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Phase diagram of the reciprocal system K^+, $Mg^{2+}//Cl^-$, NO_3^-–H_2O

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ABSTRACT

Solid–liquid phase equilibria of the reciprocal system K+, $Mg^{2+}//Cl^-$, NO_3^-–H_2O were studied in the temperature range 5 °C–115 °C. Phase diagrams obtained at the temperatures of 5 °C, 20 °C, 40 °C and 60 °C are presented. Data for higher temperatures are presented in a table. A semi-empirical model for the description of solid–liquid equilibrium for KNO_3–$MgCl_2$ diagonal of this system was developed. The model allows calculating the material balance of crystallization of KNO_3, KCl, and $KCl \cdot MgCl_2 \cdot 6H_2O$, respectively, with precision better than 1%. Experimental and calculated data on the solid–liquid equilibrium are compared up to the temperature of 115 °C.

1. Introduction

The reciprocal system K^+, $Mg^{2+}//Cl^-$, NO_3^-–H_2O can be used for the production of potassium nitrate. Raw material for this process can be potassium chloride and magnesium nitrate which can be obtained by the reaction of magnesite ($MgCO_3$) with nitric acid. For quantitative evaluation of the yield of KNO_3 which is obtained by crystallization from the aqueous solution of potassium chloride and magnesium nitrate, knowledge of the phase diagram of the reciprocal system K^+, $Mg^{2+}//Cl^-$, NO_3^-–H_2O is of primary importance.

Literature data on the phase equilibrium in this system are rather rare [1–4]. Besides, part of the literature on the phase equilibria in the mentioned system is not easily accessible [1–3] because they were published either in internal reports [3] or in the Slovak language [1,2]. This is the reason why Matveeva and Kudryashova [4] claim in their paper that no data on this reciprocal system could be found in the literature. In 1938, Bergman and Naogornyi [5] published data on the part of the reciprocal system, namely KNO_3–$MgCl_2$–H_2O for the temperature range −28–30 °C. As we will show the available data are not fully consistent. Because of that it was necessary to make a critical evaluation of the available data and in the case of uncertainties, to carry out additional experiments for proving or disproving the validity and accuracy of available data.

Literature on phase equilibria in the binary systems H_2O–KCl, H_2O–KNO_3, H_2O–$MgCl_2$ and H_2O–$Mg(NO_3)_2$ is extensive [6]. The solid–liquid phase equilibria in the reciprocal system K^+, $Mg^{2+}//Cl^-$, NO_3^-–H_2O were studied by Plančík in his diploma work [1]. Part of these results has been published in the paper by Žužiová, Khandl and Plančík [2]. Further data can be found only in the internal research report of the Department of Inorganic Technology, Slovak University of Technology in Bratislava [3]. These equilibrium data were obtained at the temperatures 5 °C, 20 °C, 40 °C and 60 °C, respectively. Recently Matveeva and Kudryashova published data on the phase equilibria in the discussed system at 25 °C and 50 °C [4]. Bergman and Naogornyi [5] published the temperature dependence of the crystallization areas of KNO_3 and KCl in the subsystem KNO_3–$MgCl_2$–H_2O for temperatures starting at −28 °C. As mentioned above, knowledge of the phase diagram of the reciprocal system in broad temperature range (5 °C–115 °C) is of

Table 1
Experimental results for the solid–liquid phase equilibria in the K^+, $Mg^{2+}//Cl^-$, NO_3^-–H_2O. The amount of water is defined in moles of water per 100 mol of non-aqueous components.

T °C	*x*(KCl) mol%	*x*($Mg(NO_3)_2$) mol%	*x*($MgCl_2$) mol%	n(H_2O) mol	Crystallizing phase
20	29	14.5	56.5	1327	KNO_3
20	27	13.5	59.5	1300	KNO_3 + KCl
20	25	12.5	62.5	1305	KNO_3 + KCl
20	23	11.5	65.5	1318	KCl
6	17	8.5	74.5	1479	KCl
6	19	9.5	71.5	1553	KNO_3 + KCl
6	21	10.5	68.5	1503	KNO_3 + KCl
6	23	11.5	65.5	1602	KNO_3
60	49	24.5	26.5	813	KNO_3 + KCl
60	46	23	31	835	KCl
60	43	21.5	35.5	872	KCl
60	40	20	40	920	KCl
99	66.67	33.33	0	560	KNO_3
110	66.67	33.33	0	450	KNO_3
115	66.67	33.33	0	411	KNO_3
116	66.67	33.33	0	404	KNO_3

