Thermodynamic analysis and calculation of the ternary phase diagram of the system water—urea—ammonium nitrate

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Phase diagrams of the binary systems water—urea, water—ammonium nitrate, and urea—ammonium nitrate were investigated. On the basis of obtained data the ternary phase diagram of the system water—urea—ammonium nitrate was calculated using a "network method". Discussion about the used thermodynamic model is based on comparison of the calculated and experimental data.

Исследованы фазовые диаграммы бинарных систем вода—мочевина, вода—нитрат аммония и мочевина—нитрат аммония. Исходя из полученных данных, с помощью «сетевого метода» была рассчитана тройная фазовая диаграмма вода—мочевина—нитрат аммония. Обсуждение применяемой термодинамической модели основывается на сравнении рассчитанных и экспериментально полученных данных.

The system water—urea—ammonium nitrate can be considered as basis of nitrogen fertilizers. For some applications other substances (*e.g.* $Cu(NO_3)_2$, $Zn(NO_3)_2$, $Co(NO_3)_2$, $(NH_4)_6Mo_7O_{24}$) are added to this mixture as trace elements. From the point of view of application of liquid fertilizers it is necessary to know the dependence of formation of crystal phases on the composition of the system and its temperature. Experimental study of multicomponent systems is laborious and time-consuming. In the present work we made an attempt to propose a method for calculation of the phase equilibria in the systems containing as components water, urea, and inorganic salts. The importance of thermodynamic model for calculation of phase equilibria consists also in a possibility of rational planning of experimental study of phase equilibria and it can be used as basis for statistical treatment of experimental data. Since based on physical principles, this method is superior to purely formal mathematical treatment.

Thermodynamic analysis of the system water—urea—ammonium nitrate is, however, interesting also from the theoretical point of view. This system consists of components of molecular and ionic nature, which makes it theoretically attractive. Calculations presented in this paper, *viz.* calculations of activities of components in the mixture, are based on formal thermodynamic models which fulfil the Gibbs—Duhem equation and the criteria of thermodynamic consistency [1]. Calculation of the equilibrium temperature of primary crystallization is based on the LeChatelier—Shreder equation which has a physical background. In this communication we show that this approach gives a set of equations suitable for the description of phase equilibria between solid and liquid phases even in complicated systems consisting of mixtures of electrolytes and non-electrolytes.

Thermodynamic data of pure components

For calculation of solid—liquid equilibria the data on temperature and enthalpy of fusion of pure components are required. In the case of existence of polymorphic forms of solid substances also the temperature and enthalpy of phase transitions are needed. For more exact calculation, especially in broader temperature range, the values of ΔC_p, *i.e.* the difference of heat capacities of pure components in undercooled liquid and solid phase, are to be known. Thermodynamic data used in this paper were taken from literature [2] and they are summarized in Table 1.

Table 1

Thermodynamic data of pure components used in the calculation

i	Component	$\theta_{\text{fus}}/°\text{C}$	$\Delta H_{\text{fus}}/(\text{kJ mol}^{-1})$	$(\Delta H_{\text{fus}}/R)/\text{K}$	$\Delta C_p/R$
1	Water	0	6.01	722.8	4.484
2	NH_4NO_3	169	5.44	654.2	0
3	Urea	132.6	15.06	1811.6	0

Calculation of the phase diagrams of binary systems

The system water—urea

Urea, similarly as water, is a non-electrolyte and therefore properties of the aqueous solutions of urea can be compared with classically ideal solutions. In this case it holds that the activity of component in solution equals its mole fraction. Calculation of the phase diagram on the side of urea is, however, complicated by the fact that urea forms in solid phase three crystallographic forms

$$\alpha \xrightarrow{0\,°\text{C}} \beta \xrightarrow{24\,°\text{C}} \gamma \xrightarrow{132.6\,°\text{C}} \text{liquidus}$$

Exact calculation of the solid—liquid equilibrium of urea would require to take into account the enthalpies of phase transitions between these forms. In the case of urea values of these quantities are not available. This topic is discussed in detail in paper [3]. As follows from Fig. 1 in the first approximation the influence of the phase transitions on the solid—liquid equilibrium of urea can be neglected. Therefore the calculation of the liquidus curve was done with thermodynamic data valid for the equilibrium of γ-form with solution (melt). As may be seen from comparison of the experimental and calculated data (Fig. 1) this approach gives satisfactory results.

