Phase Diagram of the Reciprocal System
$2NH_4^+,Mg^{2+}//SO_4^{2-},2NO_3^-$—$H_2O$

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Phase equilibria in the reciprocal system $2NH_4^+,Mg^{2+}//SO_4^{2-},2NO_3^-$—$H_2O$ were investigated in the temperature range of 70 °C—115 °C. It was found out that two double salts can exist in this system, *viz.* $(NH_4)_2Mg(SO_4)_2 \cdot 6H_2O$ (boussingaultite) and $(NH_4)_2Mg_2(SO_4)_3$ (efremovite). Boussingaultite is stable up to (107 ± 3) °C while at higher temperatures efremovite crystallizes from aqueous solutions. Boussingaultite loses its hydrate water when heated to the temperatures higher than 110 °C. However, its transformation to efremovite is very slow. Detailed phase diagram of the system $2NH_4^+,Mg^{2+}//SO_4^{2-},2NO_3^-$—$H_2O$ at the temperature of 90 °C is presented.

Industrial fertilizers may besides basic nutrition elements like nitrogen, phosphorus, and potassium contain also salts of magnesium and sulfur. For production, storage, and application of solid fertilizers knowledge of their chemical and physical properties is required. The reciprocal system $2NH_4^+,Mg^{2+}//SO_4^{2-}$, $2NO_3^-$—H_2O represents a subsystem which can be interesting as a precursor for production of industrial fertilizers containing both magnesium and sulfur in the form accessible for plants. Solubility of pure components, of the binary systems and parts of the ternary systems of the reciprocal system in question is described in literature [1—4]. However, no data on the reciprocal system $2NH_4^+,Mg^{2+}//SO_4^{2-},2NO_3^-$—$H_2O$ are available in the literature.

In the discussed reciprocal system, two double salts, *viz.* efremovite $(NH_4)_2Mg_2(SO_4)_3$ and boussingaultite $(NH_4)_2Mg(SO_4)_2 \cdot 6H_2O$ can exist. While boussingaultite can readily be prepared by crystallization from aqueous solutions at ambient temperature, efremovite is stable at elevated temperatures. There were attempts to prepare efremovite by heating of boussingaultite. However, this reaction is very slow and it seems that boussingaultite loses its crystal water without apparent changes in X-ray pattern [5]. This was the reason why in this work we paid special attention to the investigation of the temperature over which efremovite is the stable phase in the reciprocal system $2NH_4^+,Mg^{2+}//SO_4^{2-},2NO_3^-$—$H_2O$. The system was studied in the temperature range 70 °C—115 °C. We will show that efremovite can be prepared by crystallization from aqueous solution when the temperature exceeds 107 °C.

EXPERIMENTAL

Chemicals used were of grade *pro analysis*. The content of magnesium and sulfates in samples was determined by chelatometry. The content of NH_4^+ cation was determined by the formaldehyde method.

The apparatus used for investigation of equilibrium between solid and liquid phases consisted of 800 cm³ of glycerol bath placed on magnetic stirrer (Heidolph, type MR 3003) equipped with temperature regulation. Temperature of the bath was kept at chosen height with accuracy $\pm$ 1 °C. Investigated sample was placed in 200 cm³ Erlenmeyer flask. When equilibrium was achieved, temperature of the sample did not change more than $\pm$ 0.5 °C. Both the glycerol bath and the sample were mixed with constant rate 500 min⁻¹.

The equilibrium composition was achieved in the following way. All components, including distilled water, were weighed into the Erlenmeyer flask with accuracy of 10 mg. The amount of water was sufficient for dissolving all salts at chosen temperature. The system was heated and water evaporated until first crystals of solid phase appeared. Then water was gradually added again until the last crystal of solid phase dissolved. This procedure is rather slow because after each addition of water the system is closed and the required temperature has to be reached. When the last crystal dissolved, the Erlenmeyer flask was weighed and from material balance the equilibrium amount of water required for dissolution of weighed-in salts was determined.

