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Abstract

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MEASUREMENT OF THE SATURATED VAPOR PRESSURE OF SOLID BISMUTH BY THE ISOTOPIC-EXCHANGE METHOD

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In the present work, the pressure of the saturated vapor of solid bismuth has been measured for the first time. The results of measurements of the saturated-vapor pressure over the solid metal make it possible to calculate a number of thermodynamic functions, knowledge of which is at present necessary for the thermal design of nuclear power stations in which bismuth may be used as a heat-transfer medium.

The saturated-vapor pressures of liquid bismuth have been measured by a number of authors [1–5], and there is no agreement among the data of the various experimenters. Evidently, among the low-temperature measurements, the results of A. Granovskaya and A. Lyubimov [3] should be considered the most reliable. The literature data for liquid bismuth do not permit an exact calculation of the saturated-vapor pressures over the solid metal. Nevertheless, it may still be assumed that near the melting point the saturated-vapor pressures of solid bismuth should be 10^{-8}–10^{-11} mm Hg (see Fig. 3). Such low saturated-vapor pressures can obviously be measured only by applying the Langmuir method [6] and the isotopic-exchange method [7,8].

Fig. 1. Exchange chamber and heating furnace

The measurement of the saturated-vapor pressures of solid bismuth was carried out by the exchange method, using Bi^{210} (RaE) as the radioactive indicator.

RaE was isolated from old emanation tubes (3 curies of radon) and purified from RaD and polonium.

The measurements were carried out in a vacuum apparatus containing the exchange chamber, heated by a special furnace.

The exchange chamber 2 (Fig. 1) was a steel cylinder that was cut into two

Fig. 2. Vacuum apparatus for measuring low vapor pressures

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Fig. 3. Values of the saturated vapor pressures of liquid and solid bismuth

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halves fastened together by four screws. Both halves of the chamber had cylindrical recesses into which two disks 8 with an applied layer of metallic bismuth were placed. The disks were firmly secured in the chamber by means of two molybdenum rings 9. The chamber had a longitudinal through-slot, through which

a shutter 6, made of molybdenum, moved freely. The shutter had stops and one opening, the diameter of which exactly coincided with the inner diameter of the molybdenum rings. Heating of the exchange chamber was carried out by a furnace.

The furnace (Fig. 1) was made of brass and consisted of a base and a cover 2, which were joined together by the outer cylinder 10. The base and cover of the furnace had through openings through which the shutters 6 moved freely. The furnace was heated by a nichrome spiral 3, which was insulated from the metal parts by quartz cylinders 1. The temperature of the chamber and of the exchanging specimens was measured to an accuracy of 0.5° with a chromel-alumel thermocouple.

The vacuum apparatus (Fig. 2) was made of molybdenum glass and consisted of a base and a removable ground joint. In the base of the apparatus was mounted the furnace 1 with the exchange chamber, and the system 2–4–5 was placed, making it possible, with the aid of external magnets, to move the shutter without disturbing the vacuum in the apparatus. Heating of the furnace was carried out through molybdenum wires 3. In the ground joint 6 a thermocouple was fastened to a rod.

Fig. 2. Vacuum apparatus for measuring low vapor pressures

Samples for exchange were prepared by electrolytic deposition on nickel disks of active or inactive metallic bismuth. Deposition was carried out from a nitric-acid solution at a current density of 10 ma/cm^2 and a bath voltage of 2 V. In every case, specimens were prepared with the same thickness of the metallic bismuth layer.

Fig. 3. Values of the saturated vapor pressures of liquid and solid bismuth: 1 –according to data of (3); 2–according to data of (5); 3–according to data of (2); 4–according to data of (4); *a*–our data, *b*–data of (3)

Conduct of the experiment. Two nickel disks with a deposited layer of metallic bismuth, one of which contained RaE, were placed in the corresponding recesses of the exchange chamber. The specimens were first annealed in vacuum in order to create a surface of the metal in equilibrium with respect to the vapor. The exchange chamber was assembled. The shutter was set in a position in which it separated the specimens. The ground joint was placed on the base of the apparatus, and the apparatus was evacuated to a high vacuum ($5 \cdot 10^{-6}$–10^{-5} mm Hg). The furnace was heated to the prescribed temperature, and the shutter was lowered with the aid of external magnets. At the same time a stopwatch was started. The opening of the shutter coincided with the inner openings of the molybdenum rings, owing to which contact between the specimens was effected. After a certain time had elapsed

the shutter was raised and the stopwatch was switched off. Special experiments showed that, with the lid closed during heating and cooling of the chamber, no penetration of radioactive bismuth vapors into the space with the nonradioactive metal occurs. After the experiment was completed, the previously inactive specimen was placed in a special holder, and its activity was measured with an end-window counter. The activity of each specimen was measured over several weeks; in this way it was established that RaD was absent from the preparations. The activity of the preparations was compared with the specific activity, which was determined by measuring the activity of standards containing a known quantity of the initial radioactive bismuth.

