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Abstract

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ISOTOPIC EXCHANGE OF GASEOUS OXYGEN WITH SOME URANIUM COMPOUNDS

In the present work, the method of isotopic exchange with gaseous oxygen was applied to the study of the relative strength of bonding of oxygen atoms in various uranium compounds. The gaseous oxygen used, enriched in the isotope ^{18}O ($\sim 6.5\%$), was obtained by electrolysis of a sulfuric acid solution in water enriched in oxygen. Its purification from traces of hydrogen was carried out on a platinum catalyst; water was frozen out in two traps with a mixture of dry ice and acetone.

Isotopic exchange was studied with the following compounds: uranium trioxide γ-UO_3, amorphous uranium trioxide UO_3 (A), oxygen-deficient uranium dioxide α-$UO_{2.94}$, uranium oxide U_3O_8, sodium diuranate $Na_2U_2O_7$, and the α- and β-modifications of normal sodium uranate Na_2UO_4. All compounds were obtained at temperatures higher than those at which isotopic exchange was studied. By the BET method, from krypton adsorption, the specific surfaces of the compounds studied were measured. The scatter of the values obtained from sample to sample did not exceed 20%.

Table 1 gives the mean values of the specific surface area and the mean particle radii, calculated on the assumption that the latter have a spherical shape and identical sizes. During the exchange process, practically no change in the specific surface area of the preparations was observed.

Table 1

Compound	Specific surface, m^2/g	Mean particle radius, cm
U_3O_8	6.6	
α-$UO_{2.94}$	9.7	
γ-UO_3	0.60	$6.1 \cdot 10^{-5}$
UO_3 (A)	22.5	$2.0 \cdot 10^{-6}$
$Na_2U_2O_7$ (1000°)	0.26	
$Na_2U_2O_7$	1.14	$4.3 \cdot 10^{-5}$
β-Na_2UO_4	0.44	$1.2 \cdot 10^{-4}$

Fig. 1. Diagram of the apparatus for studying isotope exchange.

Figure 1: Fig. 1. Diagram of the apparatus for studying isotope exchange.

Compound	Specific surface, m^2/g	Mean particle radius, cm
α-Na_2UO_4	0.92	$5.5 \cdot 10^{-5}$

Exchange was carried out in a quartz apparatus (Fig. 1) of the static type, with forced circulation of oxygen through the sample layer. The volume of the apparatus was about 230 ml; the pump operated with a capacity of 1.5 l/min. The isotopic composition of oxygen was measured on an MS-3 mass spectrometer. A negligible volume of gas, the amount of which could be neglected, was continuously admitted into the mass spectrometer from the exchange apparatus by means of a special leak valve. The temperature of the sample was measured with a standard Pt—PtRh (10%) thermocouple; a tyratron regulator ensured temperature constancy in the device with an accuracy of ±0.1°. All experiments, except two for α-Na_2UO_4 and one for UO_3 (A), were carried out at the ratio of the number of gram-atoms of oxygen in the solid (n_t) and gaseous (n_g) phases

$$s = \frac{n_t}{n_g} = \frac{0.02298}{(0.00620 \pm 0.00005)} = 3.707 \pm 0.030.$$

The initial oxygen pressure was 250 mm Hg.

In the case of U_3O_8 and α-$UO_{2.94}$, the exchange strictly followed the exponential law. Only for the latter compound, at a degree of exchange (F) greater than 90%, was a very small deviation of the dependence $\lg(1-F)$—time observed.

