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Abstract

Full Text

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STUDY OF THE VAPOR PRESSURE OF SATURATED SELENIUM VAPORS BELOW THE MELTING POINT

(Presented by Academician V. N. Kondrat' ev, March 1, 1958)

The use of radioactive isotopes makes it possible to study vapor pressure below the melting temperature of a substance, which permits determination of the values of thermodynamic functions in these temperature intervals.

In the present communication we give the results of experiments on studying the vapor pressure of the saturated vapor of solid selenium in the temperature range 86-200° C. The measurements were carried out by the Knudsen method, using a radioactive isotope of selenium.

As is known (^1), the Knudsen method is based on the effusion of vapor through a small opening into a vacuum.

The apparatus used in our experiments for determining the vapor pressure of saturated selenium vapor (see Fig. 1) consists of a glass bulb 1, inside which a furnace 2 is installed for heating the crucible 3 with the substance under investigation.

Fig. 1. Diagram of the apparatus for determining the vapor pressure of saturated vapors

About 0.1 g of the substance under investigation is placed in the crucible, after which it is sealed at the top with platinum foil, in the center of which there is a round opening 0.359 mm in diameter. The shape and size of the opening were checked on an IZA-2 comparator. The crucible was made of graphite. The inner surface of the crucible was polished. An opening was bored in the bottom of the crucible for the thermocouple 4 to be brought out, so that the distance between the end of the thermocouple and the substance under investigation would be

Fig. 2. Plot of the dependence of $\lg p$ on reciprocal temperature: a –from ([3]), –from ([4]), –from ([5]), –our data

Figure 2: Fig. 2. Plot of the dependence of $\lg p$ on reciprocal temperature: a – from ([3]), –from ([4]), –from ([5]), –our data

minimal. To ensure rapid saturation of the vapor, the internal dimensions of the crucible were chosen as $h = 5$ mm, $d = 5$ mm.

To prevent evaporation of the substance during heating and cooling, the opening of the effusion chamber was closed with a lid 5, actuated by a lever 6 with the aid of an electromagnet 7. For tight closing of the lid, the lever is provided with a spring 8. To collect the evaporating substance, a condensation cap 9, filled with liquid air, was placed above the effusion chamber. All parts are mounted on a stainless-steel base 10.

For bringing the thermocouple leads out of the furnace, ground joint 11 is used. In order to eliminate the possible influence of the crystallization process during evaporation on the experimental results, the radioactive selenium isotope $T_{1/2} = 127$ days was subjected, before the experiments, to crystallization at a temperature of 135° for one hour, and then at a temperature of 205–210° for 15 hours (the crystallization was carried out in a vacuum of the order of 10^{-3} mm Hg). During this time the selenium crystallized completely.

The crystallized selenium was ground to a fine powder and placed in the effusion chamber. The purity of the radioactive selenium was checked by its half-life, which agrees well with the literature data ([2]). A vacuum of the order of 10^{-5}–10^{-6} mm Hg was then created in the apparatus.

Fig. 2. Plot of the dependence of $\lg p$ on reciprocal temperature: a –from ([3]), –from ([4]), –from ([5]), –our data

After the rarefaction had been attained, the furnace, supplied with stabilized current, was switched on, and the crucible was heated to the required temperature. To ensure complete saturation of the vapor before opening the lid, the crucible was held at this temperature for one hour.

The temperature was measured with a chromel-alumel thermocouple by means of a potentiometer. The tightness of the lid was also checked. For this purpose the crucible was heated to 150°, and then, without opening the lid, after cooling, the activity of the bell jar was checked. In this case the activity did not exceed the natural background.

During measurement the crucible lid was opened for a definite time, and the selenium vapors emerging through the effusion orifice condensed on the bell jar. After the furnace had cooled to room temperature, air was admitted into the apparatus, the bell jar was removed, and the condensed selenium was washed off with a carrier, which was a solution of inactive selenium in sodium sulfide.

The activity of the wash was counted on apparatus B, and by comparison with a previously prepared standard the amount of selenium was determined.

Knowing the amount of evaporated selenium g for a given exposure t (sec.), we calculated the vapor pressure of saturated selenium vapor by the following formula ([1]):

$$p = 17,14\,\frac{g}{kAt}\sqrt{\frac{T}{M}},$$

where A is the area of the orifice, cm^2, k is the Clausing coefficient, T is the absolute temperature, and M is the molecular weight of the evaporating substance in the vapor state.

Following ([1]), in calculating the saturated vapor pressure of selenium, the molecular weight of the latter was taken to be equal to six times the atomic weight. The graph in Fig. 2 gives the results of our experiments, as well as the data of other authors who studied the vapor pressure of saturated selenium vapors in different temperature regions ([3–5]).

It should be noted that the rectilinear character of the dependence of $\lg p$ on $1/T$ proves that selenium vapors in equilibrium with the solid phase in the temperature range 86–200° consist of 6-atom molecules.

According to the experimental results, the dependence of the vapor pressure of selenium vapors on temperature is expressed by the following equation:

$$\lg p\,(\text{mm}) = 8,479 - \frac{5061}{T}.$$

The results of works ([3,4]) and our data fit well on a single straight line, which indicates the reliability of both. The data of work ([5]) are clearly underestimated.

In conclusion, the authors express their gratitude to Corresponding Member of the Academy of Sciences of the Azerbaijan SSR G. B. Abdullaev for suggesting the topic and for his guidance.

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