Physical Chemistry

Academician Vikt. I. SPITSYN, I. E. MIKHAILENKO, I. V. VERESHCHINSKII

1960

SovietRxiv

Abstract

Full Text

Physical Chemistry

Academician Vikt. I. SPITSYN, I. E. MIKHAILENKO, I. V. VERESHCHINSKII
and P. Ya. GLAZUNOV

STUDY OF THE EFFECT OF EXTERNAL RADIATION ON THE RATE OF SULFUR ISOTOPIC EXCHANGE IN THE SYSTEM $K_2S^{\times}O_4$ –SO_3 AT HIGH TEMPERATURE

V. I. Spitsyn and I. E. Mikhailenko ([1,2]) established that the specific radioactivity of potassium sulfate with respect to S^{35} has a significant effect on the rate of sulfur isotopic exchange in the system $K_2S^{\times}O_{4\,\mathrm{solid}}{-}SO_{3\,gas}$ at 840°. It was of interest to study what role is played here by radiation phenomena occurring in the gas phase and on the surface of the exchanging salt under the action of β-radiation. For this purpose, isotopic exchange was carried out at low activity of potassium sulfate, but under conditions of external irradiation of the labeled preparation K_2SO_4 and SO_3 vapors by an electron beam from a betatron whose design permitted the emission of electrons outward ([3]). A diagram of the apparatus used is shown in Fig. 1.

The apparatus was located on a movable stand and placed next to the betatron in an isolated room with concrete walls for protection from radiation. The instruments were controlled remotely from a special console. The required amount of SO_3 was distilled beforehand from 60% oleum into a measuring test tube. A stream of dried air passing through the apparatus and subsequently entraining the SO_3 vapors was turned on before the start of the experiment. Uniform evaporation of sulfur trioxide at a specified rate was achieved by means of a movable heater that was automatically displaced along the measuring test tube. The working tube and the boat for the $K_2S^{\times}O_4$ sample were made of quartz. The furnace heater was a thin nichrome ribbon wound around the quartz reaction tube. A constant temperature during the experiment was maintained with an accuracy of $\pm 3°$ by means of an indirect automatic control system ([4]). In the furnace casing and its asbestos thermal insulation there was a narrow slit (9 $\times$ 70 mm), through which a stream of electrons with an energy of 5 MeV was directed onto the quartz tube and the boat contained in it. The stability of the betatron radiation was monitored by an ionization chamber used as a witness. The progress of the experiment was observed by means of a television device.

For the study of isotopic exchange, a $K_2S^{\times}O_4$ preparation with a specific activity of $4.6 \cdot 10^{-2}$ mCi/g was used. The experimental conditions were analogous to

Figure 1. Diagram of the apparatus for studying isotope exchange at high temperature under external electron irradiation.

Figure 1: Figure 1. Diagram of the apparatus for studying isotope exchange at high temperature under external electron irradiation.

those described in ([1]). Electron irradiation was carried out in two variants: 1) simultaneous irradiation of the boat with $K_2S^{\times}O_4$ and of the surrounding gas, and 2) irradiation only of the gas before its entry into the furnace (18 cm along the length of the working quartz tube). In the latter case, the slit opposite the boat was shielded with lead.

To estimate the radiation dose received by the potassium sulfate, a ferrosulfate dosimetry method was used. A $2.3 \cdot 10^{-3}$ M solution of Mohr' s salt in 0.8 N H_2SO_4 was used; the concentration of Fe^{+3} was determined spectrophotomet-

···metric with respect to absorption at 304 mμ. The volume of the dosimetric solution poured into the quartz boat was close to the volume occupied by potassium sulfate.

The dose received by the gas was determined in a special cell, placed in the position of the working tube and modeling the experimental conditions. In these calculations, differences in the scattering and secondary absorption of electrons during the transition from the dosimetric solution to solid potassium sulfate and gaseous SO_3 were neglected, as was the possible transfer of energy in the air–SO_3 mixture from one component to another. In determining the integral dose received by the samples, the specific weights, volumes, and ratios of the electron densities of the irradiated object to water, $D_e/D_e(H_2O)$, were taken into account. The results of the dose calculations are presented in Table 1.

