Rapid and Direct Measurement of Vapor Pressure of Liquid Metals

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(Received March 2, 1946)

A rapid, direct method for determining the vapor pressure of liquid metals by measuring the force of impact of evaporated particles with a vacuum microbalance is described. The vapor pressure of Bi obtained by this method in a preliminary experiment is found to be in fairly good agreement with other measurements.

STUDIES in this laboratory of various properties of thin metallic films have led to the development of a rapid, direct method for measuring the vapor pressure of the liquid metal evaporated in vacuum to form these films. In the method devised the force of impact of a stream of vapor on a surface is measured directly. The procedure for the evaporation of the metal was practically identical with that used previously.[1,2] The stream of vapor striking the bottom of a glass bucket suspended from an helical quartz spiral was interrupted with a shutter and the elevation of the bucket was measured with a micrometer microscope.

THEORETICAL

By kinetic theory the vapor pressure p of a substance at Kelvin temperature T effusing as an ideal gas through an orifice of area dS into a solid angle $d\omega$ normal to dS is

$$p = \frac{dN}{dt}(2\pi mkT)^{\frac{1}{2}}\frac{\pi}{dS}\frac{N_0}{d\omega}; \qquad (1)$$

where dN/dt is the number of moles of the substance issuing per sec. from orifice, N_0 is Avogadro's number, k is Boltzmann's constant, and m is the mass of a particle.

The pressure p_c of an ideal gas condensing completely (*without reflection*) on a surface is

$$p_c = nkT/2, \qquad (2)$$

where n is the number of molecules/volume. Making the usual substitutions $n_c = nv/(6\pi)^{\frac{1}{2}}$, $v = (3kT/m)^{\frac{1}{2}}$ in Eq. (2) yields

$$p_c = n_c(\pi mkT/2)^{\frac{1}{2}}; \qquad (3)$$

where n_c = the number of molecules condensing/ area per sec. Since $(n_c/N_0)A$ (A is the area over which condensation occurs) is the number of moles condensing/sec. it equals dN/dt in Eq. (1). Hence, putting

$$\frac{n_c}{N_0}A = \frac{p_c A}{\left(\frac{\pi}{2}mkT\right)^{\frac{1}{2}}N_0}, \qquad (4)$$

in Eq. (1) yields

$$p = 2\pi p_c A/dSd\omega;$$

or

$$p = 2\pi F/dSd\omega \qquad (5)$$

since $F = p_c A$, where F is the force of the condensing vapor on A.

EXPERIMENTAL

The apparatus is shown by Fig. 1 and is described in the accompanying legend. A micrometer microscope was placed to sight normal to the optical flat W, with its objective entering the recess shown. With the device shown by detail I, a calibrated rider (0.152_4 mg in vacuum) could be rested on and raised from the edge of the bucket B to calibrate the helical quartz spiral. The sensitivity of the microbalance under operating conditions was 4.20×10^{-7} g/micrometer-scale-division. The temperature of the liquid bismuth was measured with a tungsten-Kovar thermocouple with cold junction maintained at $0°C$. The reference line chosen to measure the elongation and contraction of the quartz spiral appeared as a thin horizontal line produced by reflection of light from the bottom of the bucket.

