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Abstract

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NEW DATA ON THE EFFECT OF THE RADIOACTIVITY OF THE SOLID PHASE ON HETEROGENEOUS PROCESSES OF ISOTOPIC EXCHANGE

In a previous communication (^{1}) the authors showed that the rate of isotopic exchange of sulfur at a temperature of 840° in the system $K_2\overset{*}{S}O_4—SO_3$ depends substantially on the specific radioactivity of the preparation of $K_2\overset{*}{S}O_4$ used. In the investigated range of activities from 0.02–0.03 to 16.2 mCi/g, the maximum degree of exchange was observed at a specific radioactivity of potassium sulfate equal to 2–2.3 mCi/g.

At present the investigation has been extended to K_2SO_4 preparations of still higher specific activity (up to $\sim$ 130 mCi/g). The new data, confirming the earlier results, make it possible to clarify somewhat the mechanism of the observed phenomenon. The apparatus and the experimental procedure were analogous to those described in (^{1}). Some of the samples were prepared by adding small amounts of Na_2SO_4 highly active in S^{35} to a solution of chemically pure K_2SO_4. It had been established earlier that an impurity of Na_2SO_4 does not affect the rate of isotopic exchange of sulfur in the system $K_2\overset{*}{S}O_4—SO_3$. Samples of $K_2\overset{*}{S}O_4$ with the highest specific radioactivity were prepared by neutralizing labeled $H_2\overset{*}{S}O_4$ with chemically pure KOH. The results obtained are given in Table 1 and in Fig. 1.

Table 1

Isotopic exchange in the system $K_2SO_4—SO_3$ at 840°

No. of K_2SO_4 preparation	Added Na_2SO_4 impurity in %	Observed specific activity, imp/min · g	Absolute activity, mCi/g	Number of experiments	Degree of exchange (average), %
1	0.04	$6.44 \cdot 10^5$	$1.7 \cdot 10^{-2}$	5	11.7
2	0.1	$9.37 \cdot 10^5$	$2.6 \cdot 10^{-2}$	6	11.5

Fig. 1. Dependence of the degree of isotopic exchange on the specific activity of K_2SO_4

Figure 1: Fig. 1. Dependence of the degree of isotopic exchange on the specific activity of K_2SO_4

No. of K_2SO_4 preparation	Added Na_2SO_4 impurity in %	Observed specific activity, imp/min • g	Absolute activity, mCi/g	Number of experiments	Degree of exchange (average), %
3	–	$5.50 \cdot 10^6$	$6.1 \cdot 10^{-2}$	5	14.2
4	0.1	$12.1 \cdot 10^6$	$3.4 \cdot 10^{-1}$	7	24.5
5	0.1	$12.5 \cdot 10^6$	$3.5 \cdot 10^{-1}$	4	26.7
6	0.4	$72.6 \cdot 10^6$	2.0	5	65.5
7	0.4	$80.4 \cdot 10^6$	2.3	5	66.9
8	0.5	$13.5 \cdot 10^7$	3.0	4	60.9
9	2.6	$28.2 \cdot 10^7$	7.8	5	33.3
10	3.0	$58.5 \cdot 10^7$	16.2	4	36.6
11	2.0	$96.4 \cdot 10^7$	27.1	4	31.4
12	1.8	$12.3 \cdot 10^8$	34.6	7	25.2
13	–	$55.1 \cdot 10^8$	61.1	4	31.5
14	–	$74.7 \cdot 10^8$	74.9	5	43.2
15	–	$17.6 \cdot 10^8$	98.8	4	52.8
16	–	$21.2 \cdot 10^9$	131.3	8	85.5

The rate of isotopic exchange at a specific radioactivity of $K_2\overset{*}{S}O_4$ of the order of 0.02–0.03 mCi/g is practically constant. It begins to increase when the activity of the preparation exceeds the level of 0.05 mCi/g.

and reaches a maximum at a specific activity of K_2SO_4 on the order of 2–2.5 mCu/g (degree of exchange about 66% in 10 min). A further increase in the specific activity of potassium sulfate from 3 mCu/g to 35 mCu/g leads to a decrease in the degree of exchange to 25%. At a specific activity of K_2SO_4 equal to 61 mCu/g, the degree of exchange again begins to increase, and for a preparation with a specific activity of 131 mCu/g it amounts to 85% in 10 min.

Fig. 1. Dependence of the degree of isotopic exchange on the specific activity of K_2SO_4

It may be assumed that the increase in the degree of isotopic exchange for preparations with specific activity from hundredths of a unit to 2–3 mCu/g is associated with the appearance of positive charges on the surface of the solid phase due to the continuous emission of β-particles. Apparently, the isotopic exchange of sulfur proceeds through the interaction of SO_3 with SO_4^{2-} ions on the surface of potassium sulfate and the formation, as an intermediate compound, of $S_2O_7^{2-}$ ions. Conditions for their formation will be more favorable in the presence of an increased number of positively charged active centers. The decrease in the degree of isotopic exchange for preparations with specific activity from 3 to 35 mCu/g may depend on partial neutralization of the positive charges of the active centers by the abundantly emitted electrons. In any case, measurement of the activation energy (see below) confirms the assumption of different mechanisms of the isotopic-exchange reaction depending on the specific activity of K_2SO_4 preparations.

