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![Fig. 1 and Fig. 2](image)

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Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

Abstract

Full Text

PHYSICAL CHEMISTRY

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ON THE INFLUENCE OF THE β-RADIATION OF S^{35} ON THE ISOTOPIC EXCHANGE OF OXYGEN IN THE SYSTEM $Na_2SO_4^{16}$–O_2^{18}

The use of preparations with high specific activities has drawn the attention of researchers to the problem of changes in the physicochemical properties of substances and in the kinetics of heterogeneous reactions under the influence of radioactive radiations of high intensity ($^{1-4}$). The aim of the present work was to study the influence of the β-radiation of S^{35}, introduced in varying amounts into sodium sulfate, on the rate of the reaction of isotopic exchange of oxygen in the system $Na_2S^*O_4^{16}$–O_2^{18} at a temperature of 600-800°. The method of investigation was the same as in (^{5}). The temperature in the experiments was maintained constant with an accuracy of ±0.5°.

Fig. 1. Dependence of the degree of oxygen exchange in the system $Na_2S^*O_4^{16}$ –O_2^{18} on temperature. Specific activity of the preparations (mCu/g): 1–0.08; 2 –0.50; 3–10

Fig. 2. Dependence of the degree of oxygen exchange in the system $Na_2S^*O_4^{16}$ –O_2^{18} on the specific activity of the solid phase

Active sodium sulfate in an amount of 4-6 g for each series of experiments was prepared by mixing solutions of active and inactive sodium sulfates, followed by evaporation and calcination of the crystals to constant weight at 600°. All preparations had the same specific surface area, equal to approximately 5 m^2/g.

To study isotopic exchange, oxygen containing about 1.5 at.% O^{18} was used. Analysis of the isotopic composition of the gas phase was carried out on an MS-1 mass spectrometer, and the determination of the amount of O^{18} transferred into the solid phase was performed with an accuracy of about 2%. The process of isotopic exchange was studied with preparations having specific activities of 0.08; 0.50; 1.25; 1.50; 1.58; 1.94; 10 and 25 mCu/g. The curves of the dependence of the composition of the gas phase on time made it possible to calculate the degree of exchange, the rate constants

Fig. 3

Figure 2: Fig. 3

reaction and the activation energy of the process. In Fig. 1, as an example, the dependence of the exchange values attained in 8 h on temperature is given for three series of experiments. From data of this kind, the values of the degree of exchange for 680 and 760° were determined, and the results are compared in Fig. 2.

Fig. 3. Dependence of the activation energy of the process of isotopic oxygen exchange in the system $Na_2SO_4^*$–O_2^{18} on the specific activity of the solid phase in the temperature interval 700-800°

In the absence of radioactive action over the indicated time interval, the degree of oxygen exchange at 750-800° is only 1-1.5%, and the activation energy is 54 kcal/mole (5). As the isotherms of degrees of exchange show (Fig. 2), in all cases the introduction of S^{35} into sodium sulfate leads to an increase in the exchange rate. With a gradual increase in the specific activity, a sharp increase in the degree of exchange is observed, reaching a maximum at 1.5 mCu/g, after which the rate of the process falls just as sharply, and then, as a result of a further increase in the specific activity from 2 to 25 mCu/g, a slower increase in the rate of the process occurs. A similar picture of the influence of radioactive radiation on isotopic exchange is also observed in other heterogeneous systems (2, 6).

The change in activation energy, as Fig. 3 shows, occurs in such a way that in the region of specific activities of $Na_2SO_4^*$ of 1-2 mCu/g it passes through a minimum (4 kcal/mole), whereas at specific activities equal to 0.08; 1.94 and 10 mCu/g, its values are respectively 61; 65.5 and 80 kcal/mole, i.e., they exceed the value found for isotopic exchange in the absence of radioactive action. The change in the values of the activation energy indicates a change in the mechanism of the reaction when the intensity of the radioactive radiation is changed.

In active preparations of sodium sulfate, a peculiar accumulation of the radiation effect with time is observed. The data of Table 1 show that isotopic exchange proceeds the more intensively, the higher the initial specific activity of the $Na_2SO_4^*$ samples and the longer their storage time.

Table 1

Dependence of the degree of exchange on the storage time of $Na_2SO_4^*$ **preparations**

No. of preparations	Experiment temperature, °C	Specific activity, mCu/g	Storage time, days	Degree of exchange in 8 h, %, before storage	Degree of exchange in 8 h, %, after storage
1	786	0.50	4	5.6	6.3
2	782	10.0	15	26.8	–
2	785	10.0	15	–	40.6
3	780	25.0	8	18.5	38.6
3	760	25.0	6	24.8*	29.6

* The preparation had been stored for 2 days before the first measurement.

A certain decrease in the activity of $Na_2SO_4^*$ preparations as a result of the decay of S^{35} should have reduced the degree of exchange if the radiation affected only the gas phase. Evidently, radiochemical phenomena have a substantial influence on the properties of the surface of the solid phase.

Radioactive $Na_2SO_4^*$ preparations acquire with time a gray-violet coloration, the intensity of which depends on the duration of storage and on the specific activity. When heated to 600°, such preparations again become colorless for a short time. Comparison of this fact with the data of Table 1 permits the supposition that the defects of the crystal lattice arising under the influence of radioactive decay can be divided into two groups: readily restored (change-

of the electron density) and are not subject to "annealing" (for example, the appearance of Cl^{35} instead of S^{35}). The accumulation of defects that persist at high temperature should facilitate diffusion processes and thereby promote the course of the process of isotopic exchange.

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