The Erlenmeyer flask was placed in glycerol bath again and small amount of water was evaporated. The

Table 1. Equilibrium Compositions of the Reciprocal System $2NH_4^+, Mg^{2+}//SO_4^{2-}, 2NO_3^- $—$H_2O$ at 70 °C

Composition					Solid phase
$x(Mg^{2+})$	$x(2NH_4^+)$	$x(SO_4^{2-})$	$x(2NO_3^-)$	Y	
mole %	mole %	mole %	mole %		
87.0	13.0	77.1	22.9	962	Boussingaultite + $MgSO_4 \cdot H_2O$
83.5	16.5	55.3	44.7	1039	Boussingaultite + $MgSO_4 \cdot H_2O$
69.1	30.9	17.3	82.7	696	Boussingaultite + $MgSO_4 \cdot H_2O$
15.0	85.0	15.0	85.0	1044	Boussingaultite
10.0	90.0	10.0	90.0	1263	Boussingaultite
50.0	50.0	25.0	75.0	1185	Boussingaultite
49.7	50.3	20.6	79.4	1003	Boussingaultite
65.0	35.0	35.0	65.0	1175	Boussingaultite
70.0	30.0	70.0	30.0	1550	Boussingaultite
74.1	25.9	62.8	37.2	1362	Boussingaultite
67.2	32.8	27.9	72.1	884	Boussingaultite
80.0	20.0	80.0	20.0	1348	Boussingaultite

$Y = n(H_2O)/(100$ mol of salts).

Table 2. Equilibrium Compositions of the Reciprocal System $2NH_4^+, Mg^{2+}//SO_4^{2-}, 2NO_3^- $—$H_2O$ at 90 °C

Composition					Solid phase
$x(Mg^{2+})$	$x(2NH_4^+)$	$x(SO_4^{2-})$	$x(2NO_3^-)$	Y	
mole %	mole %	mole %	mole %		
65.0	35.0	35.0	65.0	920	Boussingaultite + $MgSO_4 \cdot H_2O$
59.3	40.7	25.3	74.7	785	Boussingaultite + $MgSO_4 \cdot H_2O$
69.2	30.8	43.9	56.1	730	Boussingaultite + $MgSO_4 \cdot H_2O$
39.2	60.8	3.8	96.2	373	Boussingaultite + $MgSO_4 \cdot H_2O$
82.7	17.3	100.0	0	996	Boussingaultite + $MgSO_4 \cdot H_2O$
3.3	96.7	83.0	17.0	903	Boussingaultite + $(NH_4)_2SO_4$
10.0	90.0	90.0	10.0	887	Boussingaultite
10.0	90.0	50.0	50.0	973	Boussingaultite
5.0	95.0	10.0	90.0	538	Boussingaultite
19.2	80.8	11.8	88.2	705	Boussingaultite
50.0	50.0	50.0	50.0	1189	Boussingaultite
89.1	10.9	6.7	93.3	739	$MgSO_4 \cdot H_2O$
75.4	24.6	20.1	79.9	755	$MgSO_4 \cdot H_2O$
88.8	11.2	46.5	53.5	977	$MgSO_4 \cdot H_2O$

$Y = n(H_2O)/(100$ mol of salts).

crystallized solid phase was separated by filtration using fritted disk S1 or S3 and water vacuum pump. This operation was carried out in a drier heated to the temperature higher by 5 °C with respect to the equilibrium temperature. The filtration lasted less than 20 s. Fritted disk S1 could be used when solid phase consisted of coarse boussingaultite or efremovite crystals. When, however, fine crystals of $MgSO_4 \cdot H_2O$ were in equilibrium with the solution, the fritted disk S3 had to be used. The crystals were dried and analyzed by powder diffraction X-ray phase analysis using DRON UN 1 with CuK_α radiation. The solid phases were identified using the ASTM Tables. Composition of the equilibrium solid and liquid phases was analyzed by classical methods of chemical analysis.

RESULTS AND DISCUSSION

Phase equilibria in the reciprocal system $2NH_4^+$, $Mg^{2+}//SO_4^{2-}, 2NO_3^- $—$H_2O$ were investigated at the temperatures of 70 °C, 90 °C, and 115 °C. The aqueous phase is formed by concentrated salts solutions in which the activity of water is lower than one and thus boiling point of water is higher than 100 °C. This enabled us to carry out the measurements at ambient pressure of *ca.* 100 kPa at the temperatures up to 115 °C. It is a lucky coincidence that the transformation of boussingaultite to efremovite occurs in this temperature range. The equilibrium compositions of aqueous solution and corresponding equilibrium solid phases are presented in Tables 1—3. (Composition of

Table 3. Equilibrium Compositions of the Reciprocal System $2NH_4^+,Mg^{2+}//SO_4^{2-},2NO_3^- —H_2O$ at 115 °C