Since the exposures were small, the saturated vapor pressures of bismuth were calculated from the following formula, which does not take into account diffusion of the radioactive isotope into the specimen:

$$p \text{ (mm Hg)} = 17.14 \, \frac{I\sqrt{M}}{\alpha S k t \sqrt{M}}, \tag{1}$$

where I is the activity of the previously inactive specimen (counts/min), α is the specific activity of the initial active bismuth specimen (counts/min/g), S is the area of the specimen participating in the exchange (0.785 cm^2), k is the Clausing factor, in our case equal to 0.826, M is the molecular weight of bismuth in the vapor state, and t is the exposure time (sec).

In the calculations by formula (1) it was assumed that bismuth vapor consists entirely of diatomic molecules ([2,9]).

The experimental results are given in Table 1 and in Fig. 3.

Table 1

Saturated vapor pressures of solid bismuth and the standard heat of sublimation at absolute zero

T° K	p (mm Hg)	Deviation of p from the value calculated by equation (2), %	$-R \ln p$ (atm), cal	Φ'_{solid}, cal	Φ'_{gas}, cal	ΔH_0^0, kcal/mol	$\Delta H_0^0 - \Delta H_{0avg}^0$
479	$5.50 \cdot 10^{-11}$	+17.7	60.128	11.004	60.977	52.74	−1.23
485	$5.25 \cdot 10^{-11}$	−32.8	60.218	11.074	61.083	53.46	−0.51
502	$3.07 \cdot 10^{-10}$	+3.2	56.710	11.270	61.344	53.74	−0.24
507	$5.79 \cdot 10^{-10}$	+28.6	55.449	11.326	61.423	54.04	+1.07
512	$3.89 \cdot 10^{-10}$	−40.3	56.245	11.383	61.491	54.95	+0.48
515	$8.87 \cdot 10^{-10}$	+11.3	53.887	11.416	61.531	53.56	−0.41
516	$1.98 \cdot 10^{-9}$	+96	52.814	11.427	61.554	53.12	−0.85
525	$1.55 \cdot 10^{-9}$	+14.4	53.497	11.526	61.736	54.45	+0.48
528	$2.35 \cdot 10^{-9}$	+16.7	52.667	11.558	61.794	54.33	+0.36
530	$1.94 \cdot 10^{-9}$	−15.9	53.044	11.581	61.831	54.74	+0.77
532	$1.81 \cdot 10^{-9}$	−31.6	53.179	11.602	61.867	55.03	+1.06

The experimental data, treated by the method of least squares, are well described by the equation:

$$\lg p \text{ (mm Hg)} = -\frac{8397.0}{T} + 7.213, \qquad (2)$$

where T is the temperature of the exchange chamber and the specimens.

As is seen from Fig. 3, our values are in good agreement with the data of A. Granovskaya and A. Lyubimov ([3]) and with the results of works carried out in the region of high temperatures and pressures.

Starting from the obtained saturated vapor pressures of solid bismuth, the standard heat of sublimation at absolute zero ΔH_0^0 was calculated from the equation

$$\Delta H_0^0 = T\left(\Phi'_{\text{gas}} - \Phi'_{\text{solid}} - R\ln p\,(\text{atm})\right).$$

According to the general equations of thermodynamics, using data on the heat capacity of solid bismuth [10–12] and the results of spectroscopic studies [12,13] ($I = 1.4 \cdot 10^{-37}$ g $\cdot$ cm^2, $\omega = 172$ cm^{-1}), the following equations were compiled for calculating the Φ'-potentials:

$$\Phi'_{\text{solid}} = 23.896 - 12.641\lg T - 1.22 \cdot 10^{-3} - \frac{207.8}{T} \tag{3}$$

$$\Phi'_{\text{gas}} = 16.222 + 16.015\lg T + R\ln Q_{\text{vib}}, \tag{4}$$

where $Q_{\text{vib}} = \left(1 - e^{-\theta/T}\right)^{-1}$ and $\theta = 247.2°$.

The values of ΔH_0^0 obtained by calculation are given in Table 1. The mean value is $\Delta H_0^0 = 54.0 \pm 0.7$ kcal/mol.

A criterion for the reliability of the results obtained is the satisfactory scatter in the values of ΔH_0^0 relative to the mean value. The absence of a systematic trend with temperature in the values of ΔH_0^0 is also confirmation of the reliability of the obtained values of the saturated vapor pressures of solid bismuth.

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