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Abstract

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THE INFLUENCE OF RADIOACTIVE RADIATION OF THE SOLID PHASE ON THE KINETICS OF THE RECRYSTALLIZATION PROCESS OF POTASSIUM SULFATE

In previous studies (1-3) it was shown that radioactive irradiation of preparations causes the formation of smaller particles of the solid phase when it is separated from solutions or gaseous media. The surface of radioactive crystals has a larger number of irregularities in comparison with nonradioactive samples, and in some cases an intensification of dendrite formation is observed. Obviously, the indicated phenomena are connected with the action of charged particles emitted by the radioactive substance on the solution or gaseous phase and with the consequent increase in the number of nuclei that arise—centers of crystallization.

In the present communication the first results are set forth of a study of the influence of the radioactivity of the solid phase on the kinetics of its recrystallization from its saturated solution and on the magnitude of the distribution coefficient of an accompanying microimpurity. As is known (4), the rate of recrystallization of salts depends on a number of conditions (the intensity of stirring of the solution, the size of the crystals, the state of their surface, the temperature, etc.), which in our work were maintained strictly constant, with the exception of the specific radioactivity of the preparations. For the investigation the system chosen was K_2SO_4 (macrocomponent)–$^*Ce_2(SO_4)_3$ (microcomponent)–HNO_3, which, with respect to the behavior of the microcomponent, has been fairly well studied by V. I. Grebenshchikova and V. N. Bobrova (5, 6). These authors noted that in 0.5 N HNO_3 recrystallization of potassium sulfate is practically completely absent, as a result of which distribution of the microimpurity between the liquid and solid phases according to the logarithmic law takes place here ($\lambda = 15.0 \pm 2$; $D \neq$ const). But if the precipitate of the macrocomponent was separated from 1.5 N HNO_3, with rapid stirring, a homogeneous distribution of Ce^{3+} was observed ($D = 15.0 \pm 1.5$; $\lambda \neq$ const). This character of the coprecipitation of Ce^{3+} with K_2SO_4 is explained by the increase in the solubility of K_2SO_4 in 1.5 N HNO_3 as compared with 0.5 N HNO_3, respectively 0.301 g/ml and 0.163 g/ml.

We used the radioisotopes S^{35} ($T_{1/2} = 87.1$ days, $E(\beta)_{\max} = 0.167$ MeV) and Ce^{141} ($T_{1/2} = 33.1$ days, $E(\beta)_{\max} = 0.57$ MeV, $E(\gamma)_{\max} = 0.145$ MeV).

The potassium sulfate preparations were obtained in the following way. Salts of "chemically pure" grade were used, additionally recrystallized once. A solution of $Ce^{141}(NO_3)_3$ without carrier was purified by the chromatographic method; sodium sulfate, radioactive in sulfur, was freed from possible impurities of Ca^{2+} and Sr^{2+} by twofold recrystallization; its solution contained 12.3 mg/liter of stable Na_2SO_4 salt.

To equal volumes of solutions of K_2SO_4, saturated at ordinary temperature, containing identical tracer amounts of $Ce^{141}(NO_3)_3$ and different concentrations of $Na_2^*SO_4$, 1 g of dry K_2SO_4 salt was added. The concentration of stable sodium sulfate in all cases was maintained constant (0.1 g/ml), which was achieved by introducing the corresponding amounts—

part of the Na_2SO_4. The mixture was then heated to 80°, as a result of which the K_2SO_4 precipitates dissolved. The hot solutions were then slowly cooled and stirred at a temperature of $22 \pm 1°$ for 3 h. As a result of this process, potassium sulfate crystals precipitated, entraining equal amounts of Ce^{141} (~ 0.08 m Cu/g), but having different specific radioactivity with respect to S^{35}. The final pH value above the precipitates was 4.8.

Since the K_2SO_4 precipitates were formed under identical conditions and at equal supersaturations, their surface per unit weight was the same in all cases (6). A characterization of the precipitates obtained is given in Table 1. It may be considered that, upon separation of potassium sulfate from supersaturated solutions under the conditions described, a logarithmic distribution of Ce^{3+} between the liquid and solid phases takes place.

Table 1

K_2SO_4 preparations used

No.	Activity with respect to S^{35}, mCu/g	D_{Ce}	λ_{Ce}
1	0	125.6	12.5
2	0.5	150.3	12.6
3	50	34.5	11.3
			Mean 12.0 ± 0.7

$K_2^*SO_4$ crystals were separated from the liquid phase, washed several times with a saturated inactive solution of the same salt, and dried at 120°. The sieved

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

precipitate (fraction 0.3-0.5 mm) was then placed in portions of 1 g into flasks containing 25 ml of a saturated K_2SO_4 solution in 0.5 N or

Fig. 1. Kinetics of recrystallization of $K_2^*SO_4$, measured by S^{35}. System $K_2^*SO_4$ $-Ce_2^*(SO_4)_3-0.5$ N HNO_3: 1 –0.5 m Cu/g, 2 –50 m Cu/g; system $K_2^*SO_4-$ $Ce_2^*(SO_4)_3-1.5$ N HNO_3, 3 –0.5 m Cu/g, 4 –50 m Cu/g

Fig. 2. Change in the distribution coefficient D in the system K_2SO_4- $Ce_2^*(SO_4)_3-0.5$ N HNO_3: 1 –inactive K_2SO_4; preparations containing S^{35}: 2 –0.5 m Cu/g, 3 –50 m Cu/g

1.5 N HNO_3. The mixture was subjected to vigorous stirring at a temperature of $20 \pm 1^\circ$. At definite time intervals, samples were taken from the liquid phase for radiometric determination of Ce^{141} and S^{35}.