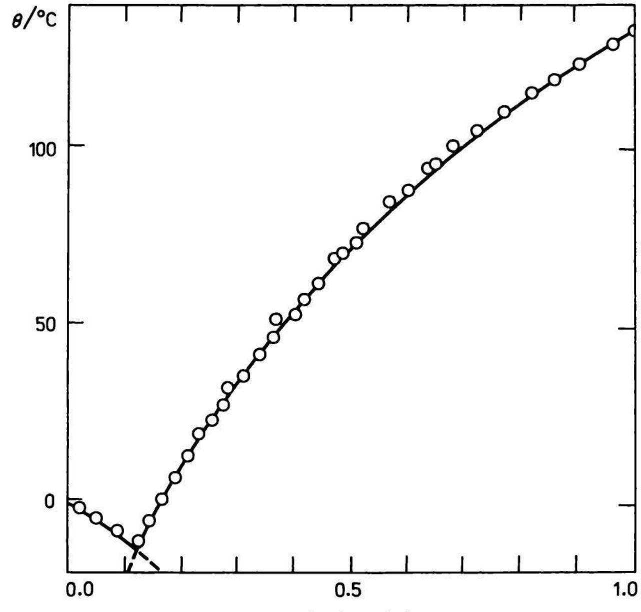

Fig. 1. Phase diagram of the system water—urea. Comparison of the liquidus curves of water and urea with chosen experimental data. One adjustable interaction parameter was used. —— Calculation; ○ experiment [6].

The calculation of the solid—liquid equilibrium was carried out according to the LeChatelier—Shreder equation [4]

$$\ln a_i = \frac{\Delta H_{\text{fus},i}}{R}\left(\frac{1}{T_{\text{fus},i}} - \frac{1}{T}\right) + \frac{\Delta C_{p,i}}{R}\left(\frac{T_{\text{fus},i}}{T} - 1 - \ln\frac{T_{\text{fus},i}}{T}\right) \qquad (1)$$

where a_i is the activity of components in solution (molten mixture), $\Delta H_{\text{fus},i}$ is the enthalpy of fusion of pure component, $T_{\mathrm{fus},i}$ is the temperature of fusion of this component and T is the equilibrium temperature of solidus—liquidus. This equation assumes that there coexists with solution a pure solid component i ($a_{i,\mathrm{s}} = 1$).

For activities of components it holds ($i = 1$ or 3)

$$\ln a_i = \ln x_i + \ln \gamma_i \tag{2}$$

For the description of deviations of the system from thermodynamic ideal behaviour the model formally identical with the so-called regular model [5] was used. According to this model it holds for the excess Gibbs energy

$$\Delta G^{\mathrm{E}}_{1,3} = R\alpha_{1,3}x_1x_3 \tag{3}$$

Then for the concentration dependence of activity coefficients in a binary system it holds

$$\ln \gamma_i = \frac{\alpha_{1,3}}{T}(1 - x_i)^2 \tag{4}$$

Combining eqns (*1*) and (*4*) we can obtain for the dependence of the equilibrium temperature solidus—liquidus on composition of solution (molten mixture) the relationship

$$T = \frac{\dfrac{\Delta H_{\mathrm{fus},i}}{R} + \alpha_{1,3}(1 - x_i)^2}{\dfrac{\Delta H_{\mathrm{fus},i}}{RT_{\mathrm{fus},i}} - \ln x_i + \dfrac{\Delta C_{p,i}}{R}\,(T_{\mathrm{fus},i}/T - 1 - \ln T_{\mathrm{fus},i}/T)} \tag{5}$$

When we consider that the parameter ΔC_p does not equal zero the relationship (*5*) is implicit with respect to temperature and it must be solved by an iterative method.

The interaction parameter $\alpha_{1,3}$ which characterizes the deviation of thermodynamic behaviour of solution from ideality can be obtained by a comparison of the experimental and calculated temperature of liquidus of water and/or urea. Using a regression method the optimum value of this parameter was found to be $\alpha_{1,3} = -150\,\mathrm{K}$. From Fig. 1, where the experimental [6] and calculated liquidus curves of water and urea are plotted, it may be seen that the agreement between calculation and experiment is good. This can be considered as justification of simplifications and approximations used at the calculation of the liquidus curves in the system water—urea.

