



Soviet-era science, translated into English

CHEMISTRY

K. N. SEMENENKO, T. N. NAUMOVA, L. N. GOROKHOV, G.
A. SEMENOVA,

1964

SovietRxiv

View the original and related papers at <https://sovietrxiv.org/items/ru-196401.17370>

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

Fig. 1. Phase diagram of $\text{FeCl}_3\text{--AlCl}_3$ according to Morozov' s data

Figure 1: Fig. 1. Phase diagram of $\text{FeCl}_3\text{--AlCl}_3$ according to Morozov' s data

Fig. 2. Phase diagram of the $\text{FeCl}_3\text{--AlCl}_3$ system according to our data

Figure 2: Fig. 2. Phase diagram of the $\text{FeCl}_3\text{--AlCl}_3$ system according to our data

Abstract

Full Text

CHEMISTRY

K. N. SEMENENKO, T. N. NAUMOVA, L. N. GOROKHOV, G. A. SEMENOVA,

Corresponding Member of the Academy of Sciences of the USSR A. V. NOVOSELOVA

INTERACTION OF Al AND Fe CHLORIDES

The interaction of Al and Fe chlorides was investigated by Morozov and co-workers by the method of polythermal analysis (^{1,2}). They showed that in the system $\text{FeCl}_3\text{--AlCl}_3$ a continuous series of solid solutions is formed. The form of the diagram is shown in Fig. 1. For our investigation of this system we used

Fig. 1. Phase diagram of $\text{FeCl}_3\text{--AlCl}_3$ according to Morozov' s data

Fig. 2. Phase diagram of the $\text{FeCl}_3\text{--AlCl}_3$ system according to our data

methods of thermographic, X-ray, and mass-spectrometric analyses, which made it possible to determine the nature of the interaction of the chlorides in different states of aggregation, as well as the nature of the phases formed in the process. Thermal analysis was carried out on a PK-61 pyrometer. Heating curves of previously melted and annealed alloys and cooling curves of molten mixtures were recorded. Samples for thermal and X-ray phase analyses were prepared by melting in vacuum weighed portions of ferric chloride (99.99%) and aluminum chloride (99.99%). The alloys were analyzed by complexometric determination of Fe and Al (³). The phase diagram of the $\text{AlCl}_3\text{--FeCl}_3$ system obtained by us is shown in Fig. 2. The positions of the liquidus curves in Figs. 1 and 2 coincide. In contrast to the literature data, we have established the existence in the system of two phases of variable composition, crystallizing on the basis of aluminum chloride (phase A) and ferric chloride (phase B). The limits of existence of phases A and B were established by X-ray phase analysis. The specimens were recorded with Co radiation in RKD cameras. The formation of solid solutions in the interaction of aluminum and iron chlorides appears quite natural. The crystal lattices of AlCl_3 and FeCl_3 are built of giant molecular

Fig. 3. Scheme of the molecule Me_2X_6

Figure 3: Fig. 3. Scheme of the molecule Me_2X_6

layers bound to one another by weak van der Waals forces. In each layer, the Al or Fe atoms occupy part of the octahedral voids of the closest packing of ... chlorine atoms. Isomorphous substitution of aluminum by iron and of iron by aluminum is possible owing to the closeness of their ionic radii: $R_{\text{Al}^{3+}} = 0.57 \text{ \AA}$,



$R_{\text{Fe}^{3+}} = 0.67 \text{ \AA}$ and the same type of coordination. One may expect the formation of a broader region of solid solution based on ferric chloride ($R_{\text{Fe}^{3+}} > R_{\text{Al}^{3+}}$), which was also established in the experimental study. Upon evaporation of pure Al and Fe chlorides, the type of coordination of Cl atoms around Me atoms changes. In the vapor, dimeric molecules Me_2Cl_6 are stable (4); their scheme is shown in Fig. 3. It was of considerable interest to investigate the possibility of isomorphous substitution of aluminum by iron not only in crystalline structures with octahedral coordination of halide atoms, but also in dimeric isolated molecules. Mass-spectrometric analysis, carried out on an MS-3 mass spectrograph in the mass-number interval 80-360, showed the presence in the vapor, above melts containing 30 and 50 mol. % FeCl_3 , of FeAlCl_6 molecules, forming the ions FeAlCl_4^{2+} , FeAlCl_5^+ . The FeAlCl_6 molecule is evidently a structural analogue of the dimeric molecules Al_2Cl_6 and Fe_2Cl_6 . It is interesting that, in studying the interaction of aluminum and iron chlorides in solution in POCl_3 (5), it was established that ferric chloride is a stronger acceptor of chloride ions than aluminum chloride. It may therefore be assumed that the $\text{Fe}-\text{Cl}^{\text{V}}$ bonds in the FeAlCl_6 molecule are shorter, and the $\text{Al}-\text{Cl}$ bonds (Fig. 3) longer, than in the pure aluminum and iron chlorides.

Fig. 3. Scheme of the molecule Me_2X_6

Moscow State University
named after M. V. Lomonosov

Received
21 IX 1963

REFERENCES

1. G. G. Urazov, I. S. Morozov, *Tr. Gos. inst. prikl. khim.*, issue 20, 1 (1934).
2. I. S. Morozov, *ZhNKh*, 1, issue 12, 2792 (1956).

3. *Complexometry*, Collection of articles and translations, 1958.
4. P. A. Akishin, N. G. Rambidi, E. Z. Zasorin, *Crystallography*, 4, issue 2, 186 (1959).
5. M. Baaz, V. Gutman, L. Hülner, *J. Inorg. and Nucl. Chem.*, 18, 276 (1961).

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

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