The limiting stage of the process of distribution of S^{35} and Ce^{141} between the solid and liquid phases is recrystallization of K_2SO_4. Therefore the increase in the activity of the solution in our experiments serves as a criterion by which the change in the precipitate can be judged.

Figure 1 shows the results of experiments obtained from measurements of S^{35} activity. The degree of recrystallization in percent (N), plotted on the ordinate axis, was calculated from the formulas

$$N = \frac{A_t}{A_\infty} \cdot 100 \quad \text{and} \quad A_\infty = \frac{A_0 \cdot B \cdot C}{(B + C) \cdot V},$$

where A_0 is the initial activity of the precipitate per unit weight, A_t is the activity of the solution at time t, A_∞ is the equilibrium activity of the solution, B is the weight of the precipitate (g), C is the weight of K_2SO_4 in the solution (g), and V is the volume of the solution (ml).

It may be concluded, first of all, that the potassium sulfate precipitate undergoes recrystallization not only in $1.5N$ HNO_3, but also in $0.5N$ HNO_3, although in works ([5],[6]) this possibility was denied. Apparently, the experimental conditions chosen in the cited studies, and in particular the time over which equilibrium was studied, were insufficient for detecting the phenomenon of recrystallization. In addition, it follows from our experiments that highly active precipitates

Fig. 3. Change in the distribution coefficient D in the system K_2SO_4- ${}^*Ce_2(SO_4)_3-1.5N$ HNO_3: 1 –inactive K_2SO_4; 2 –preparations containing S^{35}:

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

a –0.5 mCu/g, *b* –50 mCu/g

Fig. 4. Distribution of Ce^{141} between the solid and liquid phases. System K_2SO_4–$^*Ce_2(SO_4)_3$–0.5*N* HNO_3: 1 –inactive K_2SO_4, 2 –$^*K_2SO_4$, 0.5 mCu/g, 3 –$^*K_2SO_4$, 50 mCu/g. System K_2SO_4–$^*Ce_2(SO_4)_3$–1.5*N* HNO_3: 4 –inactive K_2SO_4, 5 –$^*K_2SO_4$, 0.5 mCu/g, 6 –$^*K_2SO_4$, 50 mCu/g

$^*K_2SO_4$ recrystallize in all cases faster than low-activity ones. Consequently, in the systems studied, a homogeneous distribution of *Ce should ultimately be observed. Indeed, in the course of the experiments we observed a monotonic decrease in λ, while the value of D tended with time toward a constant value (Figs. 2 and 3).

Thus, in 1.5*N* and 0.5*N* solutions of HNO_3, the coefficient D reaches constant values of 16.0 ± 2 and 22, respectively. True, in the case of 0.5*N* HNO_3 the process of distribution of *Ce between the liquid and solid phases cannot yet be considered complete. Therefore it is not excluded that, with further measurements, the value of D would also have decreased to 15-16, as was found in work ([5]). The results obtained once again confirm that, under truly equilibrium conditions, a homogeneous distribution of the microcomponent between the solid and liquid phases occurs, in accordance with V. G. Khlopin' s law.

The character of the change in the values of D (Figs. 2 and 3) also shows that radioactive precipitates recrystallize faster than inactive ones. However, one can imagine a course of the process in which D has not yet reached a constant value, while recrystallization, recorded by the isotope of the macrocomponent, has already occurred. For example, a single recrystallization is sufficient for a uniform distribution of the isotope of the macrocomponent between the phases, whereas for the microcomponent repeated repetition of the process is necessary. Therefore, it will be more correct to judge the change of the solid phase with time from the distribution of the isotopes of the precipitate itself.

Using the value $D = 15$, it is possible to calculate what amount of *Ce should be in solution under equilibrium distribution of the microcomponent, and then it is easy to show how the activity of *Ce in the liquid phase increases as recrystallization proceeds.

It follows from Fig. 4 that the rate of redistribution of *Ce between a K_2SO_4 precipitate with an activity of 50 mCi/g and its saturated solution in 0.5*N* HNO_3 is significantly higher than for inactive and weakly active precipitates. However, in 1.5*N* HNO_3 no such effect of radiation on the rate of redistribution of *Ce is observed. Evidently, in this case the process is of a more complex character, possibly because of the formation of Ce^{3+} complexes in nitric acid ([7]), which could not be taken into account in the calculations. The observed increase in the recrystallization rate of highly radioactive precipitates is apparently determined primarily by two factors: the inhomogeneity of the surface of radioactive precipitates and the action of radioactive radiation on the precipitate, the solution, and the phase boundary. The strongest influence should undoubtedly be attributed to the self-irradiation effect.

In our experiments, no clear difference was observed in the value of the coefficient D for the microcomponent *Ce as a function of the specific radioactivity of the solid phase—potassium sulfate—although this might have been expected because of the different solubility of radioactive and nonradioactive K_2SO_4 preparations.

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