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Abstract

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THE EFFECT OF THE RADIOACTIVITY OF MOLYBDENUM ANHYDRIDE ON THE RATE OF ITS EVAPORATION

In recent years a number of studies have appeared devoted to the effect of radioactive radiation from solids on heterogeneous physicochemical processes occurring with their participation ($^{1-9}$). In particular, an effect of the radioactivity of the solid phase on the kinetics of dissolution and on the solubility of certain sparingly soluble substances has been noted ($^{10-12}$). In the present work, the evaporation rate of preparations of molybdenum anhydride containing various amounts of the radioactive isotope Mo^{99} ($T_{1/2} = 68.3$ h) was studied. The latter emits high-energy β-particles, $E_{\max} = 1.23$ MeV (85%).

Samples of molybdenum anhydride with specific radioactivities from 1.0 to 28.0 mCi/g were obtained under strictly identical conditions. A mixture of calculated amounts of the initial highly active preparation and nonradioactive MoO_3 was converted by the action of NH_4OH into ammonium molybdate, the solution of which was evaporated, and the dry residue was calcined with the addition of small amounts of nitric acid to prevent reduction of hexavalent molybdenum by ammonia. The resulting MoO_3 was mixed with small additions of Nb_2O_5 and ZrO_2 and, for purification from radiochemical impurities, was sublimed at 850° in a weak stream of air. To study the evaporation rate, preparations of molybdenum anhydride with particle size 0.25-0.5 mm, obtained by sieving through appropriate sieves, were used. Samples of nonradioactive MoO_3 were prepared in an analogous manner.

The apparatus for studying the evaporation rate (Fig. 1) consists of a vertically arranged quartz tube 1, having in the middle an inner ground joint 2, into which a quartz crucible of special design 3 is inserted. At the top the tube terminates in a hermetically closing beryllium window 4, used for external irradiation of the MoO_3 preparation by electrons in separate experiments during the experiment, and also for placing the working crucible into tube 1 and removing it from it. A tube 5 for supplying air to the apparatus is soldered to the side of the upper part of the reaction tube. At the bottom of the reaction tube there is an inlet 6 for thermocouple 7, which extends under the bottom of the crucible. The reaction tube terminates below in a vapor trap 8, cooled by means of liquid nitrogen. Quartz crucible 3 is a cylinder that passes in its lower part into a truncated cone. On the outside of the cone there is a ground joint by which the crucible is fixed in the reaction quartz tube. The bottom of the crucible is a coarse-pored quartz filter. The reaction quartz tube is placed in an electric furnace 9.

The **experimental procedure** was as follows. A weighed portion of molybdenum anhydride preparation of about 300 mg was spread uniformly over the bottom of the crucible, which was placed in the reaction tube. At a temperature of 700°, maintained by a thermoregulator with an accuracy of ±2°, through the powder layer

Table 1

Evaporation rate of MoO_3 as a function of the specific radioactivity of the preparations

Preparation No.	Specific radioactivity, mCu/g	Amount evaporated in 2 h of MoO_3 (mean), g	Observed deviation from mean, %	Preparation No.	Specific radioactivity, mCu/g	Amount evaporated in 2 h of MoO_3 (mean), g	Observed deviation from mean, %
1	Inactive	0.1240	5.0	7	5.0	0.1148	3.5
2	1.0	0.1240	6.0	8	7.0	0.1458	5.0
3	2.0	0.1240	5.1	9	8.4	0.1514	7.0
4	2.5	0.1217	6.0	10	10.0	0.1556	4.5
5	3.0	0.1184	5.0	11	14.0	0.1600	5.0
6	4.0	0.1125	5.0	12	20.0	0.1623	6.0
				13	28.0	0.1669	6.0

A current of dry air was passed over the MoO_3 at a rate of 8 ml/min. Every 15 min the crucible was removed from the tube, cooled, and weighed.

The **results** of the experiments performed are presented in Fig. 2. All the data were obtained from several parallel experiments. For preparations with the same specific radioactivity, the evaporation rate of MoO_3 is a practically constant quantity. It varies depending on the level of radioactivity and, in a number of cases, differs substantially from the evaporation rate of a nonradioactive sample.