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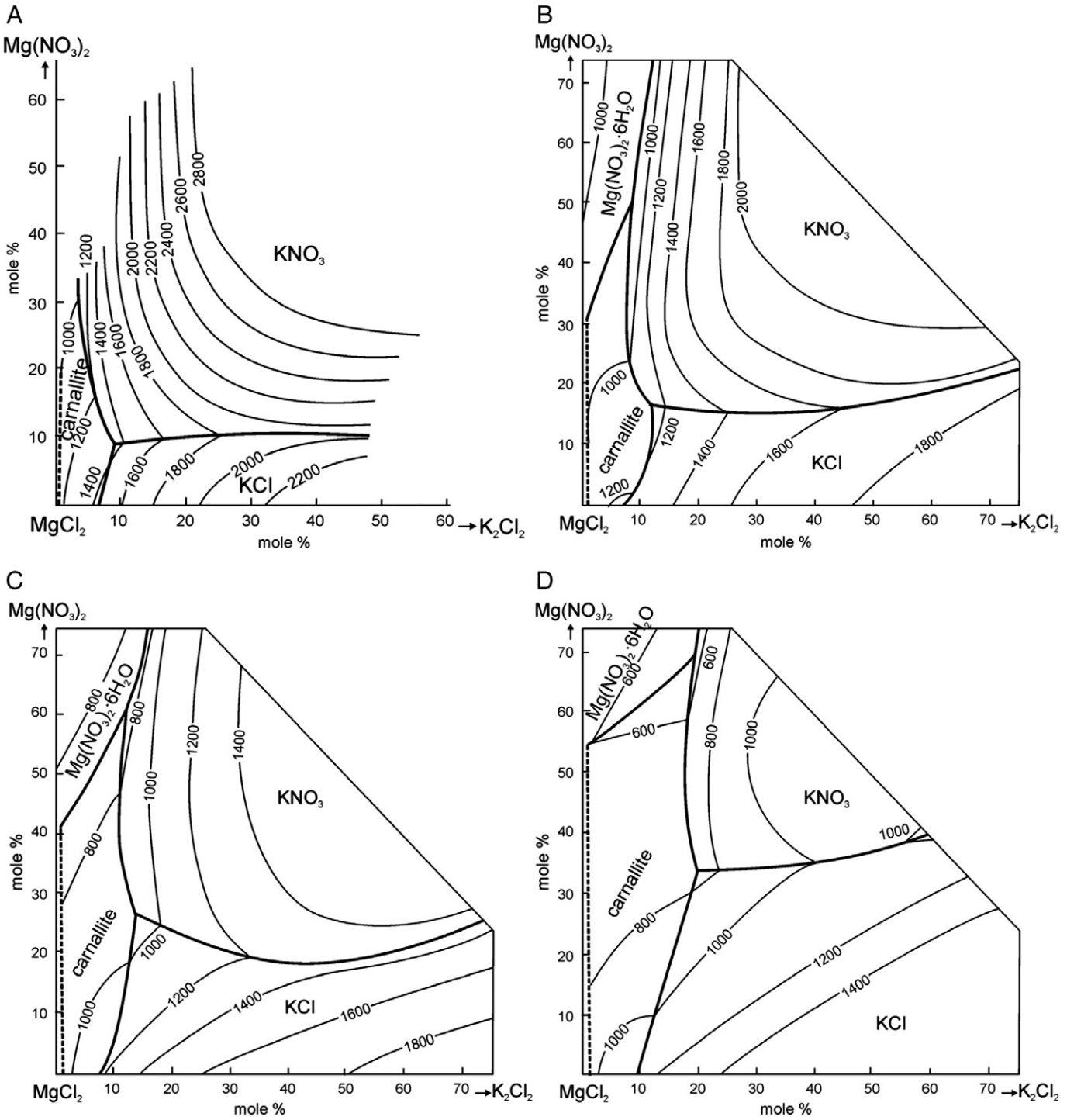

Fig. 1. Phase diagram of the system K^+, Mg^{2+}//Cl^-, NO_3^-–H_2O for different temperatures. A) 5 °C [1,2]; B) 20 °C [3]; C) 40 °C [3]; D) 60 °C [3]. Content of water is defined in moles of water per 100 mol of non-aqueous components.

primary importance for quantitative evaluation of the crystallization of KNO_3 from this system. The broad temperature range of KNO_3 crystallization is important for reaching a high yield of potassium nitrate.

2. Experimental

KCl, $MgCl_2 \cdot 6H_2O$ and $Mg(NO_3)_2 \cdot 6H_2O$ of grade "pro analysis" (Merck) were used.

For study of the solid–liquid phase equilibria, the isothermal method was used. The initial mixture (100 g) of precisely weighed components (KCl, $MgCl_2 \cdot 6H_2O$ and $Mg(NO_3)_2 \cdot 6H_2O$) was kept at the chosen temperature in a stirred, closed 250 ml three-neck flask. The flask was placed in a thermostat water bath. Temperature was measured with a digital thermometer immersed into the solution and it was kept constant with the precision of 0.1 K. Distilled water preheated to the chosen temperature was carefully added to the flask until the last crystal of the solid phase disappeared. Then the flask was weighed in order to determine the added amount of water. In the next step, the open flask was placed again into the water bath and water was evaporated until the first crystals of solid phase appeared. The crystals were separated and