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Abstract

Full Text

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INTERACTION OF HYDROGEN WITH URANIUM TRIOXIDE

(Presented by Academician V. I. Spitsyn, 11 VI 1960)

This communication presents the results of a study of the kinetics of the reduction of uranium trioxide by hydrogen in the temperature range 350–500° C and at reducing-gas pressures of 50–400 mm Hg. The experiments were carried out in a high-vacuum apparatus with continuous monitoring of the loss in weight of the sample by means of spring balances.

The experimental curves are presented in Figs. 1 and 2. Processing of the experimental data obtained leads to the rate characteristics of the process shown in Figs. 3 and 4.

Fig. 1. Dependence of the degree of reduction on time at different temperatures and $P_{H2} = 200$ mm

Thermodynamically, reduction of the higher oxides of uranium by hydrogen is possible only to the dioxide; therefore, 100% reduction was taken as complete conversion of the trioxide to the dioxide.

From Figs. 3 and 4 it is seen that, at all temperatures and pressures of the reducing gas, the initial stage of reduction proceeds at a constant rate. The magnitude of the horizontal sections corresponding to this stage increases both with increasing temperature at constant pressure and with increasing pressure at constant temperature.

At constant temperature, the dependence of the rate of the process on the hydrogen pressure at this stage is well described by the equation

$$V = kP_{H2}^{1/2}. \qquad (1)$$

The apparent activation energy of the process is 20.8 kcal/mole. Beginning from a certain degree of reduction, determined by the given temperature and pressure, the rate of the process drops sharply. The drop in rate occurs with a comparatively small change in the degree of reduction.

The final stage of reduction under the conditions of the experiments is also characterized by a constant rate. The exception is the experiment at 500° and $P_{\mathrm{H2}} = 200$ mm Hg. In this case, after the second horizontal section on the curve (Fig. 3) there is another section showing a decrease in the rate of the process as the reduction proceeds further. The apparent activation energy at 70% reduction is 30 kcal/mole. At this stage of reduction, the dependence of the rate on the hydrogen pressure, at constant temperature and $P_{\mathrm{H2}} = 50$–200 mm Hg, is described rather well by the equation:

$$V = k_1 P_{\mathrm{H2}}. \tag{2}$$

The compositions of the final products obtained by us at various temperatures are given in Table 1, from which it follows that at no temperature was the reduction brought to UO_2, and only at 500° did it proceed beyond the oxide U_4O_9. In one of the works (1) carried out in our laboratory, it was shown that dissociation of uranium trioxide in vacuum proceeds at temperatures above 430°. The temperature of onset of the reduction of UO_3 by hydrogen, determined by us, is 350°. Therefore, the assumption of preliminary dissociation of uranium trioxide during the reduction process may be excluded.

Fig. 2. Dependence of the degree of reduction on time at different hydrogen pressures and a temperature of 400°

Table 1

Compositions of the final reduction products
($P_{\mathrm{H2}} = 200$ mm, reduction time 2 hours)

Temp., °C	Ratio O : U in the final products
500	2.09
450	2.30
400	2.43
350	2.83

The kinetic picture obtained makes it possible to propose assumptions about the rate-limiting stages of particular stages of reduction. In interpreting the data, we use the phase diagram of the U—O system (2).

The first horizontal sections of the curves in Figs. 3 and 4 correspond to the reduction of UO_3 to U_3O_8. The rate-limiting stage at this stage of reduction is the surface reaction between hydrogen adsorbed on the surface of the oxide

Fig. 3

Figure 2: Fig. 3

Fig. 4

Figure 3: Fig. 4

and the oxygen of the oxide. The validity of equation (1) gives grounds to suppose that adsorption of hydrogen on the surface of uranium trioxide proceeds sufficiently rapidly and that equilibrium is established in the system for this intermediate stage of the process; moreover, the adsorption isotherm is expressed by the equation $a = k'P_{\mathrm{H2}}^{1/2}$. The appearance of the coefficient 1/2 in the latter equation can be explained by the fact that the hydrogen molecule dissociates into atoms. Thus, F. F. Vol' kenshtein (3) states: "Adsorbed hydrogen is, as a rule, not in the molecular but in the atomic state."

The rate of the surface reaction between adsorbed hydrogen and the oxygen of the oxide is directly proportional to the concentration of hydrogen on the adsorbent surface, since the oxygen concentration may be considered a constant quantity. If this stage proves to be rate-limiting, then the overall rate of the reduction process will be proportional to the hydrogen pressure to the power 1/2, as we have found experimentally.

It should be noted that an analogous dependence was established in the case of the reduction of lead, cadmium, and tin oxides by hydrogen (4). Sections

sections of the curves on which the rate decreases with an increase in the percentage of reduction correspond to the gradual transition of U_3O_8 to the phase $UO_{2.6\pm x}$ with the minimum oxygen content at the given temperature. At this time no new phase is formed, and the decrease in rate can be explained by a decrease in the oxygen concentration in the solid phase.

Fig. 3. Dependence of the process rate on the degree of reduction at different temperatures

Fig. 4. Dependence of the process rate on the degree of reduction at different hydrogen pressures

The second horizontal sections in the curves of Figs. 3 and 4 correspond to reduction of the $UO_{2.6\pm x}$ phase with the minimum oxygen content to the tetragonal phase.

The limiting stage at this stage of reduction proves to be adsorption of hydrogen on the oxide surface. This is indicated, in particular, by the fact that the total reduction rate is proportional to the hydrogen pressure.

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