Phase diagram of the system LiF—NaF—KCl*

J. GABČOVÁ and M. MALINOVSKÝ

Department of Inorganic Technology, Slovak Technical University, 880 37 Bratislava

Received 31 May 1977

Accepted for publication 16 September 1977

Dedicated to Professor Dr Ing Mikuláš Gregor, DrSc, Corresponding member of the Slovak Academy of Sciences, on his 75th birthday

The phase diagrams of the two-component system NaF—KCl and of the three-component system LiF—NaF—KCl have been reinvestigated using the classical TA method. The quasi-binary system NaF—KCl is a simple eutectic system. The coordinates of the eutectic point are 27 mole % NaF, 73 mole % KCl, $t_E = 657°C$. The system LiF—NaF—KCl has one ternary eutectic point, its coordinates are 38 mole % LiF, 38 mole % NaF, 24 mole % KCl, $t_E = 599°C$. The experimental results have been compared with theoretical calculations.

Методом ТА были исследованы фазовые диаграммы бинарной системы NaF—KCl и тернарной системы LiF—NaF—KCl. Квази-бинарная система NaF—KCl является простой эвтектической системой. Координаты эвтектической точки: 27 мол. % NaF, 73 мол. % KCl, $t_E = 657°C$. Система LiF—NaF—KCl является системой с одной тернарной эвтектической точкой, координаты которой 38 мол. % LiF, 38 мол. % NaF и 24 мол. % KCl, $t_E = 599°C$. Экспериментальные данные были сравнены с теоретическими расчетами.

The phase diagram of the system NaF—KCl has been investigated by numerous authors thus far [1—8]. Their results are confronted in Table 1. The composition of the eutectic mixture is given in the range 26.5—30.0 mole % NaF, the temperature of eutectic crystallization in the interval 630—660°C. Especially the temperature data interval exceeds essentially the allowed experimental inaccuracy. Therefore the system NaF—KCl has been reinvestigated in the whole composition range. The two further systems, LiF—NaF and LiF—KCl, which bound the phase diagram of the system LiF—NaF—KCl, have been described in [9] and [10].

---

* Based on a paper presented at the 1st Conference of Socialist Countries on Chemistry and Electrochemistry of Molten Salts, Smolenice, November 24—26, 1975.

Table 1

System NaF—KCl
Comparison of the published data

t^f_{NaF} °C	t^f_{KCl} °C	E (eutectic point)		Ref.	Notes
		mole % NaF	t_E, °C		
990	772	28.0	660	[1]	
990	772	26.5	648	[2]	
990	773	26.5	652	[3]	SES
986	772	28.0	660	[4]	Taken from the graph
992	778	27.5	630	[5]	
992	778	30.0	648	[6]	Liquidus given
990	774	26.8	648 (646)	[7]	
990	772	27.0	648	[8]	Liquidus given

SES — simple eutectic system.

Table 2

Data by *Bergman et al.* [8] concerning the systems LiF—NaF, LiF—KCl, NaF—KCl, and LiF—NaF—KCl

System	E (eutectic point)	
	mole %	t_E, °C
LiF—NaF	61 LiF	652
LiF—KCl	19 LiF	710
NaF—KCl	27 NaF	648
LiF—NaF—KCl	48 LiF; 39 NaF; 13 KCl	590

The system LiF—NaF—KCl has been studied thus far only by *Bergman et al.* [8] in 1963. They have used the visual-polythermic method in the measurements. The detailed data of the experiment were not reported.

The data of the authors [8] concerning the systems LiF—NaF, LiF—KCl, NaF—KCl, and LiF—NaF—KCl can be found in Table 2.

Experimental

The phase diagrams of the systems NaF—KCl and LiF—NaF—KCl have been investigated by TA method, described in details in [9]. The weight of the sample was 20 g. The Pt crucibles used were covered with lids. The temperature was indicated by means of a PtRh10—Pt thermocouple. The rate of cooling was maintained at 1—1.5°C/min.