The sharp increase in the degree of exchange when the specific activity of K_2SO_4 is increased above 35 mCu/g probably has a mechanism already different from that of the first branch of the curve in Fig. 1. Here, one must assume, purely radiation phenomena begin to play the decisive role, consisting in enhanced activation of SO_4^{2-} ions and individual atoms of the crystal lattice, as well as SO_3 molecules, under the energetic action of the emitted β-particles. In the following communication (^{2}), where the effect of external electron irradiation on isotopic exchange in the K_2SO_4–SO_3 system is described, it will be shown that precisely in this region, at a dose of $3 \cdot 10^{16}$ eV, which corresponds to radioactiv—

Table 2

Rate constants of the isotopic-exchange reaction between Na_2SO_4 of different specific activity and gaseous SO_3

No. of $NaSO_4$ preparation	Abs. activity, mCu/g	Temp., °C	Degree of exchange, %	Rate constant, $k \cdot 10^2$	$\frac{1}{T} \cdot 10^4$	$\ln(k \cdot 10^2)$	$E = A \cdot R$, kcal/mol
1	$1.7 \cdot 10^{-2}$	700	14.7	1.590	10.27	0.4637	24 ± 2
1	$1.7 \cdot 10^{-2}$	750	24.9	2.864	9.77	1.051	24 ± 2
1	$1.7 \cdot 10^{-2}$	800	38.1	4.894	9.32	1.587	24 ± 2
1	$1.7 \cdot 10^{-2}$	840	49.2	6.772	8.98	1.914	24 ± 2
2	1.02	700	25.8	2.984	10.27	1.0824	23 ± 2
2	1.02	750	46.8	6.212	9.77	1.8251	23 ± 2
2	1.02	800	64.7	10.41	9.32	2.3421	23 ± 2
2	1.02	840	73.1	13.13	8.98	2.5754	23 ± 2
3	10.7	700	24.3	2.784	10.27	1.0300	19 ± 2
3	10.7	740	36.0	4.464	9.90	1.4960	19 ± 2
3	10.7	800	56.0	8.210	9.32	2.1050	19 ± 2
3	10.7	840	69.3	11.810	8.98	2.4469	19 ± 2

No. of $NaSO_4$ preparation	Abs. activity, mCu/g	Temp., °C	Degree of exchange, %	Rate constant, $k \cdot 10^2$	$\frac{1}{T} \cdot 10^4$	$\ln(k \cdot 10^2)$	$E = A \cdot R$, kcal/mol
4	24.5	700	20.4	2.282	10.27	0.8252	18 ± 1
4	24.5	740	26.9	3.134	9.90	1.1400	18 ± 1
4	24.5	790	34.7	4.263	9.41	1.451	18 ± 1
4	24.5	830	56.9	8.418	9.07	2.125	18 ± 1

potassium sulfate with a specific activity of 32 mCu/g, the action of accelerated electrons on the process under study begins to be observed.

Some factors affecting the rate of isotopic exchange in the K_2SO_4—SO_3 system were subjected to more detailed study. It might have been supposed that the presence in the K_2SO_4 preparation of chlorine ions, appearing in the process of decay of S^{35}, accelerates the exchange process in the $K_2S^*O_4$—SO_3 system. For checking this assumption, experiments were carried out with a potassium sulfate preparation whose specific activity was approximately 0.06 mCu/g and whose KCl content was 0.12%. The degree of isotopic exchange was 11.6% and thus proved to be practically the same as for a preparation without additives.

Fig. 2. Dependence of the rate constant of the isotopic-exchange reaction in the $Na_2S^*O_4$—SO_3 system on reciprocal temperature

Fig. 3. Dependence of $\ln \dfrac{100}{100 - W}$ on time in the isotopic-exchange reaction between $Na_2S^*O_4$ and SO_3

In studying the process of isotopic exchange in the $K_2S^*O_4$—SO_3 system we were interested in whether the value of the activation energy of the exchange reaction changes with an increase in the content of the radioactive isotope in the sulfate being studied. The use of K_2SO_4 in this case had to be abandoned, since the temperature at which the kinetics of the process could be studied exceeded 1000°, which could lead to thermal dissociation of the salt. The necessary measurements of the kinetics of isotopic exchange were made for the $Na_2S^*O_4$—SO_3 system with sodium sulfate preparations of different radioactivity. The results of the measurements are presented in Table 2 and in Fig. 2.