The system water—ammonium nitrate

In contradistinction to the former case ammonium nitrate electrolytically dissociates in aqueous solutions. This should be respected when a suitable model for the description of thermodynamically ideal mixture is to be chosen. Similarly as in the case of urea the calculation of liquidus curve of ammonium nitrate is complicated by the existence of four crystallographic forms of this compound.

$$\alpha \xrightarrow{32\,^{\circ}\mathrm{C}} \beta \xrightarrow{84\,^{\circ}\mathrm{C}} \gamma \xrightarrow{125\,^{\circ}\mathrm{C}} \delta \xrightarrow{169\,^{\circ}\mathrm{C}} \text{liquidus}$$

Also in this case we will not consider the existence of different crystallographic forms of ammonium nitrate, which simplifies the calculation. Activities of components in the system water—ammonium nitrate are expressed according to the relationship [7]

$$\ln a_i = \ln a_i^* + \ln \gamma_i \tag{6}$$

where a_i^* is the activity of component in ideal mixture. As ammonium nitrate dissociates in solution into one cation and one anion it holds for the model activities of components [7]

$$a_1^* = \frac{x_1}{x_1 + 2x_2}; \qquad a_2^* = \left(\frac{2x_2}{x_1 + 2x_2}\right)^2 \tag{7}$$

From the point of view of application of the discussed system as liquid fertilizer we are interested especially in the region of lower temperatures at which the α-form of ammonium nitrate is stable. Thus for calculation of liquidus curve of ammonium nitrate we chose a formal approach and the "temperature of fusion" and "enthalpy of fusion" of ammonium nitrate were chosen as adjustable parameters in order to obtain the best agreement between the calculated and experimental data on primary crystallization of the α-form of ammonium nitrate.

For the description of excess Gibbs energy as a function of composition the relationship following from a lattice model [8] was used. It holds

$$\Delta G_{1,2}^{\mathrm{E}} = \frac{R\alpha_{1,2}x_1x_2}{x_1 + 2x_2} + R\alpha_2 x_2 \left[\left(\frac{2x_2}{x_1 + 2x_2}\right)^{1/3} - 1\right] \tag{8}$$

The interaction parameter α_2 corresponds to Coulombic forces between ions. Then for the activity coefficients of components it holds

$$T \ln \gamma_1 = \frac{\alpha_{1,2}2x_2^2}{(x_1 + 2x_2)^2} - \frac{\alpha_2}{6}\left(\frac{2x_2}{x_1 + 2x_2}\right)^{4/3} \tag{9a}$$

$$T \ln \gamma_2 = \frac{\alpha_{1,2} x_1^2}{(x_1 + 2x_2)^2} + \alpha_2 \left[\left(\frac{2x_2}{x_1 + 2x_2} \right)^{1/3} \left(\frac{4 + 2x_2}{3 + 3x_2} \right) - 1 \right] \qquad (9b)$$

The interaction parameters $\alpha_{1,2}$ and α_2 as well as the hypothetical temperature and enthalpy of fusion of ammonium nitrate were chosen on the basis of experimental data on solid—liquid equilibrium in the system water—NH_4NO_3 [9] (Fig. 2) using the method of regression analysis. It follows

$$\alpha_{1,2} = 297.7\,\mathrm{K} \qquad T_{\mathrm{fus}} = 459\,\mathrm{K}$$

$$\alpha_2 = -831.5\,\mathrm{K} \qquad \Delta H_{\mathrm{fus}}/R = 819\,\mathrm{K}$$

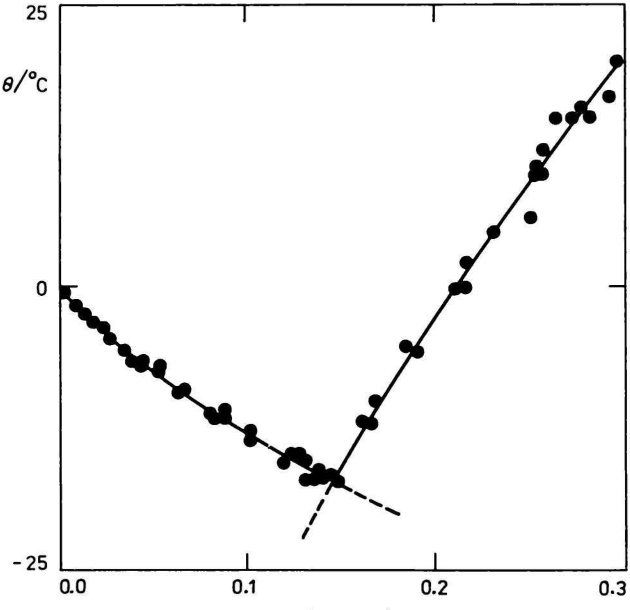

Fig. 2. Phase diagram of the system water—ammonium nitrate. Comparison of the liquidus curves of water and ammonium nitrate with experimental data. Two adjustable interaction parameters were used.