Fig. 1. Diagram of the apparatus for studying isotope exchange at high temperature under external electron irradiation.
1 –round-bottom flask with oleum; 2 –condenser; 3 –receiver for SO_3; 4, 5, 7 –three-way stopcocks; 6 –two-way stopcock; 8 –graduated test tube; 9 –quartz reaction tube; 10 –millivoltmeter with a platinum–platinum-rhodium thermocouple; 11 –lead shield; 12 –asbestos thermal insulation; 13 –quartz boat; 14 –slit in the furnace; 15 –heating element; 16 –reducer; 17 –Uorren motor; 18, 19, 20, 21, 22 –wash bottles with concentrated H_2SO_4; 23 –betatron chamber.

Table 1

Examples of calculation of the dose of electron radiation absorbed in potassium sulfate and in the gas entering into exchange (mixture of air and SO_3 vapor, $P_{SO_3} = 19$ mm)

Dose received by the ferric-sulfate solution in 10 min., eV/ml	Object under study: irradiated substance	Object under study: density, g/cm^3	Object under study: $D_e/D_e(H_2O)$	Object under study: irradiated volume, ml	Dose received in 10 min., eV: K_2SO_4 preparation	Dose received in 10 min., eV: SO_3, stationary	Dose received in 10 min., eV: SO_3, in a stream with air
$8.0 \cdot 10^{17}$	K_2SO_4	4.13	8.6	0.35	$2.8 \cdot 10^{16}$		
$2.3 \cdot 10^{16}$	SO_3	$3.6 \cdot 10^{-3}$	4	14		$4.7 \cdot 10^{15}$	$1.1 \cdot 10^{13}$

Table 2

Examples of changes in the activity of K_2SO_4 in the study of sulfur isotope exchange
in the system K_2SO_4—SO_3 under the action of external electron irradiation (SO_3, 0.58 g, passed through)

Dose received in 10 min, eV	Object of irradiation	K_2SO_4 sample, g	Weight of K_2SO_4 after experiment, g	Weight change, g	Weight change, %	Initial activity, counts/min	Activity of K_2SO_4 after experiment, counts/min	Activity of K_2SO_4 after experiment, % of initial	Degree of exchange, %	Average
$1.1 \cdot 10^{17}$	Salt and gas	0.3506	0.3513	+0.0007	+0.2	$1043 \cdot 10^3$	$7610 \cdot 10^2$	72.9	34.6	33.6
$1.1 \cdot 10^{17}$	Salt and gas	0.3950	0.3959	+0.0009	+0.2	$1176 \cdot 10^3$	$8628 \cdot 10^2$	73.4	33.2	33.6
$1.1 \cdot 10^{17}$	Salt and gas	0.3474	0.3470	−0.0004	−0.1	$1034 \cdot 10^3$	$7518 \cdot 10^2$	72.7	32.7	33.6
$1.1 \cdot 10^{17}$	Salt and gas	0.3575	0.3582	+0.0007	+0.2	$1064 \cdot 10^3$	$7839 \cdot 10^2$	73.7	33.8	33.6

Dose received in 10 min, eV	Object of irradiation	K_2SO_4 sample, g	Weight of K_2SO_4 after experiment, g	Weight change, g	Weight change, %	Initial activity, counts/min	Activity of K_2SO_4 after experiment, counts/min	Activity of K_2SO_4 after experiment, % of initial	Degree of exchange, %	Average
$1.06 \cdot 10^{13}$	Gas	0.3845	0.3849	+0.0004	+0.1	$1481 \cdot 10^3$	$1277 \cdot 10^3$	86.3	18.0	20.5
$1.06 \cdot 10^{13}$	Gas	0.4326	0.4330	+0.0004	+0.1	$1668 \cdot 10^3$	$1407 \cdot 10^3$	84.3	21.0	20.5
$1.06 \cdot 10^{13}$	Gas	0.4503	0.4508	+0.0005	+0.1	$1736 \cdot 10^3$	$1447 \cdot 10^3$	83.4	22.6	20.5
$1.06 \cdot 10^{13}$	Gas	0.3724	0.3728	+0.0004	+0.1	$1437 \cdot 10^3$	$1208 \cdot 10^3$	84.2	20.5	20.5

