature
 f_i° = pure liquid reference fugacity of component i at zero pressure
 g = gas (eqs 4-6)
 H = molal enthalpy of the liquid mixture
 \bar{H}_i = partial molal enthalpy of component i
 H_i° = molal enthalpy of component i in the ideal gas reference state

H_i° = molal enthalpy of component i in the pure liquid reference state at zero pressure
 \bar{H}_i° = molal enthalpy of component i at infinite dilution in water reference state
 $H_{i,j}$ = Henry's constant of component i in solvent j
 K_j = equilibrium constant of chemical reaction j
 L = NH_3/CO_2 load mole ratio
 l = liquid (eqs 1-14)
 l_i = see eq 22
 M_i = molecular weight of neutral species i
 m_i = molality of the i ionic species referred to 1000 g of mixed solvent
 P = pressure
 $P_{v,i}$ = vapor pressure of component i
 q_i = UNIQUAC surface parameter of component i
 R = gas constant
 r_i = UNIQUAC volume parameter of component i
 T = absolute temperature
 v_i = liquid molal volume of component i
 v_i^∞ = liquid molal volume of component i at infinite dilution
 W = $\text{H}_2\text{O}/\text{CO}_2$ load mole ratio
 x_i = mole fraction of component i in the liquid phase
 \mathbf{x} = array of the mole fractions in the liquid phase
 y_i = mole fraction of component i in the gas phase
 \mathbf{y} = array of the mole fractions in the gas phase
 z = UNIQUAC coordination number ($z = 10$)
 z_i = charge number of a ionic species i

Greek Letters

γ_i = activity coefficient of component i , rational symmetric convention
 γ_i° = activity coefficient of component i , rational unsymmetric convention
 γ_i^∞ = limiting value of the activity coefficient in the rational symmetric scale taken as $x_1 \rightarrow 1$ (pure water)
 θ_i = surface area fraction of component i
 ϕ_i = volume area fraction of component i
 Φ_i = fugacity coefficient of component i in the gas phase

Superscripts

C = combinatorial
 DH = Debye-Hückel
 R = residual

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