



---

Soviet-era science, translated into English

# Chemistry

Corresponding Member of the Academy of Sciences of the USSR A.  
V. NOVOSELOVA, Yu. M. KORENEV

1961

SovietRxiv

---

View the original and related papers at <https://sovietrxiv.org/items/ru-196101.21938>

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

## Abstract

## Full Text

### *Chemistry*

Corresponding Member of the Academy of Sciences of the USSR A. V. NOVOSELOVA, Yu. M. KORENEV and Yu. P. SIMANOV

## STUDY OF THE SYSTEM KF–ZrF<sub>4</sub>

Zirconium fluoride forms double salts of complex composition with alkali-metal fluorides. Thus, in the system NaF–ZrF<sub>4</sub>, studied by Barton et al. (1), two congruently melting compounds, Na<sub>3</sub>ZrF<sub>7</sub> and Na<sub>7</sub>Zr<sub>6</sub>F<sub>31</sub>, were found; three compounds melting incongruently—Na<sub>5</sub>Zr<sub>2</sub>F<sub>13</sub>, Na<sub>2</sub>ZrF<sub>6</sub>, and Na<sub>3</sub>Zr<sub>4</sub>F<sub>19</sub>; and one compound—Na<sub>3</sub>Zr<sub>2</sub>F<sub>11</sub>—existing only in the solid state.

According to the literature data, KF and ZrF<sub>4</sub> form the compounds: K<sub>3</sub>ZrF<sub>7</sub>, K<sub>2</sub>ZrF<sub>6</sub>, and KZrF<sub>5</sub>. The fusibility diagram of the system KF–ZrF<sub>4</sub> (up to 65% ZrF<sub>4</sub>) was investigated in works (2,3), apparently by the visual-polythermal method, since in work (2) the phase fields below the solidus line are not indicated on the diagram of this system. In work (3) there are likewise no indications of transformations in this system in the solid state.

In the present work we carried out differential thermal analysis and an X-ray phase study of the system KF–ZrF<sub>4</sub>. According to the data of work (4), zirconium fluoride undergoes a polymorphic transformation at 405 ± 5°. Schulze (5) determined the parameters of the low-temperature monoclinic modification of ZrF<sub>4</sub>:  $a = 9.46 \text{ \AA}$ ;  $b = 9.87 \text{ \AA}$ ,  $c = 7.64 \text{ \AA}$ ;  $\beta = 94^\circ 30'$ . According to Barton's determination (1), ZrF<sub>4</sub> melts at 912°. Sense et al. (6) determined the dependence of the vapor pressure of ZrF<sub>4</sub> on temperature; according to their data, the sublimation temperature of ZrF<sub>4</sub> is 903°.

**Starting substances.** For the study of the system we obtained potassium fluoride by dehydrating KF · 2H<sub>2</sub>O; zirconium fluoride was prepared from (NH<sub>4</sub>)<sub>3</sub>ZrF<sub>7</sub> by distilling off ammonium fluoride in a stream of CO<sub>2</sub>. The synthesis of (NH<sub>4</sub>)<sub>3</sub>ZrF<sub>7</sub> was carried out by the method described in work (7).

For the preparation of melts containing less than 33.3% ZrF<sub>4</sub>, we used potassium fluoride and the available preparation K<sub>2</sub>ZrF<sub>6</sub>. Melts containing more than 33.3% ZrF<sub>4</sub> were prepared by fusing calculated amounts of K<sub>2</sub>ZrF<sub>6</sub> and (NH<sub>4</sub>)<sub>3</sub>ZrF<sub>7</sub> in a stream of CO<sub>2</sub>. Because of the volatility of ZrF<sub>4</sub>, melts with a content of it greater than 75% were not studied. The results of analyses of the starting preparations and the melts obtained for potassium, zirconium, and fluorine agreed well with the calculated values. The errors of determination did not exceed 0.2–0.25%.

Fig. 1. System KF–ZrF<sub>4</sub>. Phase fields diagram

Figure 1: Fig. 1. System KF–ZrF<sub>4</sub>. Phase fields diagram

**Thermal and X-ray phase analysis of the system KF–ZrF<sub>4</sub>.** Differential thermal analysis was carried out on an N. S. Kurnakov pyrometer using a platinum–platinum–rhodium thermocouple. Aluminum oxide served as the standard. Melts for thermal analysis were taken in an amount of 0.5 g. For melts containing up to 33.3% ZrF<sub>4</sub>, cooling and heating curves were recorded. For melts with a ZrF<sub>4</sub> content greater than 33.3%, only cooling curves were recorded, since during slow heating of the melts their composition changed noticeably. In order to reduce the loss of ZrF<sub>4</sub>, the melts were placed in a furnace preheated to a temperature slightly exceeding the melting temperature of the melt, and then after several minutes the furnace was switched off and the cooling curve was recorded. The temperatures were noted from the beginning of the effect on the differential curve.