A needed shutter (not shown by Fig. 1) entering through a side tube at $180°$ from I was used either to interrupt the vapor beam or to allow its
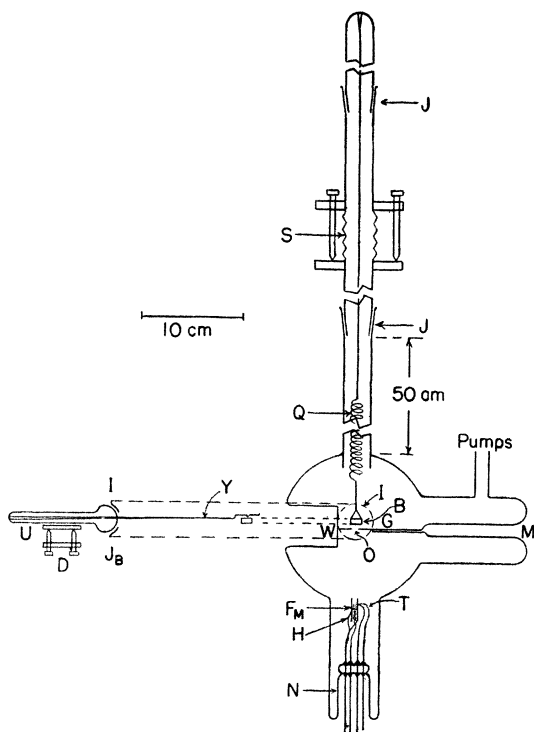
[1] A. H. Weber and S. C. Kirsch, Phys. Rev. **57**, 1042 (1940).
[2] E. Rudberg and J. Lempert, J. Chem. Phys. **3**, 627 (1935).

FIG. 1. Vacuum tube and microbalance. J, ground glass joints; J_B, ball and socket ground glass joint; S, bronze sylphon with screws for adjusting length and centering of spiral; Q, helical quartz spiral supported from above by a glass rod; B, glass bucket on the lower surface of which the metallic vapor particles condense; O, circular hole in glass plate G; W, optical flat (window); F_M, molybdenum furnace having orifice of area dS containing 99.8 percent c.p. Bi in upper cylindrical cavity; H, heating coil of 10-mil tungsten wire in lower cylindrical cavity; N, 50-mil lead-in wires; T, hot junction of tungsten-Kovar thermocouple; I, side tube entering at 90° from plane of Fig. 1 for glass rider-rod Y (used in manipulating rider on and off edge of bucket B); M, cylindrical recess through which illumination of reference line is produced; U, handle with rest D.

passage through the hole O. Thus readings taken with shutter "open" and "closed" after thermal equilibrium was established yielded directly the force of impact F of the vapor beam on the bucket bottom. The vapor pressure was calculated from Eq. (5).

RESULTS

Preliminary results for the vapor pressure of Bi are given in Table I.

Comparison of several Bi vapor pressure determinations is shown by Fig. 2. Curve 1 represents the data of Weber-Kirsch[1] in the temperature interval 876.1–911.4°K and extrapolated

(dashed section) for the higher temperatures. The corresponding equation is

$$\log_{10} p_{mm} = -52.23(205/T) + 9.03. \qquad (6)$$

Curve 2 is obtained by extrapolating for the temperature range here considered the equation[3]

$$\log_{10} p_{mm} = -52.23(200/T) + 8.87. \qquad (7)$$

The vapor pressure as determined by Ko[4] in the temperature range 1100–1220°K is shown by curve 3 and is represented by

$$\log_{10} p_{mm} = -52.23(195/T) + 8.56. \qquad (8)$$

Since the vapor pressure of bismuth in the present investigation was obtained for one temperature only, no curves can be drawn to represent these results; hence the mean vapor pressure at 969.9°K of Table I is shown by a circle on Fig. 2. Values of the vapor pressure of bismuth at 969.6°K read from the curves of Fig. 2 are listed in Table II.

Two correction factors applying to measurement of vapor pressure of Bi by molecular effusion have not generally been taken into consideration; the effect of a short canal between the evaporating surface and the effusion orifice, and the diatomic character of Bi vapor. During the evaporation the surface of liquid Bi in the furnace is lowered. As the ratio of depth/diameter approaches unity,[5] the probability of the particles

TABLE I. Summarized date for vapor pressure of Bi. $dS = \pi(0.194 \text{ cm}^2)$, diameter of $O = 0.716$ cm, distance from dS to $O = 4.99$ cm, $T = 969.6$°K.