The simple eutectic NaF—KCl system is a stable diagonal section of the ternary reciprocal system $Na^+, K^+||F^-, Cl^-$. On the NaF side 15 mixtures and on the KCl side 14 mixtures have been measured. The determined values of the temperature of primary and eutectic crystallizations are assembled in Table 3. The eutectic mixture has the following parameters: 27 ±0.5 mole % NaF, 73 ±0.5 mole % KCl, $t_E = 657$ ±1°C. These results agree satisfactorily with the data in [1, 2], however, they differ from the data reported in [3—8], especially as to the value of the eutectic temperature t_E. The reason of these differences lies evidently in the methods of measurement and the purity of the salts used.

Table 3

Measured values of the temperature of primary (TPC) and eutectic (t_E) crystallization and calculated values of the temperature of primary crystallization (t_{calc}) in the system NaF—KCl

Mole %		TPC	t_E	t_{calc}
NaF	KCl	°C	°C	°C
99.5	0.5	987.0	—	—
99.0	1.0	983.5	—	—
98.0	2.0	977.5	652.0	—
97.0	3.0	970.5	654.5	—
96.0	4.0	965.0	656.0	—
95.0	5.0	959.0	657.0	—
90.0	10.0	929.0	657.5	925.8
80.0	20.0	885.0	657.5	874.1
70.0	30.0	839.0	658.0	831.0
60.0	40.0	797.0	658.0	792.1
50.0	50.0	753.0	658.0	754.6
40.0	60.0	716.0	657.0	715.6
30.0	70.0	669.0	657.5	672.0
29.0	71.0	—	656.5	—
28.0	72.0	—	655.5	—
27.0	73.0	—	657.0	—
26.0	74.0	—	657.5	—
25.0	75.0	664.0	658.5	662.9
24.0	76.0	666.0	656.5	—
23.0	77.0	669.5	656.0	—
22.0	78.0	676.0	656.5	—
21.0	79.0	678.0	656.0	—
20.0	80.0	683.0	656.0	678.5
10.0	90.0	724.0	651.0	716.3
5.0	95.0	747.0	643.0	740.6
4.0	96.0	752.0	642.0	—
3.0	97.0	756.5	640.0	—
2.0	98.0	761.5	637.0	—
1.0	99.0	767.0	635.0	—
0.5	99.5	769.5	—	—

The system LiF—NaF—KCl is a planar diagonal section of the quaternary reciprocal system Li^+, Na^+, $K^+||F^-$, Cl^-, the composition polyhedron of which is a triangular prism (Fig. 1). In studying this system 12 sections of the 2nd kind and 3 sections of the 1st kind have been investigated, altogether 36 internal mixtures. Most measurements were repeated several times. The deviation of the determined values did not exceed ±3°C. The phase diagram of the system LiF—NaF—KCl with marked lines of the monovariant equilibrium and isotherms for every 50°C is shown in Fig. 2. The system LiF—NaF—KCl is a system with one ternary eutectic point, the coordinates of which are: 38 ±2 mole % LiF, 38 ±2 mole % NaF, 24 ±2 mole % KCl, $t_E = 599$°C. The inaccuracy in determination of the temperature coordinate of the ternary eutectic point does not exceed ±3°C and therefore it is

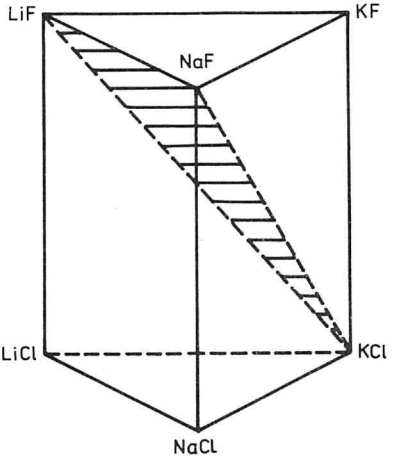

Fig. 1. Composition polyhedron of the quaternary reciprocal system Li^+, Na^+, $K^+||F^-$, Cl^-.