For the X-ray investigation, the alloys were ground and, with the aid of zapon lacquer, applied to a Pyrex whisker. Potassium fluoride and alloys with a high content of it were photographed in sealed capillaries made of Pyrex glass. X-ray patterns were recorded in RKD-57 cameras using Fe radiation.

In view of the fact that a number of effects connected with its transformations were detected on the heating curves of  $K_2ZrF_6$ , we recorded X-ray patterns of  $K_2ZrF_6$  at 260 and 340° in a Unicam camera (8) on a BSVLT tube with a copper anode. At a higher temperature it was impossible to carry out the recording because of the interaction of  $K_2ZrF_6$  with quartz.\*

The phase diagram of the system  $KF-ZrF_4$ , constructed by us on the basis of thermal and X-ray phase analysis, is presented in Figs. 1 and 2.

The zirconium fluoride synthesized by us was a monoclinic modification, described in (5). On its heating curve, endothermic effects at 612 and 685°, corresponding to transformations in the solid state, were found; on repeated heating the effect at 612° was absent.

In view of the strong volatility of  $ZrF_4$  on heating, beginning at 880° a strong deviation of the differential curve is noted on the thermogram. The endothermic effect corresponding to the melting of  $ZrF_4$  is found at  $903 \pm 5^\circ$ . If a closed platinum crucible with  $ZrF_4$  is placed in a furnace preheated to 930–940° and then, after switching off the furnace, the cooling curve is recorded, then the effect of solidification of  $ZrF_4$  is observed at  $903 \pm 5^\circ$ ; on further cooling a polymorphic transformation occurs at 685°. Potassium fluoride, according to our data, melts at 850°. In the system

Fig. 1. System  $KF-ZrF_4$ . Phase fields: **1** –  $KF + \text{liq.}$ ; **2** –  $K_3ZrF_7 + \text{liq.}$ ; **3** –  $K_5Zr_2F_{13} + \text{liq.}$ ; **4** – solid solution + liq.; **5** –  $\delta-K_2ZrF_6 + \text{liq.}$ ; **6** –  $\gamma-K_2ZrF_6 + \text{liq.}$ ; **7** –  $\gamma-KZrF_5 + \text{liq.}$ ; **8** –  $\delta-K_2ZrF_6 + \text{liq.}$ ; **9** –  $\alpha-ZrF_4 + \text{liq.}$ ; **10** –  $KF +$

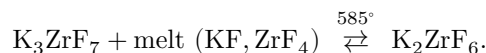
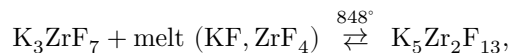
Fig. 2. Line diagrams of compounds in the KF–ZrF<sub>4</sub> system

Figure 2: Fig. 2. Line diagrams of compounds in the KF–ZrF<sub>4</sub> system

$K_3ZrF_7$ ; **11**  $-K_3ZrF_7 + K_5Zr_2F_{13}$ ; **12** –solid solution; **13** –solid solution  $+\delta-K_2ZrF_6$ ; **14** –solid solution  $+\gamma-K_2ZrF_6$ ; **15** –solid solution  $+\alpha-K_2ZrF_6$ ; **16**  $-\gamma-K_2ZrF_6 + \gamma-KZrF_5$ ; **17**  $-\gamma-K_2ZrF_6 + \beta-KZrF_5$ ; **18**  $-\gamma-K_2ZrF_6 + \alpha-KZrF_5$ ; **19**  $-\gamma-K_2ZrF_6 + K_7Zr_6F_{31}$ ; **20**  $-\alpha-K_2ZrF_6 + \beta-K_3Zr_2F_{11}$ ; **21**  $-\gamma-K_2ZrF_6 + \alpha-K_3Zr_2F_{11}$ ; **22**  $-\alpha-K_2ZrF_6 + \alpha-K_3Zr_2F_{11}$ ; **23**  $-\beta-K_3Zr_2F_{11} + K_7Zr_6F_{31}$ ; **24**  $-\alpha-K_3Zr_2F_{11} + K_7Zr_6F_{31}$ ; **25**  $-\alpha-KZrF_5 + K_7Zr_6F_{31}$ ; **26**  $-\alpha-KZrF_5 + \alpha-ZrF_4$ ; **27**  $-\beta-KZrF_5 + \alpha-ZrF_4$ ; **28**  $-\gamma-KZrF_5 + \alpha-ZrF_4$ .

