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Abstract

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THE SATURATED VAPOR PRESSURE OF LIQUID ANTIMONY AND ITS ASSOCIATION STATE

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The saturated vapor pressure of solid antimony was determined by Niwa and Iosiyama (1) and later by Nesmeyanov and Iofa (2). Studies relating to liquid antimony are described in a number of works (3–8), of which only the first three give original experimental data.

In calculating vapor-pressure values in works (1, 2, 5), it was assumed that the vapor consists of Sb_4 molecules and has a constant molecular composition throughout the region investigated; this was regarded by some authors as being indicated by the linear dependence of $\log P$ on $1/T$. However, such a dependence cannot serve as a definitive criterion for assessing the absence of dissociation in saturated vapors. An example is provided by the behavior of saturated selenium vapors, whose association states change with temperature while the indicated linear dependence is nevertheless preserved (9, 10). It is easy to show that the linear dependence is preserved when the heats of evaporation and dissociation are equal, or when the vapor pressures of the pseudocomponents are equal, if equilibrium between them is established in both phases.

At high temperatures antimony vapors are substantially dissociated (11), and Eucken assumes (12) that in this region a curvature of the dependence under consideration should occur, since only in this case can the data (4) be reconciled with the reliably determined boiling temperature (13).

We proposed a radiometric method for determining vapor density, applicable in the presence of γ-radioactive isotopes. It is similar to the method of Dayton and Kimberly (14), used to determine the vapor elasticity of white phosphorus. By this method we determined the densities of antimony vapor.

Two vessels are placed in furnaces, of which one is thermostated at a specified temperature T_1, while the second, containing the vessel into which the substance under study is introduced, is at a variable temperature T_2. This temperature is always lower than T_1 and lies in the region of saturated-vapor pressure. The

Fig. 1

Figure 1: Fig. 1

vessels are connected by a heated capillary, whose cross section ensures, at established equilibrium, the absence of a noticeable pressure difference at the different vessel temperatures caused by the superposition of the Knudsen effect. If the vapor-pressure curve is known, as well as the temperature and volume of the vessel in the first furnace, then the vapor density in it can be established remotely, by radiometric determination of the mass. In this way it is easy to measure isotherms of vapor densities. When the second furnace is thermostated and the temperature of the first is varied continuously, the measurements are carried out isobarically.

When working with a predetermined mass, it is necessary in both furnaces to maintain conditions corresponding to the unsaturated state of the vapors, and to measure the activities in the vessels simultaneously. One of the vessels must be at a constant temperature corresponding to practically complete association or dissociation. In such a case the pressure can be determined by lowering the temperature in one of the vessels to the saturated state, which is detected by a sharp increase in radioactivity.

The investigations were carried out according to the first variant. The work used furnaces similar to the large furnace described earlier (^{10,15}), placed in lead chambers with walls 2 cm thick. The volume of the quartz vessel in the first furnace was 55.973 ml. The volume of the part of the capillary whose radiation reached the counter was 1.119 ml. The temperature was measured by calibrated platinum-platinum-rhodium thermocouples, by the compensation method, with an accuracy of ±1°. In each of the furnaces the measurement was made at six points by moving the thermocouples in sheaths soldered into the vessels, and on the capillary in a quartz sheath. The capillary and sheath were wound together with platinum heating wire and well thermally insulated. The axial temperature gradient in the furnace from the center to the end did not exceed 2°. The temperature at the capillary throughout the entire experiment (recording a series lasted up to 30 hours) was $1000° \pm 10°$. The furnaces were shifted relative to one another so that radiation from the vessel in the second furnace did not reach the counter installed in front of the hinged door of the chamber opposite an opening that corresponded exactly to the position of the vessel in the first furnace. The counter was placed in a thermostat with a built-in hollow tube to prevent changes in the intensity of the γ-rays by a thick layer of water.

Fig. 1. 1 –$T_1 = 950°$; a –upward run, b –downward run. 2 –$T_1 = 900°$, v –upward run. When decays are taken into account and recalculation is made to identical T_1, the straight lines coincide.

The radioactive antimony was diluted with a twenty-fold amount of spectrally pure antimony, containing $1 \cdot 10^{-5}\%$ impurities, and after fivefold sublimation in high vacuum was introduced by distillation into the vessel placed in the second furnace. After distillation the line to the high vacuum was sealed off. The total activity of the amount loaded was 2 mCi.