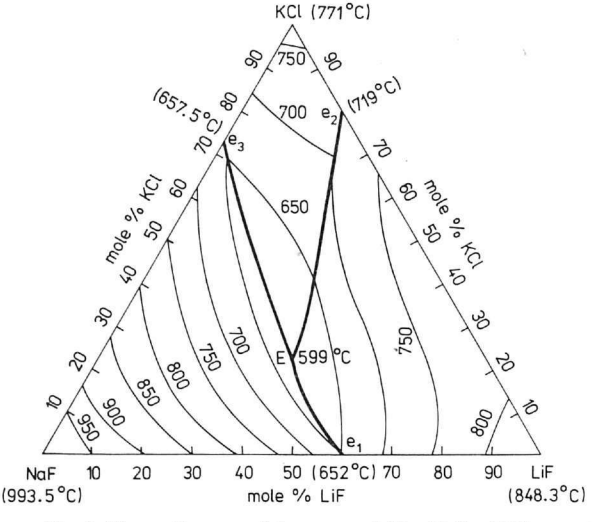

Fig. 2. Phase diagram of the system LiF—NaF—KCl.

evident that the temperature given by *Bergman et al.* [8], *i.e.* 590°C, is too low. The inaccuracy in determining the composition coordinates of the ternary eutectic point in systems of the given type is in general ± 2 to 3 mole %. The data reported by *Bergman et al.* [8], *i.e.* 48 mole % LiF, 39 mole % NaF, 13 mole % KCl differ from the determined values much more than the admissible error. This difference may be caused by a too high rate of cooling as well as the insufficient purity of salts (*Bergman et al.* [8] do not give the exact description of the experiment). It should be emphasized that after elongation into the unstable region (beyond the eutectic point) each curve of the monovariant equilibrium — if the equilibrium system is considered — has to pass between the stable parts of the two other monovariant curves [11]. The angle of two curves of monovariant equilibrium must not exceed 180° [12]. The diagram by *Bergman et al.* [8] does not satisfy these two conditions, the reason being probably the same as it has been mentioned above.

Theoretical

In [13] *Gabčová* and *Malinovský* calculate the isotherms and curves of the monovariant equilibrium for the three-component system LiF—NaF—NaCl. The isotherms and curves of monovariant equilibrium in the ternary system have been graphically constructed on the basis of the theoretically calculated courses of liquidus curves of binary systems. It has been shown that the isotherms and curves of the monovariant equilibrium which have been obtained using the universal relationship [14] are the closest to the experimental results.

This method of calculation has been applied to the system LiF—NaF—KCl. The course of liquidus curves in two-component systems LiF—NaF, LiF—KCl, and NaF—KCl has been calculated by means of the Le Chatelier—Shreder equation, where the activity has been expressed using the universal relationship [14]: $a_i = x_i^k$, where

$$k = \frac{k_{j/i}^{St}}{1 + b(1 - x_i)}$$

Here, a_i denotes the activity of the i-th substance, x_i denotes the mole fraction of the i-th substance, $k_{j/i}^{St}$ is the Stortenbeker correction factor, b denotes the parameter calculated on the basis of the experimental eutectic point data.

Then

for the system LiF—NaF: $b_{LiF} = -0.4685$, $b_{NaF} = -0.3372$;
for the system LiF—KCl: $b_{LiF} = 9.3795$, $b_{KCl} = 9.0624$;
for the system NaF—KCl: $b_{NaF} = 1.7604$, $b_{KCl} = 2.5770$.

