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Abstract

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BEHAVIOR OF ALKALI-METAL IMPURITIES DURING THE CRYSTALLIZATION OF CESIUM SALTS FROM THE MELT

(Presented by Academician V. I. Spitsyn on 29 March 1965)

Recently there has been growing interest in salts of a high degree of purity and, in particular, in cesium salts.

For obtaining salts of a high degree of purity, methods of crystallization from the melt are very promising: bulk, directional, and zone recrystallization. Removal of impurities in these processes in salts of one and the same element, under identical crystallization conditions, proceeds with different efficiency. Therefore, the study of the behavior of impurities in different salt forms of one element is of theoretical and practical interest, since it makes it possible to judge the influence of the individual properties of a given salt form on the degree of isomorphism, and also to choose the substance most suitable for purification.

The most difficult impurity to separate in cesium salts is rubidium and, to a lesser extent, potassium. In the present work we have studied the behavior of these impurities and of sodium during crystallization from the melt of the salts CsCl, CsJ, $CsClO_3$, $CsNO_3$, CsCNS, and $Cs_2Cr_2O_7$. In the work, the indicated salts of "chemically pure" grade were used.

Fig. 1. Distribution curves of impurities along an ingot in cesium salts after directional crystallization

The behavior of an impurity in crystallization processes is characterized by the distribution coefficient. To determine the numerical value of the distribution coefficient, it is convenient to use the method of directional crystallization. In the present work the directional-crystallization procedure described earlier (^{1}) was used. According to this procedure, an ampoule containing the substance

Figure 2

Figure 2: Figure 2

(length 150 mm, diameter 10 mm), placed horizontally, is pulled from the heater at a specified rate. To stir the melt, the ampoule is rotated about its axis at a rate of 800 rpm. After the experiment, the ingot is cut into sections and analyzed for impurity content. The analysis was carried out by flame photometry with an accuracy of ±10 relative percent.

The distribution curves of alkali-metal impurities along the ingot in cesium salts, obtained at an ampoule withdrawal rate of 1.6 cm/hour, are shown in Fig. 1, where y denotes the relative concentration of the impurity in the ingot, and p the relative length of the ingot. The anion that is common to the mixture of cesium salts and the impurity alkali metal is denoted by X. In addition to the curves shown in Fig. 1, there were also obtained ⋯

the same distribution curves of alkali-metal impurities in CsCNS at ampoule drawing rates of 0.4 and 6.4 cm/h.

To determine the distribution coefficient from the experimental data we used the equation

$$\lambda(p) = \frac{y(p)(1-p)}{1-\int_0^p y(p)\,dp}, \tag{1}$$

which is given in (2). This equation makes it possible to calculate the value of λ from the distribution curve at different impurity concentrations in the liquid phase, which increase as the amount of solid phase increases. The results of calculations by equation (1) show that the distribution coefficient of rubidium and potassium in the cesium salts studied remains practically constant when the concentration in the liquid phase is changed by a factor of 2-3. The integration in the calculations was carried out graphically. The average values of the distribution coefficients for alkali-metal impurities are given in Table 1. The initial impurity concentration is given in this table in weight percent, calculated as metal. Purification of cesium salts from sodium, with the exception of cesium iodide and cesium dichromate, proceeds so effectively that it does not appear possible to determine the distribution coefficients of this impurity.

Fig. 2. Dependence of the impurity distribution coefficients on the crystallization rate in CsCNS: 1 –RbCNS, 2 –KCNS

Figure 2 presents the dependence of the distribution coefficient for the systems CsCNS–RbCNS and CsCNS–KCNS on the crystallization rate. It is seen from the figure that, with increasing crystallization rate, the distribution coefficient of rubidium and potassium impurities under the indicated crystallization conditions (constant rate of stirring of the melt) changes only slightly.