—— Calculation; ● experiment [9].

The system urea—ammonium nitrate

The system urea—ammonium nitrate consists of one substance of molecular nature and one of ionic nature. Thus from the point of view of model activity this system is similar to the former one. Therefore for the thermodynamic analysis of this system we may use similar reasoning as in the former case.

There are only a few data on the phase equilibria in the discussed system [10]. Thus the calculation of the phase equilibria may yield further information also for the binary system. As in the previous cases we neglected the existence of different crystalline forms of urea and/or ammonium nitrate. From the point of view of liquid fertilizers we are interested mainly in the contribution of the system urea—ammonium nitrate to the excess Gibbs energy of the ternary system water—urea—ammonium nitrate. For this purpose it is sufficient to estimate the deviation of this system from ideality from the eutectic point. The following data are considered to be most reliable [11]: $\theta_{\text{eut}} = 47\,°\text{C}$, $x_{\text{eut}}(\text{CO(NH}_2)_2) = 55\,\%$. Excess Gibbs energy $\Delta G^{\text{E}}_{3,2}$ was determined according to the relationship analogous to eqn (*8*). In this case instead of index 1 (water) stands index 3 (urea). Value of the parameter α_2 remains the same as in the former case. Parameter $\alpha_{3,2}$ was chosen to obtain the best fit between the experimental and calculated coordinates of the eutectic point. For calculation of the excess molar Gibbs energy the following relationship was used

$$\Delta G^{\text{E}}_{3,2} = \frac{R\alpha_{3,2}x_2x_3^2}{x_3 + 2x_2} + R\alpha_2x_2\left[\left(\frac{2x_2}{x_3 + 2x_2}\right)^{1/3} - 1\right] \qquad (10)$$

From this relationship we can readily derive corresponding relationships for $\ln \gamma_3$ and $\ln \gamma_2$. The best fit with experiment was obtained for $\alpha_{3,2} = -500\ \text{K}$.

Calculation of ternary phase diagram of the system water—urea—ammonium nitrate

The ternary phase diagram was calculated using the so-called "network method" [12]. According to this method the calculation is divided into two steps. In the first step the concentration triangle is divided into a regular triangular network and at each point of this network the temperature of solid—liquid equilibrium of all components is calculated. In the second step an interpolation procedure is used for calculation of isotherms and their intersections. The temperatures of solid—liquid equilibrium were calculated according to eqn (*5*). In the case of water an iterative procedure was used. Activities of components were calculated on the basis of general relationship (*6*). In paper [7] it is shown that for the model activities of components in the ternary system of this type it holds

$$a_1^* = \frac{x_1}{1 + x_2}; \qquad a_2^* = \left(\frac{2x_2}{1 + x_2}\right)^2; \qquad a_3^* = \frac{x_3}{1 + x_2} \qquad (11)$$

The activity coefficients in the ternary system can be calculated under the assumption that excess Gibbs energy is estimated with good approximation as a sum of contributions of excess Gibbs energies of binary systems [13]

$$\Delta G^{\mathrm{E}} = \Delta G^{\mathrm{E}}_{1,2} + \Delta G^{\mathrm{E}}_{1,3} + \Delta G^{\mathrm{E}}_{3,2} \qquad (12)$$

We found that calculation of solid—liquid equilibria in the ternary system based on the above stated assumption did not give satisfactory results. It follows that neglection of the ternary interaction term $\Delta G^{\mathrm{E}}_{1,2,3}$ in eqn (*12*) is not justified. For improving agreement between the experimental and calculated data we used the simplest relationship for ternary interactions

$$\Delta G^{\mathrm{E}}_{1,2,3} = R\alpha_{1,2,3}x_1x_2x_3 \qquad (13)$$

It was found that using $\alpha_{1,2,3} = -500\ \mathrm{K}$ we obtain substantial improvement between the experimental and calculated data in the middle part of phase diagram.