Table 3

Effect of external electron radiation on the degree of isotope exchange in the system $K_2^{\times}SO_4$—SO_3 (temperature 840°, duration of experiments 10 min, $K_2^{\times}SO_4$ samples 0.35–0.45 g, SO_3 0.58 g, gas-flow rate 37 l/h, P_{SO_3} 19 mm)

Series of experiments	Dose rate according to the ferrosulfate solution, eV/ml · sec	Dose received in 10 min, eV	Object of irradiation	Number of experiments	Degree of exchange, % (average)
1	Experiments without irradiation	–	–	4	14.4
2	$1.8 \cdot 10^{13}$	$3.4 \cdot 10^{15}$	Salt and gas	4	14.7
3	$1.3 \cdot 10^{14}$	$2.8 \cdot 10^{16}$	Salt and gas	12	28.7
4	$5.1 \cdot 10^{14}$	$1.1 \cdot 10^{17}$	Salt and gas	10	33.7
5	$3.9 \cdot 10^{13}$	$1.1 \cdot 10^{13}$	Gas	4	20.5
6	$7.4 \cdot 10^{13}$	$2.1 \cdot 10^{13}$	Gas	8	20.3

The study of isotope exchange was carried out at different dose rates; for each value, from 4 to 12 experiments were performed. Radiochemical decomposition of potassium sulfate was never observed.

Table 2 gives examples of changes in the activity of potassium sulfate in the study of isotope exchange under irradiation. The average results of all experiments are given in Table 3.

From the data presented it follows that external electron irradiation of the solid phase in the system K_2SO_4—SO_3, at a dose of the order of 10^{15} eV/10 min, has practically no effect on the rate of exchange. Increasing the irradiation dose to 10^{16}—10^{17} eV leads to an increase in the degree of exchange, which occurs in direct proportion to the logarithm of the dose (Fig. 2).

Fig. 2. Dependence of the degree of sulfur exchange in the system $K_2^{\times}SO_{4\,\mathrm{solid}}$—$SO_{3\,\mathrm{gas}}$ on the integral dose of external electron irradiation (per 10 min).

It should be noted that the radiation of β-particles by radioactive preparations of $K_2^{\times}SO_4$ has a much greater effect on the rate of exchange. For example, an electron-irradiation dose of $3.4 \cdot 10^{15}$ eV/10 min for solid potassium sulfate (Table 3, 2nd series of experiments) would correspond to an intrinsic radioac-

of this salt, equal to 2.3 mCu/g (in this calculation the number of β-particles emitted by the preparation over 10 min was taken into account; the accumulation of the irradiation effect before the beginning of the experiments ([5]) was not considered here). The degree of exchange of the indicated radioactive preparation was 66.9% ([2]) and was increased, in comparison with weakly radioactive samples of $K_2\overset{\times}{S}O_4$, by a factor of 2.5–3. External irradiation of similar intensity under the given conditions has no effect.

The electrons bombarding the surface of labeled potassium sulfate apparently excite SO_4^{2-} ions and individual atoms in the existing active exchange centers. Electron irradiation also has an activating effect on gaseous SO_3 (Table 3, 5th and 6th series of experiments). Here, evidently, SO_3 and SO_2 ions of different sign are formed. However, the indicated effect is manifested comparatively weakly: exchange increases by approximately 40% and, within the investigated dose limits (1—$2 \cdot 10^{13}$ eV/10 min.), practically does not change.

Institute of Physical Chemistry
Academy of Sciences of the USSR

Received
10 XII 1959

CITED LITERATURE

[1] Vikt. I. Spitsyn, I. E. Mikhailenko, DAN, **121**, 319 (1958).
[2] I. E. Mikhailenko, Vikt. I. Spitsyn, DAN, **131**, No. 1 (1960).

[3] B. A. Kononov, *Izv. Tomsk. politekhnich. inst. im. S. M. Kirova*, **87**, 322 (1957).
[4] A. P. Rudenko, *System of indirect automatic temperature regulation in electric furnaces*, Moscow, 1958.
[5] Vikt. I. Spitsyn, *Izv. AN SSSR, OKhN*, 1958, No. 11, 1296.

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