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# PHYSICAL CHEMISTRY

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Fig. 1. Change in the  $O^{18}$  content in the gas phase during isotopic exchange in the system  $Na_2WO_4^{16}-O_2^{18}$  at  $720^\circ$ . Samples of  $Na_2WO_4$ : 1 –1.0 g, 2 –4.4 g, 3 –7.4 g

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## Abstract

## Full Text

PHYSICAL CHEMISTRY

Academician Vikt. I. SPITSYN, V. G. FINIKOV, and G. N. ZYKOVA

# ISOTOPIC EXCHANGE BETWEEN $O_2^{18}$ AND MOLTEN $Na_2WO_4^{16}$

Using the procedure described in (1), we studied isotopic exchange between gaseous oxygen containing 1.360 at.%  $O^{18}$  and molten  $Na_2WO_4$  of normal isotopic composition at 720, 745, and  $764^\circ C$  (the temperature was maintained to an accuracy of  $\pm 0.5^\circ$ ). The surface of the melt, which had the form of a rectangle measuring  $4 \times 0.5$  cm, was practically the same in all experiments. To determine the dependence of the kinetic characteristics on the thickness of the melt layer, three series of experiments were carried out with samples of 1.0, 4.4, and 7.4 g of sodium tungstate, corresponding to layer depths of approximately 1, 5, and 8 mm. The isotopic analysis of the oxygen in the gas phase on an MS-4 mass spectrometer was carried out by V. L. Litvakov, to whom the authors express their gratitude. From the change in the  $O^{18}$  content in the gas with time, for known sodium tungstate sample weights and gas-flow rate through the system, the degrees of exchange, the reaction rate constants, and the activation energies of the exchange process were calculated.

Fig. 1. Change in the  $O^{18}$  content in the gas phase during isotopic exchange in the system  $Na_2WO_4^{16}-O_2^{18}$  at  $720^\circ$ . Samples of  $Na_2WO_4$ : 1 –1.0 g, 2 –4.4 g, 3 –7.4 g

Figure 1 shows the change in the  $O^{18}$  content in the gas phase with time at a temperature of  $720^\circ$ . Attention is drawn to the constancy of the reaction rate over many hours.

Table 1

Degrees of exchange attained in the system  $Na_2WO_4^{16}-O_2^{18}$  in 8 h (percent)

Fig. 2

Figure 2: Fig. 2

Sodium tungstate sample, g	720	745	764
1.0	45.6	57.9	65.4
4.4	22.4	28.6	33.9
7.4	10.6	13.4	13.8

Table 2

Reaction rate constants of oxygen isotopic exchange in the system  $\text{Na}_2\text{WO}_4^{16} - \text{O}_2^{18}$  ( $\text{h}^{-1}$ )

Sodium tungstate sample, g	720	745	764
1.0	0.0631	0.1040	0.1229
4.4	0.0317	0.0421	0.0525
7.4	0.0140	0.0179	0.0186

On the surface of the melt there were about  $10^{15}$  O ions per  $1 \text{ cm}^2$ . The number of collisions with the melt surface was  $2 \cdot 10^{23} \text{ s}^{-1} \cdot \text{cm}^{-2}$ . A calculation made from the experimental results shows that every second at  $720^\circ$  there occurred  $5 \cdot 10^{14}$ ,  $15 \cdot 10^{14}$ , and  $1.5 \cdot 10^{14}$ —or, on average,  $7 \cdot 10^{14}$ —acts of transition of  $\text{O}^{18}$  into the liquid phase, respectively, for samples of 1.0, 4.4, and 7.4 g, i.e., the same number or somewhat fewer than the number of oxygen ions in the surface layer. The theory of absolute reaction rates gives the relation

$V = N_q e^{-E/RT}$ , where  $V$  is the reaction rate ( $\text{molecules} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ ), and  $N_q$  is the number of impacts on the surface ( $\text{molecules} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ ). Substitution of the above quantities into this relation gives an activation energy equal to 38.4 kcal/mole. For temperatures of 745 and  $764^\circ$ , the results are analogous.

Table 1 contains data on the degrees of exchange attained at the temperatures studied after 8 h.

The use of the formula  $Kt = \ln \frac{100}{100 - \alpha}$ , where  $K$  is the reaction rate constant,  $t$  is time, and  $\alpha$  is the degree of exchange in percent, made it possible to calculate the reaction rate constants given in Table 2. The strictness of the linear dependence of the experimental data is shown in Fig. 2, on which the results corresponding to a temperature of  $720^\circ$  are plotted. The apparent activation energies, calculated by the least-squares method,

**Fig. 2.** Dependence of  $\ln \frac{100}{100 - \alpha}$  on time for the isotopic exchange of oxygen in the system  $\text{Na}_2\text{WO}_4^{16} - \text{O}_2^{18}$  at  $720^\circ$ . Charges of  $\text{Na}_2\text{WO}_4$ : 1 —1.0 g, 2 —4.4 g,

Fig. 3

Figure 3: Fig. 3

3 –7.4 g

**Fig. 3.** Dependence of the activation energy of the isotopic-exchange process in the system  $\text{Na}_2\text{WO}_4^{16}-\text{O}_2^{18}$  on the size of the  $\text{Na}_2\text{WO}_4$  charge

proved to be 30.6, 22.7, and 13.2 kcal/mole and are in linear dependence on the size of the charge (Fig. 3). Extrapolation to an infinitely small (the real value is a monomolecular) layer gives an activation-energy value of 33.5 kcal/mole.

It seems possible to give the following interpretation of the results obtained. In the present case, isotopic exchange is effected by exchange between gaseous oxygen, most likely in the form of atoms, and the oxygen of sodium tungstate anions located on the surface of the melt, through substitution of atoms upon impact. This exchange proceeds at a very low rate; the number of effective impacts on the surface is very small, since only  $10^{-13}\%$  of the molecules are in a state of thermal dissociation ( $10^4$  atom pairs  $\cdot\text{cm}^{-3}$  in our case). The linear increase in activation energy with decreasing layer thickness (increasing mass) of molten sodium tungstate, and its tendency toward the limiting value of 33.5 kcal/mole, which differs from the theoretically calculated value by only 12%, provide grounds for regarding the value found as a quantitative characteristic of the strength of the oxygen bond in the sodium tungstate anion. The lower accuracy of the quantities used in the theoretical calculation makes it possible to consider the value 33.5 kcal/mole closer to the true one.

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## REFERENCES

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

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