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Abstract

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STUDY OF THE VAPOR PRESSURE OF SOME THALLIUM COMPOUNDS

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In the present work we give the results of measurements of the vapor pressure of thallium sulfide and its oxide, used for the preparation of thallium sulfide photocells (1,2). Data on the vapor pressure of these compounds and on their thermodynamic functions are absent from the literature.

The vapor pressure was determined by the Knudsen method with the aid of the apparatus shown schematically in Fig. 1. The principle of operation of the apparatus and the course of the measurements are analogous to those described in (3). This apparatus, unlike that described in (3), makes it possible, without breaking the vacuum, to change the condensation caps 14: after carrying out each experiment the cooling system 13 is raised by lever 15 with the aid of an electromagnet, and the next cap is brought into the working position by mechanism 16, also actuated by an electromagnet. In this way it is possible to carry out 10 experiments at different temperatures without breaking the vacuum.

To carry out the experiment we synthesized Tl_2S and Tl_2O_3. In the synthesis of the compound Tl_2S (4), distilled thallium and sulfur sublimed three times were placed in stoichiometric ratio in an ampoule, in which a vacuum of the order of 10^{-5} mm Hg was then created. The ampoule was then slowly heated to 450–460°C and kept at this temperature for a long time. The conversion of metallic thallium into Tl_2O_3 was carried out in a stream of oxygen at 200°C. As a thallium “indicator” in the distillation, the radioactive isotope Tl^{204} with a half-life of 2.71 years, emitting electrons with an energy of 0.765 MeV, was used.

In the case of Tl_2S, both components were taken radioactive (Tl^{204} and S^{35}, emitting electrons with an energy of 0.169 MeV), since such an arrangement of the experiment makes it possible to calculate the saturated vapor pressure for both components. The radiation intensity was measured on a type B apparatus

Fig. 1. Schematic of the apparatus.

Figure 1: Fig. 1. Schematic of the apparatus.

with an end-window counter with a thin mica window. The vapor pressure was calculated by the formula

$$P = 17{,}14\,\frac{I}{KAtI_0}\sqrt{\frac{T}{M}},$$

where I is the radiation intensity of the condensed substance (counts/min); I_0 is the specific activity of the evaporated substance (counts/min $\cdot$ g); K is the Clausing coefficient; A is the area of the orifice (cm^2); t is the exposure time (sec.); T is the absolute temperature; M is the molecular weight of the substance in the vapor state.

Extrapolation of the experimentally obtained dependence of $\lg P$ on reciprocal temperature to a pressure of 760 mm Hg gives a boiling-point value considerably lower than that of Tl_2O_3. The boiling point of distilled

the substance turned out to be close to the boiling point of Tl_2O. This indicates the transition of Tl_2O_3 into Tl_2O, which is noted in the literature ([5]). Therefore the obtained values of the vapor pressure were recalculated for Tl_2O.

The results of measurements of the saturated vapor pressure of Tl_2O are given in Fig. 2. From the slope of the curve, the heat of sublimation was calculated; it proved to be equal to 30.21 kcal/degree $\cdot$ mol.

Fig. 1. Schematic of the apparatus. *1* –glass bell jar, *2* –iron plate, *3* –rubber gasket, *4* –base, *5* –quartz tube, *6* –furnace, *7* –crucible, *8* –platinum foil, *9* –calibrated orifice, *10* –cover, *11* –lever, *12* –thermocouple, *13* –cooling system, *14* –condensation caps, *15* –lever for raising the cooling system, *16* –mechanism for replacing the caps.

Processing of the experimental data by the least-squares method leads to the following dependence of $\lg P$ on temperature:

$$\lg P\ (\text{mm}) = 11.51 - \frac{6612}{T}.$$

Solving this equation for the pressure $P = 760$ mm gives $T = 766°$K, which corresponds to the value of the boiling point of Tl_2O given in ([6]). The total intensity of the radiation of Tl_2S was measured with an aluminum filter and without it. The intensity of the radiation of the components was determined by calculation ([7]). Such determination is possible because the energies of the electrons emitted by thallium and sulfur differ severalfold.

Fig. 2. Change in the logarithm of the saturated-vapor pressure of Tl_2S (a) and Tl_2O (b) as a function of reciprocal temperature

Figure 2: Fig. 2. Change in the logarithm of the saturated-vapor pressure of Tl_2S (a) and Tl_2O (b) as a function of reciprocal temperature

The results of measurements of the vapor pressure of Tl_2S are given in Fig. 2. The dependence of $\lg P$ on temperature for Tl_2S shows that the saturated-vapor pressures obtained from both components fall on a single straight line. Such agreement shows that Tl_2S does not decompose upon evaporation. The dependence of the saturated-vapor pressure $\lg P$ on temperature can be expressed by the following formula:

$$\lg P \text{ (mm)} = 7.354 - \frac{4484}{T}.$$

The sublimation energy proved to be equal to 20.45 kcal/deg · mol.

The heats of sublimation of Tl_2S and of the individual components entering into the composition of this compound differ greatly. This makes it possible to assume that Tl_2S can be purified by vacuum sublimation.

Fig. 2. Change in the logarithm of the pressure of the saturated vapors of Tl_2S (*a*) and Tl_2O (*b*) as a function of reciprocal temperature.

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