We recorded one preliminary and three main series of experiments, at a temperature of the first furnace of 900 and 950°. Radiometric measurements were made both during an upward and a downward temperature run. The points agreed well with one another. Radioactivity readings were taken each time for five minutes.

The results obtained are presented in Fig. 1 in coordinates $\log i - 1/T$. They correspond to experiments 2 ($T_1 = 950^\circ$) and 4 ($T_1 = 900^\circ$). The points fit well on straight lines with identical slopes.

If $\log P$ is a linear function of $1/T$, then one may write

$$\log i = -\frac{\lambda}{4.576} T + \text{const} + \log \frac{A}{KR} + \log \frac{V_\nu}{T_1} = -\frac{\lambda}{4.576} T + \text{const}' + \log \nu,$$

where i is the activity, K is the coefficient for conversion to mass, A is the atomic weight, V is the volume of the vessel, T_1 is the constant temperature in the first furnace, R is the gas constant expressed in the corresponding units, and ν is the total degree of association.*

For dissociation of the type $A_2 \rightleftarrows 2A$, $\nu = 2 : (1 + X)$, where X is the degree of dissociation. According to the law of mass action equation,

$$X = \left[K_p : (4P + K_p)\right]^{\frac{1}{2}}.$$

It follows from this that at $K_p \gg 4P$ and $K_p \ll 4P$, ν depends linearly on $1/T$. The intermediate region represents a curvilinear dependence, except in those cases when ν can be expressed as a power function of P. Then $\log \nu$ is linearly related to $\log P$ and, consequently, to $1/T$. This leads to preservation of the linear dependence of $\log i$ on reciprocal temperatures over the entire pressure interval, but with a change in slope, which we also observed in work with selenium.

After completion of all the experiments, part of the antimony was distilled into the vessel in the first furnace, the capillary having been melted off at a place from which radiation did not reach the counter, and the standard radioactivity was established at 950°. The cooled vessel was then opened and the antimony was transferred into solution by the method of Chervyak (^{16}). After dilution, the activity of an aliquot portion of the solution was determined, this being done in a lead house. This activity was compared with the activity of a solution prepared by the same method from an accurately weighed amount of antimony taken from the vessel in the second furnace. The antimony sample was 31.84 mg ± 9.12%. Taking into account corrections for decay by the day of the last analyses, 1000 counts in our experiments corresponded to 1.8795 ± 0.0218 mg of antimony.

The measurements of all the experiments were recalculated to activity in order to establish the standard radioactivity. The results were expressed by formulas for the linear dependence of $\log m$ on reciprocal temperatures, obtained by the method of least squares.

When recalculating the data of experiments carried out at 900 and 950°, complete agreement was obtained at one temperature, which can occur only for identical values of ν at these temperatures. Identical values of ν at two different temperatures can occur only in the absence of dissociation. This unambiguously indicates that the unsaturated, and consequently also the saturated, vapors of antimony at temperatures up to 1000° consist practically only of Sb_4 molecules.

The obtained dependences of $\log m$ on $1/T$ were recalculated into dependences of $\log P$ on reciprocal temperatures. The average value for three series gives

$$\log P = -\frac{6403.35}{T} + 6.1938.$$

The latent heat of vaporization according to this equation is 29.30 ± 0.60 kcal. This value differs from the value determined in work (⁵) by 2.37 kcal. The latent heat of fusion, as the difference between the latent heats of evaporation and sublimation, according to the equations of works (¹) and (²), respectively, is 14.88 ± 0.60 and 19.79 ± 0.60 kcal. The latter value agrees well with reliable literature data, namely 19.08 kcal.

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* The formula used by us is valid only in the case of equality of T_1 and the temperature in the capillary (T_3). If they differ, the term $\log V_\nu / T_1$ must be replaced by $\log(T_3 V_1 \nu_1 + T_1 V_3 \nu) : T_1 T_3$. We neglected this refinement, taking into account the small correction thereby introduced.

per mole of Sb_4 (¹⁷). Extrapolation to the triple point gives a value of 0.1278 mm. From the equations in works (¹) and (²), and also from the equation derived by us from the data of (⁵), we obtain 0.1347, 0.2602, and 0.1772.

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