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Abstract

Full Text

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K. N. Semenenko, T. N. Naumova, L. N. Gorokhov,

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

On the Interaction of Aluminum and Beryllium Chlorides

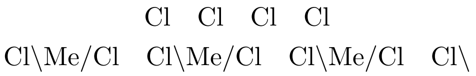
The interaction of beryllium and aluminum chlorides is of interest from the theoretical standpoint, since it is an example of a reaction between two compounds very similar in the character of their bonding and in the type of their crystal lattice.

The interaction of beryllium and aluminum chlorides in different states of aggregation was investigated by methods of thermographic and X-ray analysis; electrical conductivity was measured, and the composition of the vapor over the melts was studied by mass-spectrometric and chemical methods. The phase diagram of the system $AlCl_3$—$BeCl_2$, constructed from the results of X-ray phase and thermal analysis, is presented in Fig. 1.

The melts $BeCl_2$—$AlCl_3$ showed a tendency to solidify with supercooling and with formation of glasses; to reduce glass formation and attain a more equilibrium state, the melts were annealed at 70° for 150–200 hours. The eutectic in the system $BeCl_2$—$AlCl_3$ lies at a temperature of 90–100° and a composition of 52 mole % $BeCl_2$. In regions A and B, two solid solutions crystallize, structurally similar to pure $AlCl_3$ (α-phase) and $BeCl_2$ (the limits of existence of the phases were established by X-ray methods).

In the formation of the α-phase–the solid solution of $BeCl_2$ in the $AlCl_3$ lattice –the tendency, characteristic of aluminum, toward octahedral coordination of chlorine atoms is manifested. The crystal lattice of the α-phase may be represented as the lattice of pure aluminum chloride, with the layers arranged according to a definite law and with Al atoms placed in octahedral voids and Be atoms in tetrahedral voids; the order of arrangement of the layers and the distances between them, in comparison with pure $AlCl_3$, practically do not change.

Fig. 1. Phase diagram of the system $BeCl_2$—$AlCl_3$



$$\begin{array}{c} \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \\ \text{Cl}\backslash\text{Me}/\text{Cl} \quad \text{Cl}\backslash\text{Me}/\text{Cl} \quad \text{Cl}\backslash\text{Me}/\text{Cl} \quad \text{Cl}\backslash \end{array}$$

To explain the nature of the transformation at 140°, accompanied by a large thermal effect,* a study was undertaken of the melts and the vapor in the $BeCl_2$—$AlCl_3$ system.

The melts investigated have the same nature as a melt of pure aluminum chloride, containing dimeric Al_2Cl_6 molecules linked to one another by weak van der Waals forces ([1]).

* The effect at 140°, which is associated with a transformation in the melt, is not plotted on the diagram.

The electrical conductivity of the melts is practically no different from the electrical conductivity of pure aluminum chloride ($\sim 10^{-5}\ \Omega^{-1} \cdot \text{cm}^{-1}$), and remains low in absolute magnitude, which is characteristic of molecular melts built up from discrete molecules.

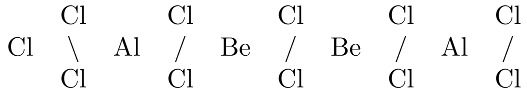
Interesting results were obtained in studying the vapor pressure over the melts by a static method with chemical analysis of the distillate. It turned out that in melts containing 10-50 mole % $BeCl_2$, the activity of beryllium chloride in the vapors $\alpha - P\text{BeCl}_2$ (over the melt)$/P\text{BeCl}_2$ (over the pure chloride) at temperatures of 200-250° is much greater than unity ($\alpha = 16$-18), which indicates the possibility of the existence in the vapors of a compound containing beryllium chloride. The heat of vaporization of aluminum chloride from melts of the above compositions of $BeCl_2 - AlCl_3$, determined from data on the temperature dependence $\lg p = f(1/T)$, is about 10 kcal/mole and is almost equal to the heat of vaporization of pure aluminum chloride from a melt of aluminum chloride—11 kcal/mole ([2]). The heat of vaporization of the compound containing beryllium chloride has a similar value—10 kcal/mole—and is much less than the heat of vaporization of pure $BeCl_2$ from its melt—26.2 kcal/mole ([2]).*

In aluminum chloride the transition to dimeric molecules Al_2Cl_6 with tetrahedral coordination of the Cl atoms occurs on melting or evaporation ([1], [3]). In a melt containing beryllium chloride, the transition temperature is lowered—aluminum chloride, which at 140° is present in the melt in the form of Al_2Cl_6 molecules, reacts with beryllium chloride to form the bridged molecule $AlBeCl_5$, whose properties practically do not differ from those of the bridged molecule Al_2Cl_6.

Mass-spectrometric studies of the vapor** over a melt of composition 35 mole % $BeCl_2$ showed that the compound actually exists. In the mass spectrum of the vapors the ions $BeAlCl_4^+$, $BeAlCl_5^+$ were detected, which corresponds to the formula $BeCl_2 \cdot AlCl_3$

$$\text{Cl—Be}\ \begin{matrix}\text{Cl}\\ \text{Cl}\end{matrix}\text{Al}\ \begin{matrix}\text{Cl}\\ \text{Cl}\end{matrix}$$

It is not excluded that these ions arise by dissociative ionization of molecules of more complex composition, for example,



$$\begin{array}{cccccccccc} & \mathrm{Cl} & & \mathrm{Cl} & & \mathrm{Cl} & & \mathrm{Cl} & & \mathrm{Cl} \\ \mathrm{Cl} & \backslash & \mathrm{Al} & / & \mathrm{Be} & / & \mathrm{Be} & / & \mathrm{Al} & / \\ & \mathrm{Cl} & & \mathrm{Cl} & & \mathrm{Cl} & & \mathrm{Cl} & & \mathrm{Cl} \end{array}$$

in which the coordination saturation of Be is achieved, or of composition $BeAl_2Cl_8$.

Complex formation in the $BeCl_2 - AlCl_3$ system is of special interest, since in this case substances very close in bond type participate in the formation of the compound. The complex-forming ability of beryllium and aluminum atoms is approximately the same, so that in the complex it is impossible to single out the complex-former—both atoms participate in its formation to the same extent.

Moscow State University
named after M. V. Lomonosov

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3. E. V. Pershina, Sh. Raskin, *Optics and Spectroscopy*, **13**, 488 (1962).

* The heat of vaporization of pure beryllium chloride characterizes not only the weakening of van der Waals forces between individual molecules, but also the rupture of Be—Cl bonds in the polymeric chains $(BeCl_2)_n$, leading to the formation in the vapor of monomeric molecules Cl—Be—Cl.

** The mass-spectrometric studies were carried out on an MS-3 instrument in the mass-number range 50–300 at a vapor pressure of 0.1 mm Hg. The vapor pressure in the effusion chamber was 10^{-1}-10^{-2} mm Hg.

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

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