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Abstract

Full Text

PHYSICAL CHEMISTRY

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EFFECT OF THE INTENSITY OF RADIOACTIVE RADIATION OF S^{35} ON THE RATE OF ISOTOPIC EXCHANGE OF SULFUR IN THE SYSTEM

K_2SO_4–SO_3

In studying the isotopic exchange of sulfur between solid sulfates of alkali elements and gaseous sulfuric anhydride under high-temperature conditions ([1]), the authors observed that the level of radioactivity of the preparations under investigation affects the rate of isotopic-exchange processes. This phenomenon was subjected to more detailed investigation.

Fig. 1. Diagram of the apparatus for studying isotopic exchange in the K_2SO_4 –SO_3 system.

The action of the beta radiation of S^{35} on the degree of isotopic exchange of sulfur between solid potassium sulfate labeled with S^{35} and gaseous sulfuric anhydride was studied. The investigation was carried out under identical conditions at a temperature of 840° with preparations of K_2SO_4 differing in the magnitude of their specific activity. A diagram of the apparatus used is shown in Fig. 1. The round-bottom flask (1), condenser (2), test tube (4) with a ground joint and gas-inlet tubes, and the wash bottles (7), (8), (9) were made of molybdenum glass; tube (6) and the boat in it were made of quartz glass. A 60% oleum of "chemically pure" grade was poured into the flask; distillation of SO_3 was carried out at a temperature of 60–70°. Through the condenser and the three-way stopcock (3), with the two-way stopcock (5) closed, sulfuric anhydride entered a graduated test tube (4) with a scale division of 0.05 ml. A measured amount of SO_3 was carried by a stream of dry air through stopcock (5) into the reaction space of the quartz tube (6).

Fig. 2. Dependence of the degree of isotopic exchange on the specific activity of K_2SO_4

Figure 2: Fig. 2. Dependence of the degree of isotopic exchange on the specific activity of K_2SO_4

After passing over the substance, the sulfuric anhydride was trapped in wash bottles with concentrated H_2SO_4 (7) and 0.1 N NaOH solution (8) and (9). A definite weighed portion of the radioactive potassium sulfate preparation was placed in the quartz boat. Before the beginning of each experiment and after it, dry air, entering through the side arm of the three-way stopcock (3), was passed through the entire apparatus. The temperature of the furnace (10) was measured with a platinum–platinum-rhodium thermocouple. During the experiments the temperature, equal to 840°, was maintained with an accuracy of $\pm 5°$. In each experiment the weighed portion of sulfate was 0.3–0.4 g; the amount of SO_{3} was 0.3 ml, or 0.6 g. The rate of the stream of dry air carrying along the sulfuric anhydride reached 37 l/h. The time of passage of SO_3 over the preparation under study was 10 min. The weighed portion of sulfate remained in the heated zone of the furnace for 20 min. The sulfur-labeled K_2SO_4 preparations were prepared by introducing into their solutions a small amount of

amount of active sodium sulfate. The solutions were then evaporated to dryness and the precipitate was calcined at 800°. The same specific surface of the K_2SO_4 samples was achieved by subjecting the carefully ground preparations to sieving into fractions. The particle size ranged from 0.17 to 0.10 mm.

After the experiment, the weighed portion of active sulfate was dissolved in a volumetric flask. A definite volume of the solution was evaporated on a sheet of filter paper placed in a round aluminum dish. The activity of the preparation was always measured under identical geometrical conditions with respect to an end-window counter. The solutions of highly active preparations obtained after the experiments were diluted in such a way that the pulse-counting rate for all preparations was of approximately the same order (1500–2000 pulses/min). With each K_2SO_4 preparation of different specific activity, 4–6 isotope-exchange experiments were carried out. Examples of the changes in the activity of potassium sulfate that occurred are given in Table 1, and the mean results of the isotope-exchange measurements—in Table 2 and in Fig. 2. The degree of exchange was calculated by the formula

Fig. 2. Dependence of the degree of isotopic exchange on the specific activity of K_2SO_4

$$W = (A_0 - A_1)/B,$$

where W is the degree of exchange in percent, A_0 is the activity of the initial salt, taken as 100%, A_1 is the activity of the reaction product in percent of the activity

of the initial compound; $B = \frac{N_1}{N_1 + N_2}$; N_1 is the atomic concentration of the element under study (sulfur) in the passed SO_3; N_2 is the atomic concentration of sulfur in the radioactive preparation.

It follows from the results presented that the rate of isotopic exchange at a specific radioactivity of K_2SO_4 of the order of 0.02–0.03 μc/g is practically constant and is about 12%. It then rises to 26.7% when the activity of potassium sulfate reaches 0.35 μc/g. The maximum degree of exchange, 66.9%, is observed at a specific activity of about 2.3 μc/g. A further increase in the specific activity of potassium sulfate to 8–16 μc/g then leads to a decrease in the degree of exchange to 33–37%. The region of still higher specific activities has not yet been investigated by us.