Composition					Solid phase
$x(Mg^{2+})$	$x(2NH_4^+)$	$x(SO_4^{2-})$	$x(2NO_3^-)$	Y	
mole %	mole %	mole %	mole %		
56.6	43.4	25.5	74.5	822	Efremovite + $MgSO_4 \cdot H_2O$
50.0	50.0	50.0	50.0	1085	Efremovite
40.0	60.0	60.0	40.0	906	Efremovite
26.8	73.2	36.6	63.4	771	Efremovite
40.0	60.0	22.4	77.6	627	Efremovite
67.3	32.7	24.0	76.0	934	$MgSO_4 \cdot H_2O$
70.0	30.0	30.0	70.0	1034	$MgSO_4 \cdot H_2O$

$Y = n(H_2O)/(100 \text{ mol of salts})$.
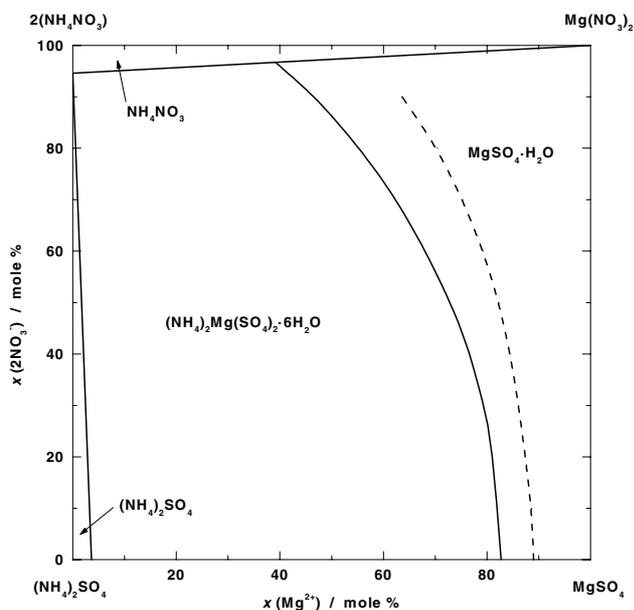
Fig. 1. Phase diagram of the reciprocal system $2NH_4^+,Mg^{2+}$ $//SO_4^{2-},2NO_3^- —H_2O$. Full line: $\theta = 90$ °C; dashed line: $\theta = 70$ °C.

the reciprocal system is expressed using Jänecke's projection [6].)

The most detailed investigation of the phase equilibria in the system $2NH_4^+,Mg^{2+}//SO_4^{2-},2NO_3^- —H_2O$ were carried out at temperature 90 °C. Phase diagram of the investigated system measured at this temperature is presented in Fig. 1. In this figure, data ob-

tained for the temperature of 70 °C are plotted as well. One can see that at 70 °C the crystallization field of boussingaultite broadened in respect to the temperature of 90 °C. The other parts of the phase diagram did not change in the limit of error.

When the phase equilibria were investigated at 115 °C, the equilibrium solid phase was $(NH_4)_2Mg_2$-$(SO_4)_3$ (efremovite) instead of $(NH_4)_2Mg(SO_4)_2 \cdot 6H_2O$ (boussingaultite). Detailed study of the temperature over which efremovite coexists in equilibrium with solution revealed that this temperature is (107 ± 3) °C.

REFERENCES

1. Silock, H. L. (Editor), *Solubility of Inorganic and Organic Compounds*, Vol. 3, Part 1. Pergamon Press, Oxford, 1979.
2. *Spravochnik eksperimental'nykh dannykh po rastvorimosti solennykh sistem*, Tom I—IV. Publishing House GKHI, Leningrad, 1954—1962.
3. *Gmelins' Handbuch der Anorganischen Chemie,* System Nummer 27, Magnesium, Teil B. Verlag Chemie, Weinheim, 1937 (Nachdruck 1953).
4. *Landolt-Börnstein, Lösungsgleichgewichte,* II. Band, 2. Teil. Springer Verlag, Berlin, 1962.
5. Žáček, V., *Acta Universitatis Carolinae – Geologica 3*, 315 (1988).
6. Nývlt, J., *Solid-Liquid Phase Equilibria*, p. 44—49. Academia, Publishing House of the Czechoslovak Academy of Sciences, Prague, 1977.