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Abstract

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ON THE SOLUBILITY OF POTASSIUM OZONIDE IN LIQUEFIED AMMONIA

SYSTEM NH_3–KO_3

(Presented by Academician I. I. Chernyaev, 12 XI 1960)

It is known from the literature that KO_3, one of the representatives of the higher oxygen compounds–ozonides–is fairly readily soluble in liquefied ammonia. This property was used to isolate it from the products of ozonation of KOH ([1,2,4]). However, the absence in the literature of quantitative data on the polythermal solubility of potassium ozonide in liquefied ammonia makes it impossible to obtain KO_3 in its purest form and to isolate it as single crystals. In this connection, the literature contains no indications of a purity of KO_3 higher than 93.3% ([1]), and experimental data on the actual structure of KO_3 are entirely lacking. Authors have had to confine themselves to comparison with the similar structure of potassium azide–KN_3 ([3]).

Taking all these circumstances into account, we undertook a study of the phase diagram of the system NH_3–KO_3. In the region of KO_3 crystallization (see Fig. 1), the data were obtained on the basis of the isothermal solubility of potassium ozonide in liquid ammonia at temperatures of −35, −45, −55, −65, and −75°C. In the region of NH_3 crystallization, the investigation was carried out by the well-known visual-polythermal method.

The data, corresponding to the average results of three to four measurements in the temperature interval from −33 to −80°, i.e., in the region of existence of liquid ammonia in this system at ordinary pressure, are summarized in Table 1 and in the diagram NH_3–KO_3 (Fig. 1).

Table 1

Solubility data for potassium ozonide in liquid ammonia

Temp., °C	$\frac{KO_3\ (g)}{100\ g\ NH_3}$	Temp., °C	$\frac{KO_3\ (g)}{100\ g\ NH_3}$
−77.7	0	−75	5.91
−78.1	1.21	−65	7.85
−78.6	2.75	−55	10.05
−79.3	3.93	−45	12.31

Fig. 1

Figure 1: Fig. 1

Temp., °C	$\frac{KO_3\ (g)}{100\ g\ NH_3}$	Temp., °C	$\frac{KO_3\ (g)}{100\ g\ NH_3}$
−80.0*	5.1	−35	14.82

* Composition established graphically.

The diagram obtained by us belongs to the simplest type of eutectic diagrams, with a eutectic composition of about 5.1 g KO_3/100 g NH_3 at a temperature of −80°.

An increase in temperature leads to an increase in the solubility of potassium ozonide in liquefied ammonia with $K = 0.22$ g KO_3 per 1° and near the tempera-

the boiling temperature of the latter reaches its limiting value. According to the data obtained, at −35° the solubility was found to be about 15 g KO_3/100 g NH_3. The lowering of the freezing (melting) temperature of ammonia in this system correspondingly varies from −77.7 to −80°.

The availability of the data obtained for the NH_3–KO_3 system makes it possible, on the one hand, to obtain KO_3 in its purest form by the method of polythermal crystallization (region ED), and, on the other hand, to concentrate dilute ozonide solutions obtained after extraction

Fig. 1

of it from ozonized alkali by the freezing-out method (region AE). The use of polythermal crystallization enabled us comparatively easily to obtain individual samples of potassium ozonide with a KO_3 content of 98.1% by weight.

In studying the system, ammonia of high purity was used, prepared by triple distillation of liquid ammonia and drying with metallic sodium. Potassium ozonide was freed by preliminary recrystallization from the ordinarily present $KOH \cdot H_2O$ (1), and thus its influence in the system was reduced to a minimum. The data obtained, in addition to being of known scientific interest, may have substantial importance for the technology of obtaining potassium ozonide.

The experimental part will be set forth in greater detail in a special article.

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REFERENCES

1. I. A. Kazarnovskii, G. P. Nikol' skii, T. A. Abletsova, DAN, **64**, 69 (1949).

2. T. R. Whaley, S. Kleinberg, *J. Am. Chem. Soc.*, **73**, 79, 82 (1951).

3. G. S. Zhdanov, Z. V. Zvonkova, ZhFKh, **25**, issue 1, 100 (1951).

4. S. Z. Makarov, E. I. Sokovnin, DAN, **135**, No. 3, 606 (1960).

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