Fig. 4. Change in the rate of isotopic exchange in the $Na_2S^*O_4$—SO_3 system

The activation energy was determined from the Arrhenius formula $K = K_0 e^{-E/RT}$. The rate constant of the reaction was calculated from the formula $\ln \dfrac{100}{100 - W} = kt$, where W is the degree of exchange, t is the duration of the experiments, 10 min. The possibility of applying this equation is determined by the linear dependence of the left-hand side of the equality on time (Fig. 3). From the data presented it is seen that the mechanism of the isotopic-exchange reaction between $Na_2S^*O_4$ and SO_3 changes on going from preparations with specific activity of 0.02 and 1 mCu/g to 11 and 25 mCu/g.

The dependence of the rate of isotopic exchange in the $Na_2S^*O_4$—SO_3 system on the specific activity of Na_2SO_4 has the same character as in the $K_2S^*O_4$—SO_3 system. Sodium and potassium sulfates are similar in their nature. All this makes it possible to draw analogous conclusions for the mechanism of exchange in the $K_2S^*O_4$—SO_3 system.

The process of isotopic exchange of sulfur in the system we studied is clearly divided into two phases: during a short interval of time, on the order of 5 min.,

the exchange rate is very considerable—the exchange reaches 40%—and rapidly decreases. Here, evidently, exchange occurs in a thin surface layer of K_2SO_4. Then the exchange rate for each subsequent 5 min remains at an almost constant value of 10%, smaller than for the first 5 min (Fig. 4). In this case the rate of the process is evidently limited by diffusion of $SO_4{}^{2-}$ ions in the solid phase.

Isotopic exchange between radioactive sulfur anhydride and stable potassium sulfate was also studied (Table 3). It was found that after 5 min of passage of sulfur anhydride, a constant value of the radioactivity of potassium sulfate is reached. The appearance of a relatively high concentration of S^{35} atoms on the surface of the solid salt is undoubtedly the reason for the decrease in the exchange rate. Evidently, diffusion into the solid salt proceeds considerably more slowly than is observed for the escape of S^{35} atoms from the solid phase into the gaseous phase during exchange of labeled K_2SO_4 with inactive SO_3.

Table 3

Isotopic exchange in the system K_2SO_4–$\overset{*}{S}O_3$ at 840°.
Charge of K_2SO_4 0.28 g; initial activity of SO_3 6.2 mCi/g

Time of passage of $\overset{*}{S}O_3$, min	Amount of $\overset{*}{S}O_3$, g	Specific activity of K_2SO_4 after the experiment, mCi/g (average of 4 experiments)
5	0.2881	0.28
10	0.5762	0.20
15	0.8643	0.28
20	1.1524	0.27

As is known, SO_3 at temperatures above 400° begins to dissociate with formation of SO_2. Therefore, isotopic exchange was studied in the system $K_2\overset{*}{S}O_4$–SO_2 with a specific activity of K_2SO_4 equal to $5.9 \cdot 10^{-2}$ mCi/g, at different temperatures. Sulfurous gas, dried over $CaCl_2$ and conc. H_2SO_4, entered the reaction quartz tube at a rate of 13 l/hr and passed over a boat with labeled potassium sulfate. Then the remaining activity of $K_2\overset{*}{S}O_4$ was measured and the degree of isotopic exchange was calculated.

Table 4

Study of isotopic exchange of sulfur in the system $K_2\overset{*}{S}O_4$–SO_2 at different temperatures. Amount of SO_2 0.6 g

Temp., °C	Charge of K_2SO_4, g	Change in K_2SO_4 weight after experiment, %	Initial activity, imp/min	Activity of K_2SO_4 after experiment, imp/min	Activity of K_2SO_4 after experiment, % of initial	Degree of exchange, %
600	0.3732	–0.1	$1784\cdot10^3$	$1805\cdot10^3$	100.9	
600	0.3374	+0.1	$1614\cdot10^3$	$1665\cdot10^3$	103.0	
600	0.3479	–0.2	$1663\cdot10^3$	$1640\cdot10^3$	101.0	
600	0.3477	–0.1	$1663\cdot10^3$	$1648\cdot10^3$	99.1	
700	0.3295	–0.1	$1577\cdot10^3$	$1483\cdot10^3$	94.0	6.2
700	0.2900	–0.2	$1388\cdot10^3$	$1307\cdot10^3$	94.2	6.9
700	0.3074	–0.1	$1471\cdot10^3$	$1422\cdot10^3$	93.3	6.8
700	0.2732	–0.1	$1308\cdot10^3$	$1237\cdot10^3$	94.6	7.5
840	0.3147	–	$1582\cdot10^3$	$1393\cdot10^3$	88.0	14.4
840	0.3373	–0.1	$1696\cdot10^3$	$1527\cdot10^3$	90.0	13.1
840	0.3532	–0.1	$1776\cdot10^3$	$1570\cdot10^3$	88.4	14.2

It has been established that sulfur exchange occurs at 700° and above. The rates of isotopic exchange at 840° in the systems K_2SO_4–SO_3 and $K_2\overset{*}{S}O_4$–SO_2 practically do not differ from one another.

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2. Vikt. I. Spitsyn, I. E. Mikhailenko et al., DAN, **131**, No. 2 (1960).

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