The calculated values for the course of liquidus curves of the system NaF—KCl are presented in Table 3 and those of the systems LiF—NaF and LiF—KCl in [9] and [10], respectively. The isotherms and the curves of monovariant equilibrium in the ternary system LiF—NaF—KCl have been constructed on the basis of

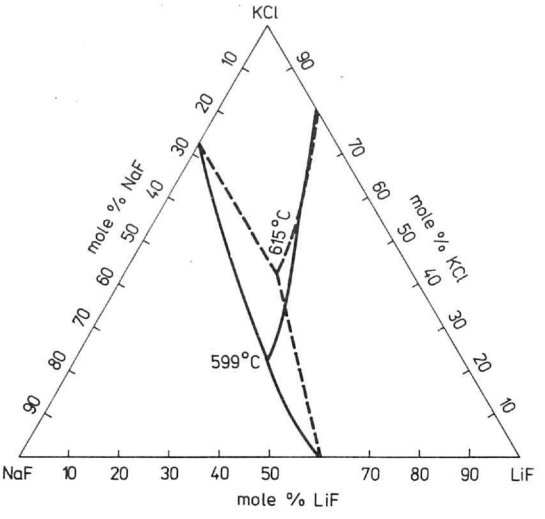

Fig. 3. Phase diagram of the system LiF—NaF—KCl.
— Experimental; – – – – $a_i = x_i^k$.

theoretically calculated liquidus curves in the binary systems. (The detailed procedure can be found in [13].) The theoretically determined curves of monovariant equilibrium are compared with the experimental ones in Fig. 3. In contrast to the system LiF—NaF—NaCl, where the calculated diagram is in a good accordance with the experiments [13], there are considerable differences between the calculation and the experiments in the case of the system LiF—NaF—KCl, namely with respect to the course of curves of the monovariant crystallization of KCl + NaF and LiF + NaF. The maximum deviation in the composition coordinate of the eutectic point makes 17 mole %, in the temperature coordinate it is 16°C. In contrast to the system LiF—NaF—NaCl, where 2 kinds of cations and anions are present, there are three cations (Li^+, Na^+, K^+) and two anions in the system LiF—NaF—KCl. The aggregate interaction of ions is therefore essentially more complicated than in the previous case. This fact is also reflected in the character of the corresponding phase diagram.

References

1. Polyakov, V. D., *Izv. Sektora Fiz. Khim. Anal. Akad. Nauk SSSR* ***11,*** 208 (1938).
2. Polyakov, V. D., *Izv. Sektora Fiz. Khim. Anal. Akad. Nauk SSSR* ***13,*** 308 (1940).
3. Rassonskaya, I. S. and Bergman, A. G., *Zh. Neorg. Khim.* ***23,*** 14 (1953).
4. Ishaque, M., *Bull. Soc. Chim. Fr.* ***1952,*** 130.
5. Sauerwald, F. and Dombois, H. E., *Z. Anorg. Allg. Chem.* ***227,*** 60 (1954).

6. Flood, H., Fykse, O., and Urnes, S., *Z. Elektrochem.* ***59,*** 364 (1955).
7. Bukhalova, G. A. and Yagubyan, E. S., *Zh. Neorg. Khim.* ***5,*** 2503 (1960).
8. Bergman, A. G., Berezina, I. S., and Bakumskaya, E. L., *Zh. Neorg. Khim.* ***8,*** 2144 (1963).
9. Malinovský, M. and Gabčová, J., *Chem. Zvesti* ***30,*** 783 (1976).
10. Gabčová, J., Peschl, J., Malinovský, M., and Koštenská, I., *Chem. Zvesti* ***30,*** 796 (1976).
11. Anosov, V. Yu. and Pogodin, S. A., *Osnovnye nachala fiziko-khimicheskogo analiza*, p. 61. Izd. Akad. Nauk SSSR, Moscow—Leningrad, 1947.
12. Ricci, J. E., *The Phase Rule and Heterogeneous Equilibrium*, p. 243. Van Nostrand, New York, 1951.
13. Gabčová, J. and Malinovský, M., *Chem. Zvesti* ***30,*** 813 (1976).
14. Malinovský, M. and Koštenská, I., *Chem. Zvesti* ***28,*** 493 (1974).

Translated by M. Uhrová