(t) from linearity. For $Na_2U_2O_7$, the deviation from linearity began earlier, and at smaller degrees of exchange, the lower the temperature was. This fact can be explained by the influence of the rate of diffusion of oxygen into the interior of the solid-phase particles. Diuranate calcined in air for several days at a temperature of 1000° showed a linear dependence

Fig. 1. Diagram of the apparatus for studying isotope exchange. 1 —reactor; 2 —crucible with the substance under study; 3 —heat reflector; 4 —pocket for the thermocouple; 5 —furnace; 6 —circulation pump; 7 —pole pieces of the electromagnets; 8 —three-way stopcock; 9 —leak valve; 10 —Teflon seal; 11 —transition, quartz-molybdenum glass; 12 —kovar

$\lg(1-F)$ on t. Obviously, this can be attributed to a greater ordering of the surface of the substance, as a result of which the rate of exchange proper on the surface decreased to a greater extent than the rate of diffusion. However, because of the fairly large scatter in the exchange rates observed for individual specimens (especially in the case of calcined diuranate, for which the half-exchange periods of different specimens differed by a factor of 2-4), this conclusion cannot be strictly substantiated. On the other hand, taking into account the activation-energy values of the exchange and diffusion processes given below, as well as the dependence of $1-F$ on the diffusion coefficient (D), it must be admitted that the more linear character of the exchange curves at high temperatures speaks in favor of this conclusion.

For U_3O_8, α-$UO_{2.94}$, and $Na_2U_2O_7$ calcined at 1000°, measurements at different temperatures were carried out on a single specimen, which eliminated scatter caused by the individuality of the surface properties of the specimen.

For the other compounds studied, the dependence of $\lg(1-F)$ on t was sharply nonlinear because of the slowness of the diffusion process. For β-Na_2UO_4, the half-exchange periods could be determined from the slope of the initial portion of the exchange curves. In the case of γ-UO_3, UO_3 (A), and α-Na_2UO_4, diffusion almost immediately proved to be the controlling stage of the exchange process.

For preparations that showed a dependence of the exchange process on diffusion, the self-diffusion coefficients of oxygen were determined. For this purpose, use was made of the solution of Fick' s general diffusion equation obtained

by Wagner (see (1)):

$$1-F=6(s+1)\sum_{k=1}^{\infty}\frac{e^{-x_k^2\tau}}{x_k^2+9s(s+1)}.$$

Here $\tau = tD/R^2$, where R is the radius of the particles of the solid phase, and x_k are the roots of the transcendental equation:

$$\operatorname{ctg} x_k=\frac{1}{x_k}+\frac{x_k}{3s}.$$

With the aid of an M-20 electronic computer, τ was calculated for values of F from 0 to 1 at small intervals. The calculations were carried out for $s = 1.930$; 3.707 and 18.46. The value D/R^2 was found from the slope of the linear portion of the $\tau - t$ curves, within which the greater part of the exchange took place. In the case of γ-UO_3, for which the observed degrees of exchange were very small, in determining D/R^2 the slopes of the $\tau - t$ curves corresponding to identical degrees of exchange were used, which made it possible to reduce the effect of particle-size inhomogeneity, especially pronounced at the very beginning of the exchange.

Fig. 2. Dependence of $\lg T_{1/2}$ on reciprocal temperature.
I–$Na_2U_2O_7$ (1000°); II–Na_2UO_7; III–β-Na_2UO_4; IV–U_3O_8; V–α-$UO_{2.94}$; coincident points are marked by a double outline; for $Na_2U_2O_7$ (1000°), U_3O_8, and α-$UO_{2.94}$, points obtained in experiments on individual samples are shown by outlines with a blackened top.

Table 2 gives the coefficients, found by the least-squares method, of the equation relating the half-exchange period (in minutes) or the self-diffusion coefficient (in cm^2/sec) to the absolute temperature (T, °K):

$$-\lg T_{1/2} \text{ (or } \lg D) = a - b/T.$$

For greater clarity, the scatter observed in measurements on individual samples and the dependences $-\lg T_{1/2}$ and $\lg D/R^2$ on reciprocal temperature are shown graphically in Figs. 2 and 3.

The activation energies of the isotopic exchange proper and of diffusion, with indication of the temperature interval in which they were determined, are given in Table 3 (confidence limits are indicated for 95% probability).