\* When the present work had been completed, a paper (9) appeared in print on the thermal stability and polymorphism of  $K_2ZrF_6$ .

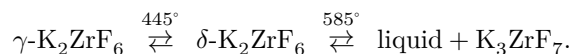
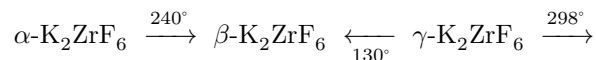
In the KF–ZrF<sub>4</sub> system the following compounds were found:  $K_3ZrF_7$ ,  $K_5Zr_2F_{13}$ ,  $K_2ZrF_6$ ,  $K_3Zr_2F_{11}$ ,  $K_7Zr_6F_{31}$ ,  $KZrF_5$ . The fluorozirconates  $K_3ZrF_7$  and  $KZrF_5$  melt congruently at temperatures of 923 and 455°, respectively. The fluorozirconates  $K_5Zr_2F_{13}$  and  $K_2ZrF_6$  are formed by peritectic reactions:



The fluorozirconates  $K_3Zr_2F_{11}$  and  $K_7Zr_6F_{31}$  exist only in the solid state below 327 and 380°, respectively. The eutectic between KF and  $K_3ZrF_7$  lies at 760° and 13% ZrF<sub>4</sub>; between  $K_3ZrF_7$  and  $KZrF_5$  at 430° and 47% ZrF<sub>4</sub>, and between  $KZrF_5$  and ZrF<sub>4</sub> at 440° and 60% ZrF<sub>4</sub>.

**Fig. 2.** Line diagrams of compounds in the KF–ZrF<sub>4</sub> system

Several modifications were found for the fluorozirconate  $K_2ZrF_6$  (Fig. 3). The transformations of  $K_2ZrF_6$  may be represented by the scheme:



The fluorozirconate  $KZrF_5$  undergoes polymorphic transformations at 400 and 424°. The fluorozirconate of composition  $K_3Zr_2F_{11}$  undergoes a polymorphic transformation at 313°.  $K_3ZrF_7$  has one modification, crystallizing in a face-centered cubic lattice

Fig. 3. Line diagrams of the  $\alpha$ ,  $\beta$ ,  $\gamma$  modifications of  $\text{K}_2\text{ZrF}_6$

Figure 3: Fig. 3. Line diagrams of the  $\alpha$ ,  $\beta$ ,  $\gamma$  modifications of  $\text{K}_2\text{ZrF}_6$

**Fig. 3.** Line diagrams of the  $\alpha$ ,  $\beta$ ,  $\gamma$  modifications of  $\text{K}_2\text{ZrF}_6$

$$a = 8.966 \pm 0.003 \text{ kX}$$

and forms a solid solution with  $\text{K}_2\text{ZrF}_6$  (in the region 73–75% KF).

Moscow State University  
named after M. V. Lomonosov

Received  
18 III 1961

### CITED LITERATURE

1. C. J. Barton, W. R. Grimer et al., *J. Phys. Chem.*, **62**, 665 (1958).
2. Materials of the U.S. Atomic Energy Commission, *Nuclear Reactors*, **2**, Nuclear Reactor Technology, IL, 1957, p. 584.
3. Abstracts of Reports, All-Union Conference on the Physical Chemistry of Molten Salts and Slags, Sverdlovsk, 1960, p. 12.
4. G. Creten, Gordo, C. R., **246**, No. 15, 2266 (1958).
5. E. R. Schulze, *Zs. Kristallogr.*, **84**, 477 (1934).
6. R. A. Sense, M. J. Snyder, R. B. Tilley, *J. Phys. Chem.*, **58**, 995 (1954).
7. H. M. Haendler, C. M. Wheder, D. M. Robinson, *J. Am. Chem. Soc.*, **74**, 2352 (1952).
8. H. Lipson, A. Wilson, *J. Sci. Instrum.*, **18**, 144 (1941).
9. G. A. Yagodin, V. I. Tarasov, *ZhNKh*, **5**, issue 9, 1987 (1960).

*Note: Figure translations are in progress. See original paper for figures.*

*Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.*