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Fig. 1. Design of the effusion chamber.

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Abstract

Full Text

PHYSICAL CHEMISTRY

L. Kh. GENOV, An. N. NESMEYANOV, and Yu. A. PRISELKOV

MEASUREMENT OF THE VAPOR PRESSURE OF THALLIUM BY THE RADIOACTIVE-TRACER METHOD

(Presented by Academician V. I. Spitsyn, 6 IV 1961)

Data on the vapor pressure of liquid thallium, obtained by a number of investigators¹⁻⁶, agree poorly with one another and require verification and refinement. Until the present work, there had been no data on the vapor pressure of solid thallium.

We carried out measurements of the vapor pressure and evaporation coefficient of liquid and solid thallium over a wide temperature range by an integral variant of the Knudsen effusion method and by the method of evaporation from an open surface (the Langmuir method), using the radioactive isotope thallium Tl^{204} . For the work an apparatus was constructed, analogous to that described in⁷. In contrast to the latter, the effusion chamber and the evaporation cup were heated by a resistance furnace introduced into the vacuum chamber.

Fig. 1. Design of the effusion chamber.

1 –chamber body, 2 –chamber cover, 3 –molybdenum cup, 4 –crucible support, 5 –thallium, 6 –beryllium oxide crucible, 7 –ceramic cover, 8 –diaphragm with effusion aperture, 9 –cover heater, 10 –quartz spiral, 11 –chamber-body heater, 12 –ceramic tubes (12 pieces), 13, 14 –chromel-alumel thermocouples

The design of the chamber is shown in Fig. 1. The body (1) and cover (2) of the chamber were made of “Armco” iron, and the internal parts (3, 4) of molybdenum. Metallic thallium was placed in a crucible (6) (made of sintered beryllium oxide), closed with a cover of ceramic (7) and molybdenum foil (8). The crucible was sealed in the same manner as indicated in⁷. The cover and the chamber body were heated by two separate spirals, so that a limiting temperature gradient could be produced to prevent condensation of metal vapors on the diaphragm. The temperature of the diaphragm and of the crucible bottom was measured by two chromel-alumel thermocouples connected to PMS-48 potentiometers. The error in the temperature measurements due to heat removal through the

thermocouples was negligible and was not taken into account in the calculations. The accuracy of temperature measurement was $\pm 0.5^\circ$.

In the work, high-purity thallium was used; it contained the radioactive isotope of thallium Tl^{204} and had the following impurities: Fe, In, Cd, Cu, Sn, and Pb in amounts less than $1 \cdot 10^{-4}\%$ for each element. The specific activity was 2 mCi/g. Radiometrically, the absence of radioactive impurities in Tl^{204} was shown.

The evaporation rate was determined from the radioactivity of the vapor condensate. The condensed thallium vapors were washed from the receiver with a solution of nitric acid (1 : 3), which contained inactive thallium as a carrier. The solution was then neutralized with an excess of ammonia (2 : 1), heated to 60–70°C, and thallium chromate was quantitatively precipitated from it with potassium dichromate.

The precipitate was filtered on a Büchner funnel, washed with a 1% potassium dichromate solution, and dried. The activity of the precipitate was measured with an end-window counter and compared with the activity of the reference preparation.

The vapor pressure of thallium was calculated by the formula:

$$P = 17,14 G \sqrt{\frac{T}{M}}, \quad (1)$$

where P is the pressure in mm Hg; M is the molecular weight of the vapor; T is the tempera-

Table 1

Vapor pressure of thallium

No.	$T, ^\circ\text{K}$	$\tau, \text{sec.}$	g, g	$G, \frac{\text{g}}{\text{cm}^2 \cdot \text{sec}}$	$P, \text{mm Hg}$	$\Delta H_0^\circ, \frac{\text{kcal}}{\text{mol}}$
$S = 3,835 \cdot 10^{-4} \text{ cm}^2$	$S = 3,835 \cdot 10^{-4} \text{ cm}^2$	$S = 3,835 \cdot 10^{-4} \text{ cm}^2$	$S = 3,835 \cdot 10^{-4} \text{ cm}^2$	$S = 3,835 \cdot 10^{-4} \text{ cm}^2$	$S = 3,835 \cdot 10^{-4} \text{ cm}^2$	$S = 3,835 \cdot 10^{-4} \text{ cm}^2$
1	719	10800	$6,85 \cdot 10^{-6}$	$1,656 \cdot 10^{-6}$	$5,324 \cdot 10^{-5}$	43,07
2	816	3600	$53,5 \cdot 10^{-6}$	$3,875 \cdot 10^{-5}$	$1,327 \cdot 10^{-3}$	43,62
3	882	3600	$358 \cdot 10^{-6}$	$2,593 \cdot 10^{-4}$	$9,233 \cdot 10^{-3}$	43,63
4	912	3600	$846 \cdot 10^{-6}$	$6,128 \cdot 10^{-4}$	$2,219 \cdot 10^{-2}$	43,42
5	656	14400	$0,60 \cdot 10^{-6}$	$1,091 \cdot 10^{-7}$	$3,350 \cdot 10^{-6}$	43,09