Under equilibrium conditions the distribution coefficient is determined by the course of the liquidus and solidus curves on the phase diagram. Phase diagrams of systems formed by potassium and rubidium salts with cesium salts are known for chlorides (3) and for nitrates (4). Phase diagrams

Table 1

Values of the distribution coefficients of rubidium and potassium salts in cesium salts, obtained from directional crystallization data

Salt	Melting temp., °C	Initial concentration of rubidium	Initial concentration of potassium	Crystallization rate, cm/h	λ_{Rb}	λ_K	λ_{Na}
CsCl	638	0.120	0.005	1.6	0.78	0.61	–
CsI	621	0.044	0.004	1.6	0.62	0.32	0.20
$CsClO_3$	392	0.135	0.008	1.6	0.64	0.25	–
$CsNO_3$	414	0.200	0.075	1.6	0.54	0.22	–
CsCNS	195	0.320	0.040	0.4	0.76	0.50	–
CsCNS	195	0.320	0.040	1.6	0.78	0.52	–
CsCNS	195	0.320	0.040	6.4	0.84	0.64	–
$Cs_2Cr_2O_7$	398	0.140	0.022	1.6	0.88	0.63	0.62

for the systems CsCl–RbCl and CsCl–KCl are shown in Fig. 3. In these systems there is a continuous series of solid solutions with a minimum. The equilibrium distribution coefficients for RbCl and KCl, determined from the phase diagrams by means of tangents drawn to the initial portions of the solidus and liquidus curves, are respectively 0.70 and 0.60. In the system $CsNO_3$–KNO_3 there also exists a continuous series

solid solutions, but, since only the liquidus line is known, it is not possible to determine the equilibrium distribution coefficient from the melting diagram. In the system $CsNO_3$–KNO_3 there are limited solid solutions; the equilibrium distribution coefficient for KNO_3, determined from the melting diagram in an analogous way, is equal to 0.45. The values of the distribution coefficients obtained in the systems CsCl–RbCl and CsCl–KCl by the method of directional crystallization, as is evident from the data of Table 1, are close to the equilibrium values. However, in the system $CsNO_3$–KNO_3 the experimental value of the distribution coefficient is considerably smaller than the equilibrium one, which is evidently due to the mismatch between the solidus line on the melting diagram and the equilibrium line. Since the melting diagrams of the other systems are unknown, it is impossible to compare the experimental values with those calculated from melting diagrams, but it may be assumed that they are also close to the equilibrium ones.

Fig. 3. Melting diagrams of the systems CsCl—RbCl and CsCl—KCl

Figure 3: Fig. 3. Melting diagrams of the systems CsCl—RbCl and CsCl—KCl

Fig. 4. Dependence of the distribution coefficients of rubidium and potassium salts in cesium salts on the radius of the common anion: 1 —rubidium salts, 2 —potassium salts

Figure 4: Fig. 4. Dependence of the distribution coefficients of rubidium and potassium salts in cesium salts on the radius of the common anion: 1 —rubidium salts, 2 —potassium salts

Fig. 3. Melting diagrams of the systems CsCl—RbCl and CsCl—KCl

The data obtained by us make it possible to trace the change in the distribution coefficients, which characterize the degree of isomorphism of a given impurity with the main substance, for impurities of rubidium and potassium as a function of the size of the common anion. This dependence is presented in Fig. 4. The radii of simple ions were taken by us from the handbook (^{5}) according to Belov and Bokii. The radii of the ClO_3^- and NO_3^- ions are given in work (^{6}). The radii of the CNS^- and $Cr_2O_7^{2-}$ ions were calculated by us. In doing so, the radius of a complex ion was taken to be equal to the radius of the smallest sphere into which the given complex ion can be inscribed.

Fig. 4. Dependence of the distribution coefficients of rubidium and potassium salts in cesium salts on the radius of the common anion: 1 —rubidium salts, 2 —potassium salts

It is evident from Fig. 4 that, with increasing radius of the common anion, the distribution coefficient decreases, passes through a minimum, and then increases again. The minimum corresponds to mixtures of nitrate salts. Let us note that from the thermodynamic data presented in work (^{7}) it follows that melts of nitrate salts are the most ideal of all salt melts. Consequently, the smallest distribution coefficient corresponds to the most ideal mixtures.

It follows from the data presented in the present work that purification of cesium nitrate from rubidium and potassium nitrates by crystallization methods from melts will proceed more effectively than purification of other cesium salts. Studies carried out by us on the distribution of various nonisomorphic impurities during crystallization from a melt of potassium nitrate (^{8}) and sodium nitrate (^{9}) showed that purification of the indicated salts from these impurities proceeds quite successfully. Purification of cesium nitrate by crystallization methods from a melt from alkaline-earth and heavy metals by analo-

with purification of potassium nitrate and sodium nitrate, will also, apparently, proceed effectively.

Thus, among the cesium salts, the most suitable substance for deep purification from impurities by the method of zone recrystallization is cesium nitrate, which can serve as the starting form for obtaining other cesium salts of high purity.

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