It may be assumed that the beta particles emitted by sulfur-35, at sufficient intensity of their radiation, cause excitation of the ions forming the K_2SO_4 crystal lattice and, in particular, of the SO_4^{2-} ions. Apparently, in this state the SO_4^{--} ions from the solid phase are more readily able to exchange sulfur atoms with gaseous sulfur anhydride, SO_3 radicals, SO_2, etc. This leads to an increase in the exchange rate by several times in comparison with weakly active preparations.

As for the maximum in the magnitude of exchange at a specific activity of 2 μc/g, the reason for its occurrence is still not clear. It is possible that, under excessively intense radioactive radiation, ionization of SO_3 molecules begins to occur to a noticeable extent near the surface of the solid potassium sulfate. This may hinder their adsorption and, correspondingly, exchange. On the other hand, charges may arise on the surface of potassium sulfate under intense radiation, producing the same consequences.

It should be noted that the addition of sodium sulfate by itself does not affect the rate of isotopic exchange of sulfur in potassium sulfate. For a K_2SO_4 preparation with a specific activity of $1.7 \cdot 10^{-2}$ μc/g and a Na_2SO_4 content of 0.4%, the rate of isotopic exchange proved to be 11.9%, which practically does not differ from the exchange value at the same specific activity but with a lower Na_2SO_4 content (0.04%).

In the experiments described, we also do not have a simple radiation-chemical

chemical decomposition of potassium sulfate, which would be accompanied, for example, by the elimination of SO_2 and the loss of a corresponding amount of activity. Calcination of the active K_2SO_4 preparation in a stream of air under the same conditions as in the exchange experiments with SO_3 showed a complete absence of change in weight, as well as in the content of S^{35}.

Table 1

Examples of changes in the activity of potassium sulfate in isotope-exchange experiments with SO_3
Temperature 840°. SO_3 charge 0.58 g.

K_2SO_4 preparation	K_2SO_4 charge, g	Weight of K_2SO_4 after experiment, g	Change in weight, g	Change in weight, %	Initial activity, imp/min	Activity of K_2SO_4 after experiment, imp/min	Activity of K_2SO_4 after experiment, %	Degree of exchange, %
1	0,3362	0,3362	–	–	$2164 \cdot 10^2$	$1942 \cdot 10^2$	89,8	11,7
2	0,4034	0,4039	+0,0005	+0,1	$4625 \cdot 10^2$	$4160 \cdot 10^2$	90,0	12,0
3	0,3780	0,3785	+0,0005	+0,1	$4713 \cdot 10^3$	$3719 \cdot 10^3$	78,9	27,5
4	0,3756	0,3761	+0,0005	+0,1	$2726 \cdot 10^4$	$1344 \cdot 10^4$	49,3	65,9
5	0,3129	0,3129	–	–	$2514 \cdot 10^4$	$1187 \cdot 10^4$	47,2	66,1
6	0,3512	0,3512	–	–	$9897 \cdot 10^4$	$7310 \cdot 10^4$	73,9	33,4
7	0,3563	0,3561	−0,0002	−0,1	$1669 \cdot 10^5$	$1212 \cdot 10^5$	72,4	35,4

A phenomenon close to that described above was observed by Gordon and Hart ([2]): treatment with Co^{60} gamma rays of a solution of gaseous deuterium in light water led to isotopic exchange of deuterium and protium, which by itself does not proceed at a noticeable rate under the same conditions. These authors believe that in this case exchange takes place through products of radiolysis of water.

	Initial activity of the K_2SO_4 charge, imp/min	Activity after experiment, imp/min
1	$1440 \cdot 10^5$	$1439 \cdot 10^5$
2	$1186 \cdot 10^5$	$1186 \cdot 10^5$

Table 2

Isotopic exchange of sulfur between potassium sulfate and SO_3 at 840°

K_2SO_4 preparation	Introduced Na_2SO_4 impurity, %	Observed specific activity, imp/min, g	Absolute activity, $\mu c/g$	Number of experiments	Degree of exchange, %
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
3	0,1	$12{,}5 \cdot 10^6$	$3{,}5 \cdot 10^{-1}$	4	26,7
4	0,4	$72{,}6 \cdot 10^6$	2,0	5	65,5
5	0,4	$80{,}4 \cdot 10^6$	2,3	5	66,9
6	2,6	$28{,}2 \cdot 10^7$	7,8	5	33,3
7	3,0	$58{,}5 \cdot 10^7$	16,2	4	36,6

In heterogeneous systems similar to the one we studied, an important role must be played by the energetic action of radioactive radiation on the adsorption layer of gaseous or liquid products formed on the surface of the solid phase. The processes of isotopic and chemical exchange occurring on the surface of a solid, and the adsorption, catalytic, and other properties of solids, may depend on this action. At the same time, a radiation-chemical action of the radiation on the gaseous or liquid phase in contact with the radioactive solid is not excluded. In addition, within the volume of the solid and on its surface, recoil nuclei may create defects in the crystal lattice, which play the role of additional active centers for the phenomena of adsorption and isotopic exchange.

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