Table 2

Compound	Exchange a	Exchange $b \cdot 10^{-3}$	Diffusion a	Diffusion $b \cdot 10^{-3}$
U_3O_8	10.28	9.08		
α-$UO_{2.94}$	9.98	8.51		
γ-UO_3			+1.1, at 375°	15.8
UO_3 (A)			$D \approx 10^{-21}$	
$Na_2U_2O_7$ (1000°)	5.32	6.98		
Na_2UO_7	4.73	5.67	−1.5	11.14
β-Na_2UO_4	3.93	4.39	−3.7	8.06
α-Na_2UO_4			−6.6	7.06

When comparing the activation energies of exchange and diffusion (for $Na_2U_2O_7$, β-Na_2UO_4, and, with a known approximation, for γ-UO_3 and α-$UO_{2.94}$), it may be noted that the former are approximately half as large as the latter. Evidently this should be attributed to the uncompensated bonds of oxygen atoms located on the crystal surface, owing to which their detachment from the lattice requires a lower activation energy.

Despite the presence, in the compounds studied, of oxygen atoms occupying different positions in the crystal lattice ($^{2-6}$), isotopic exchange proceeds as if all the oxygen atoms

Table 3

Compound	Activation energy of exchange, kcal/mol	Activation energy of self-diffusion, kcal/mol
U_3O_8	41.6 ± 0.7 (450–525°)	
α-$UO_{2.94}$	39.0 ± 2.1 (375–475°)	72 ± 16 (600–650°)

Fig. 3. Dependence of $\lg D/R^2$ on reciprocal temperature. I—γ-UO_3; II—α-Na_2UO_4; III—$Na_2U_2O_7$; IV—β-Na_2UO_4

Figure 2: Fig. 3. Dependence of $\lg D/R^2$ on reciprocal temperature. I—γ-UO_3; II—α-Na_2UO_4; III—$Na_2U_2O_7$; IV—β-Na_2UO_4

Compound	Activation energy of exchange, kcal/mol	Activation energy of self-diffusion, kcal/mol
γ-UO_3		
$Na_2U_2O_7$ (1000°)	32.0 ± 2.3 (675—775°)	
$Na_2U_2O_7$	26.0 ± 2.1 (500—700°)	51.0 ± 4.0 (500—700°)
β-Na_2UO_4	20.1 ± 2.7 (500—650°)	36.9 ± 1.4 (400—650°)
α-Na_2UO_4		32.4 ± 3.5 (500—700°)

were equivalent. For U_3O_8, α-$UO_{2.94}$, and $Na_2U_2O_7$ this follows directly from the linear dependence of $\lg(1-F)$ on t and from the possibility of bringing the exchange practically to completion. For the other compounds studied there are indirect confirmations of this, for example, the coincidence of the τ—t curves obtained for different values of s. Apparently, energetically the oxygen atoms in the compounds studied either do not differ or differ only very little, which leads to their identical behavior in the exchange process. This may be explained by the fact that the oxygen atoms located closer to uranium (usually called uranyl oxygen atoms) are bound to a smaller number of uranium atoms (and of the alkali element in the uranates) than the more remote ones, and on average their bond energies in the lattice are equal. In view of the above, it is difficult to agree that uranyl and non-uranyl oxygen atoms have a sharply different character of bonding in the crystal lattice.

Fig. 3. Dependence of $\lg D/R^2$ on reciprocal temperature. I—γ-UO_3; II—α-Na_2UO_4; III—$Na_2U_2O_7$; IV—β-Na_2UO_4

It is interesting that between the values of the activation energy and the U : O ratio in the compounds studied a certain parallelism is observed, which is apparently connected with the change in the bond energy per oxygen atom on average. In the case of U_3O_8 and α-$UO_{2.94}$ this can be shown by comparing the ratio of their activation energies of isotopic exchange with the ratio of the heats of formation[7–10] calculated per oxygen atom. They are respectively equal to 41.6 : 39.0 = 1.067 and 106.7 : 99.8 = 1.069. For the uranates such a comparison cannot be made, since it is not known to what extent sodium ions affect the strength of the bond of the oxygen atoms in these compounds.

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