Chemistry

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Abstract

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VAPOR PRESSURE OF RHENIUM DISULFIDE, DIOXIDE, AND TRIOXIDE

Recently, interest in rhenium has increased considerably in connection with the expansion of the fields of application of rhenium and of its raw-material sources ([1–3]). The study of the possibility of concentrating and isolating rhenium during the pyrometallurgical processing of sulfide materials requires knowledge of the physicochemical properties of its compounds. The vapor pressure of ReS_2, ReO_2, and ReO_3 was studied by the effusion method ([4,5]). Other data on the vapor pressure of the indicated rhenium compounds are absent from the literature.

In the present work we give the results of a study of the saturated vapor pressure of rhenium disulfide, dioxide, and trioxide by the effusion method. The starting substances were prepared in evacuated quartz ampoules according to a known procedure ([6]). The metallic rhenium used for their preparation contained 0.0005% Al, 0.009% Fe, 0.008% Ca, 0.022% K, 0.001% Cu, and 0.005% Mo. In the synthesis of rhenium disulfide, sulfur of special purity was used.

The ReS_2 obtained contained 73.88% rhenium and 25.20% sulfur, with theoretical contents of 74.33% Re and 25.61% S. The rhenium oxides had the following composition: ReO_2, 85.93% rhenium (theoretically 85.34% Re), and ReO_3, 79.54% rhenium (theoretically 79.51% Re). The materials were ground to the minus 0.1 mm fraction.

The investigation was carried out in an apparatus whose difference from that described earlier ([7]) consisted in the fact that the thermocouple was introduced into the reaction zone, directly to the sample, by means of a water-cooled ground joint. After a high vacuum had been reached ($1 \cdot 10^{-5}$—$1 \cdot 10^{-6}$ mm Hg), the effusion vessel with the sample of material was placed in the isothermal zone of the furnace by an electromagnet.

A small quartz ampoule served as the effusion vessel; the orifice at the blown-out end of the ampoule was made by grinding. The edges of the orifice had insignificant thickness, which made it possible to take the correction coefficient in the calculation formula as equal to unity ([8]). The area of the ampoule orifice was measured on a metallographic microscope.

Verification of the experimental apparatus and evaluation of the selected method

Figure 1

Figure 1: Figure 1

for making the orifices in the ampoules and determining their area were carried out by measuring the known value of the vapor pressure of potassium chloride at 618—800°.

The results obtained, which agree well with the data of other authors, made it possible to establish that the chosen method of investigation provides reliable results.

The equilibrium vapor pressure was calculated by the Knudsen formula, transformed into the form:

$$\lg P = \lg \Delta q + \frac{1}{2}\lg T - \frac{1}{2}M - \lg a - \lg \tau + \overline{4}.4558, \tag{1}$$

where P is the vapor pressure in mm Hg, Δq is the weight of the evaporated substance in mg, T is the absolute temperature, a is the area of the orifice in cm^2, τ is the duration of the experiment in minutes, and M is the molecular weight of the substance in the vapor.

The sizes of the holes in the ampoules used for each substance are given in the figures. A small change in the size of the hole had no effect on the change in the rate of vapor effusion per unit area of the hole, which indicates that the equilibrium vapor pressure in the ampoules was reached. Fluctuations in the furnace temperature during the experiment did not exceed $±$3°. The ampoule with the sample was weighed with an accuracy of $±$0.02 mg.

Figure 1 gives experimental data on determining the vapor pressure of rhenium disulfide in the range 505-700°. The values obtained are in close agreement with the data of previous investigators (^{4}). The dependence of the saturated vapor pressure of ReS_2 on temperature can be expressed by the equation:

$$\lg P = -\frac{4976}{T} + 3.214 \tag{2}$$

Fig. 1. Change in the vapor pressure of rhenium disulfide with change in temperature. 1 —according to our data: I —$a = 1.813 \cdot 10^{-3}$; II —$a = 3.64 \cdot 10^{-3}$; III —$a = 9.961 \cdot 10^{-4}$; 2 —according to data of (^{4})

(P in millimeters), whence the change in the isothermal-isobaric potential is

$$\Delta Z_T^0 = 22665 - 1.523 \cdot T.$$

Figure 2

Figure 2: Figure 2

Figure 3

Figure 3: Figure 3

The enthalpy of sublimation is equal to 22.66 kcal/mole. An estimate of the magnitude of the dissociation pressure of rhenium disulfide at 500-700°, according to the data of P. A. Isakova and V. D. Ponomarev (4), showed that the vapor pressure of sulfur at 500° is 0.009% and at 700° 3.2% of the equilibrium pressure, which is below the experimental error.

Fig. 2. Change in the vapor pressure of rhenium dioxide with change in temperature. 1 –according to data of (5); 2 –according to our data: I $-a = 3.135 \cdot 10^{-3}$; II $-a = 2.76 \cdot 10^{-3}$; III $-a = 6.578 \cdot 10^{-4}$

Fig. 3. Change in the vapor pressure of rhenium trioxide with change in temperature. 1 –according to data of (5); 2 –according to our data: I $-a = 3.20 \cdot 10^{-3}$; II $-a = 1.023 \cdot 10^{-3}$; III $-a = 3.02 \cdot 10^{-4}$

The results of measurements of the saturated vapor pressure of rhenium dioxide and trioxide are shown in Figs. 2 and 3, from which it is evident that our data differ significantly from the literature values obtained by the transpiration method. It should be noted that the maximum relative error of the effusion method in the present study was 5-6%. As for the transpiration method, in addition to errors characteristic of this method (9), when working with substances that are readily oxidized upon heating, to which ReO_2 and ReO_3 belong, an additional error may arise due to insufficient purification of technical nitrogen from oxygen and water vapor.

The saturated vapor pressure of ReO_2 was studied in the range 650-785°; above 785° disproportionation of rhenium dioxide becomes noticeable.

The dependence of $\lg P$ on temperature is described by the equation:

$$\lg P = -\frac{14347}{T} + 11.65 \tag{3}$$

(P in millimeters). The isothermal-isobaric sublimation potential is $\Delta Z_T^0 = 65637 - 40.11 \cdot T$, and $\Delta H_T^0 = 65.64$ kcal/mol.

For rhenium trioxide in the interval 325–420°, the dependence of $\lg P$ on temperature is expressed by the following formula:

$$\lg P = -\frac{10882}{T} + 15.16, \tag{4}$$

whence $\Delta Z_T^0 = 49785 - 56.1 \cdot T$ and $\Delta H_T^0 = 49.78$ kcal/mol.

The vapor pressure of ReO_2 and ReO_3, calculated from formulas (3) and (4), reaches 760 mm Hg at temperatures of 1363 and 614°, respectively.

Consequently, during the oxidizing roasting of sulfide concentrates, rhenium trioxide, like the heptoxide, will pass into the gas phase.

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