In Fig. 3 the calculated phase diagram of the system H_2O—$CO(NH_2)_2$—NH_4NO_3 is shown. Part of this phase diagram was experimentally studied in our laboratory [14]. In literature [15] one can find this phase diagram published in the whole concentration range. From the comparison of papers [14] and [15] it follows that there is a good agreement between the phase diagrams published in the cited papers.

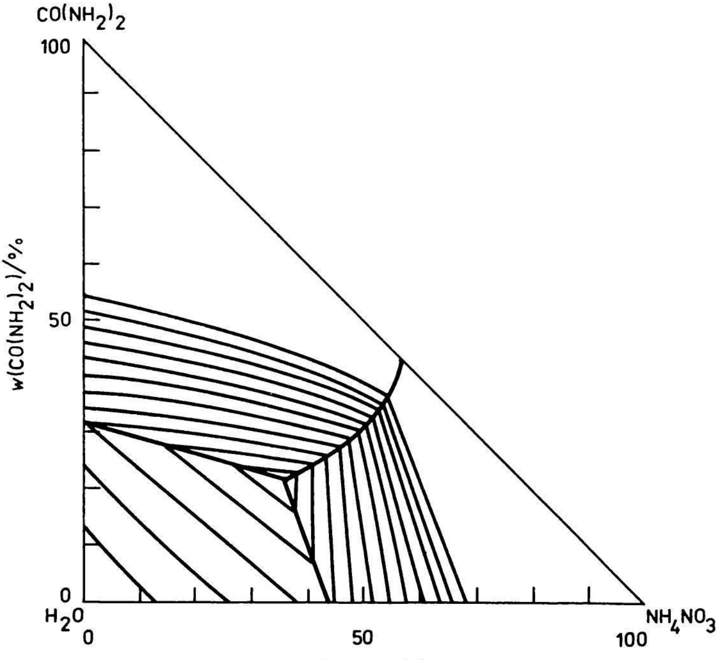

Fig. 3. Calculated phase diagram of the ternary system H_2O—$CO(NH_2)_2$—NH_4NO_3. Isotherms are plotted in the range −25 °C to 25 °C in the interval of 5 °C.

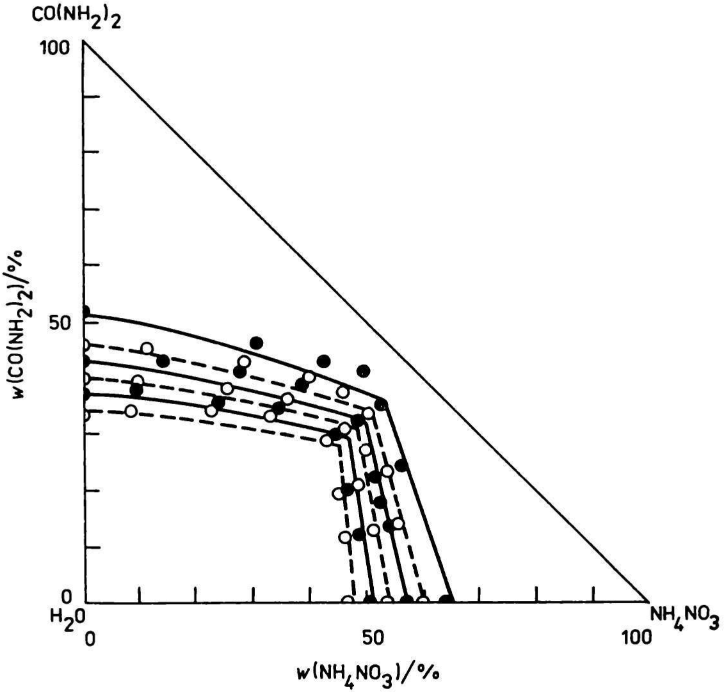

Fig. 4. Comparison of experimental determined points of the phase diagram of the system H_2O —$CO(NH_2)_2$—NH_4NO_3 with calculation.
Full lines and symbols ● are related to the isotherms $\theta/°C = 20; 5; -5$. Dashed lines and symbols ○ are related to the isotherms $\theta/°C = 10; 0; -10$.

In this paper we preferred for comparison of the calculated and experimental data the results [14] because they are available in numerical form, which is more precise than reading from a graph of phase diagram. From Fig. 4 it follows that the agreement between calculated and experimental temperature of primary crystallization of components in the ternary system is good, which proves that the used thermodynamic model is suitable for calculation of solid—liquid equilibria in the discussed ternary system.

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