The data shown in Fig. 3 and in Table 1 indicate the dependence of the amount of MoO_3 evaporated in 2 hours on the specific radioactivity of the preparations studied. It may be concluded that, at specific radioactivities up to 2.5–3 mCu/g, the MoO_3 samples have an evaporation rate identical to that of the nonradioactive preparation. At specific radioactivities from 2.5 to 4 mCu/g, a certain decrease in the evaporation rate is observed. In the range of radioactivity values from 4 to 9 mCu/g, a rapid increase in the evaporation rate occurs, slowing down with further increase in the specific radioactivity.

Fig. 1. Diagram of the apparatus for studying the evaporation rate

Figure 1: Fig. 1. Diagram of the apparatus for studying the evaporation rate

Figure 2

Figure 2: Figure 2

P. and M. Curie (^{13}) had already discovered the appearance of electric charges on the surface of radioactive preparations as a result of their emission of β-particles. One of us, together with co-workers (^{10}), noted that this phenomenon can substantially affect the dissolution processes of radioactive substances. The charges formed on the surface of a sample during radioactive irradiation must also influence evaporation processes. Indeed, the appearance of charges should lead to enhanced interaction between the surface of the solid and the vapor molecules located near the phase boundary. In MoO_3 molecules, the central molybdenum atom is surrounded by three negatively charged oxygen atoms. Therefore, the positive charge of the surface of solid MoO_3, caused by the continuous emission of β-particles, should hinder the transition of MoO_3 molecules into the vapor.

Fig. 1. Diagram of the apparatus for studying the evaporation rate

To test this assumption, the following experiment was carried out. Into a crucible containing a radioactive MoO_3 sample, a grounded platinum wire was introduced directly into the preparation. The results of the measure-

measurements of the evaporation rate under these conditions are shown in Fig. 4. The minimum, clearly visible in Fig. 3, disappears in this case. The curve of the dependence of the amount of evaporation of MoO_3 on the specific radioactivity of the preparation in this case has a smoother course than is observed without charge removal. Thus, it should be considered established that the charge arising on the surface of MoO_3 is indeed the cause of the decrease in the evaporation rate in the range of specific radioactivities 2.5-4 mCu/g.

Fig. 2. Evaporation rate of MoO_3 preparations of different specific radioactivity. 1 —nonradioactive MoO_3 and preparations with specific radioactivity 1.0 and 2.0; 2—3.0; 3—4.0; 4—5.0; 5—7.0; 6—8.4; 7—14.0; 8—28 mCu/g

It may be assumed that the increase in the evaporation rate of MoO_3 with increasing specific radioactivity above 4-5 mCu/g is already to a considerable extent dependent on radiation phenomena in the gas phase. A powerful flux of β-particles ionizes the evaporating MoO_3 molecules and causes, in particular, the formation of MoO_3^+ ions, which promotes their repulsion from the surface. In addition, radioactive radiation strongly changes the structure of the crystal surface, promoting its development. Electron-microscopic photographs showed a large difference in the form of the surface of radioactive and nonradioactive MoO_3 preparations (14). The latter have an even and smooth surface. In the case of radioactive samples, beginning precisely with a specific activity of

Figure 3

Figure 3: Figure 3

Figure 4

Figure 4: Figure 4

4 mCu/g and higher, the crystal surface of MoO_3 begins to contain many irregularities, projections, and depressions, the number of which increases with increasing specific radioactivity.

Fig. 3. Dependence of the amount of evaporation of MoO_3 on the specific radioactivity of the preparations

Fig. 4. Influence of surface charge removal on the evaporation rate of MoO_3. 1 —experiments without charge removal, 2 —experiments with charge removal

It should be noted that the evaporation rate of MoO_3 under external irradiation of the preparation by a flux of electrons with an energy of 800 keV practically begins to increase only at dose rates on the order of 10^{16} eV/g·sec. The influence of radioactive radiation is observed already at considerably lower dose rates.

Thus, using MoO_3 preparations as an example, it has been shown that the kinetics of evaporation of radioactive solids depends on the level of their radioactivity. In this, several factors play an essential role: the surface charge

surface, arising from the emission of charged particles, a change in the character of the surface of the crystals under the action of radiation, and radiation phenomena in the gas phase.

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