Elevation of bucket by vapor beam (scale divisions)	$F \times 10^3$ (dynes)	Vapor pressure p (mm-Hg)
19.0	7.82	0.0194
19.0	7.82	0.0194
14.0	5.76	0.0142
16.5	6.79	0.0167
12.0	4.94	0.0122
19.5	8.02	0.0198
15.0	6.17	0.0152
15.0	6.17	0.0152
16.0	6.58	0.0163
15.0	6.17	0.0152
18.0	7.41	0.0183
19.0	7.82	0.0194
18.0	7.41	0.0183
12.5	5.14	0.0127

Mean 0.0166±0.0017

[3] Int. Crit. Tab. **3**, 205 (1926).
[4] C. C. Ko, J. Frank. Inst. **217**, 173 (1934).
[5] R. Fraser, *Molecular Rays* (Cambridge University Press, New York, 1931), p. 16.
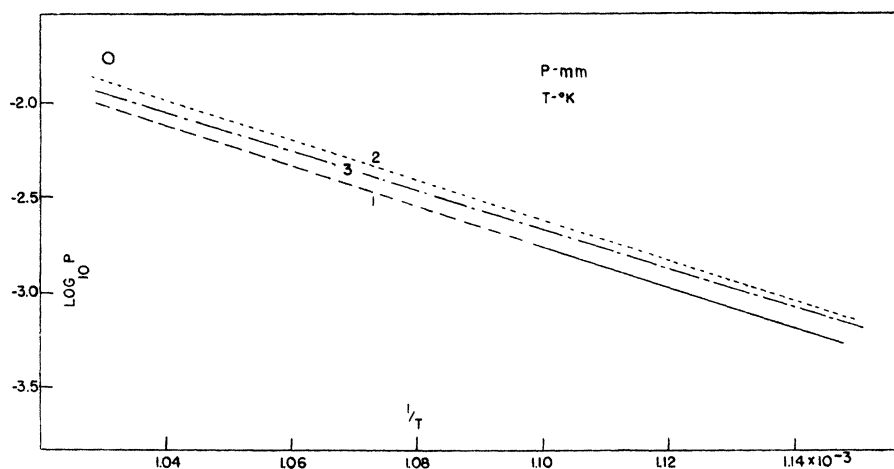
Fig. 2. Comparison of Bi vapor pressure determinations.

passing through the canal becomes 0.7. Hence the vapor pressure near the liquid surface may be greater by as much as 10/7 (provided a depth/diameter ratio equal to 1 is assumed) than the measurements made on the beam which has effused indicate. Another effect of a canal is to cause departure of the effusing particles from the cosine distribution law. This collimation of the vapor-beam by the canal is zero[6] if $\theta = 0$ as it does in the present experiments. Nor is a depth/diameter correction necessary (in the present experiments) for the cavity in the furnace F_M (Fig. 1) was brimful with Bi so that the ratio of depth/diameter is zero and the probability of passage through the canal is unity. Ko in his experiments on the heat of dissociation of Bi gives evidence that Bi vapor is diatomic.[4] The vapor pressure calculated by Eq. (1) must be corrected by multiplying by $1/\sqrt{2}$ if the vapor is diatomic instead of monatomic since the measurement of dN/dt involves the operation of dividing the mass

Table II. Vapor pressure of Bi in mm-Hg at 969.6°K.

| Direct pressure method | Extrapolated values | | |
	Weber-Kirsch	Ko	I.C.T.
0.0166	0.00966	0.0112	0.0129

[6] R. Fraser, reference 5, p. 17.

of metal condensed by the *atomic* weight of Bi. Such a correction is not involved in the direct pressure method used in the present experiments as can be seen by examining Eq. (5). The conditions under which the Weber-Kirsch experiments[1] were performed were such that the corrections due to the canal effect and to the diatomic effect cancel each other approximately.

Errors in the direct pressure method arise chiefly from vibrations of the quartz spiral, a factor difficult to control, and slight temperature changes in and around the tube. The chief advantages of this method are its directness and rapidity, a pair of readings (with shutter "open" and with shutter "closed") being made in 2–3 minutes as compared with several hours for the previous method.[1] The results of the vapor pressure measurements by this method are of a preliminary nature, the chief purpose of the present investigation was to test the reliability of the method.