No.	$T, ^\circ\text{K}$	$\tau, \text{sec.}$	g, g	$G, \frac{\text{g}}{\text{cm}^2 \cdot \text{sec}}$	$P, \text{mm Hg}$	$\Delta H_0^{\circ}, \frac{\text{kcal}}{\text{mol}}$
6	689	10800	$2,30 \cdot 10^{-6}$	$5,553 \cdot 10^{-7}$	$1,750 \cdot 10^{-5}$	42,74
7	749	7200	$12,23 \cdot 10^{-6}$	$4,430 \cdot 10^{-6}$	$1,453 \cdot 10^{-4}$	43,30
8	790	7200	$72,1 \cdot 10^{-6}$	$2,610 \cdot 10^{-5}$	$8,796 \cdot 10^{-4}$	42,71
9	819	3600	$78,8 \cdot 10^{-6}$	$5,704 \cdot 10^{-5}$	$1,957 \cdot 10^{-3}$	42,89
10	872	3600	$299,5 \cdot 10^{-6}$	$2,169 \cdot 10^{-4}$	$7,654 \cdot 10^{-3}$	43,15
11	924	3600	$1225 \cdot 10^{-6}$	$8,821 \cdot 10^{-4}$	$3,215 \cdot 10^{-2}$	42,68
$S = 2,691 \cdot 10^{-3} \text{ cm}^2$	$S = 2,691 \cdot 10^{-3} \text{ cm}^2$	$S = 2,691 \cdot 10^{-3} \text{ cm}^2$	$S = 2,691 \cdot 10^{-3} \text{ cm}^2$	$S = 2,691 \cdot 10^{-3} \text{ cm}^2$	$S = 2,691 \cdot 10^{-3} \text{ cm}^2$	$S = 2,691 \cdot 10^{-3} \text{ cm}^2$
12	663	7200	$2,73 \cdot 10^{-6}$	$1,409 \cdot 10^{-7}$	$4,350 \cdot 10^{-6}$	43,18
13	737	5200	$66,4 \cdot 10^{-6}$	$3,429 \cdot 10^{-6}$	$1,116 \cdot 10^{-4}$	42,90
14	802	3600	$337,5 \cdot 10^{-6}$	$3,483 \cdot 10^{-5}$	$1,183 \cdot 10^{-3}$	42,86
15	840	3600	$910,4 \cdot 10^{-6}$	$9,397 \cdot 10^{-5}$	$2,898 \cdot 10^{-3}$	43,28
16	835	1800	$549 \cdot 10^{-6}$	$1,133 \cdot 10^{-4}$	$3,969 \cdot 10^{-3}$	43,23
17	902	900	$1066 \cdot 10^{-6}$	$4,402 \cdot 10^{-4}$	$1,585 \cdot 10^{-2}$	43,24
$S = 9,079 \cdot 10^{-2} \text{ cm}^2$	$S = 9,079 \cdot 10^{-2} \text{ cm}^2$	$S = 9,079 \cdot 10^{-2} \text{ cm}^2$	$S = 9,079 \cdot 10^{-2} \text{ cm}^2$	$S = 9,079 \cdot 10^{-2} \text{ cm}^2$	$S = 9,079 \cdot 10^{-2} \text{ cm}^2$	$S = 9,079 \cdot 10^{-2} \text{ cm}^2$
18	646	7200	$53,6 \cdot 10^{-6}$	$8,200 \cdot 10^{-8}$	$2,499 \cdot 10^{-6}$	42,84
19	760	1860	$1105 \cdot 10^{-6}$	$6,762 \cdot 10^{-6}$	$2,235 \cdot 10^{-4}$	43,25
$S = 1,413 \text{ cm}^2$	$S = 1,413 \text{ cm}^2$	$S = 1,413 \text{ cm}^2$	$S = 1,413 \text{ cm}^2$	$S = 1,413 \text{ cm}^2$	$S = 1,413 \text{ cm}^2$	$S = 1,413 \text{ cm}^2$
20	519	10800	$0,56 \cdot 10^{-6}$	$3,644 \cdot 10^{-11}$	$9,951 \cdot 10^{-10}$	42,73
21	544	7200	$1,93 \cdot 10^{-6}$	$1,897 \cdot 10^{-10}$	$5,306 \cdot 10^{-9}$	42,94
22	562	3600	$3,2 \cdot 10^{-6}$	$6,253 \cdot 10^{-10}$	$1,777 \cdot 10^{-8}$	42,88

No.	T , °K	τ , sec.	g , g	G , $\frac{\text{g}}{\text{cm}^2 \cdot \text{sec}}$	P , mm Hg	ΔH_0° , $\frac{\text{kcal}}{\text{mol}}$
23	572	3600	$5,60 \cdot 10^{-6}$	$1,107 \cdot 10^{-9}$	$3,174 \cdot 10^{-8}$	43,06
24	579	1800	$4,7 \cdot 10^{-6}$	$1,829 \cdot 10^{-9}$	$5,275 \cdot 10^{-8}$	43,24
25	610	1200	$17,1 \cdot 10^{-6}$	$1,007 \cdot 10^{-8}$	$2,981 \cdot 10^{-7}$	43,13
26	640	1200	$62,2 \cdot 10^{-6}$	$4,082 \cdot 10^{-8}$	$1,238 \cdot 10^{-6}$	43,41
27	665	900	$200 \cdot 10^{-6}$	$1,607 \cdot 10^{-7}$	$4,962 \cdot 10^{-6}$	43,13
28	708	900	$1,262 \cdot 10^{-6}$	$9,924 \cdot 10^{-7}$	$3,166 \cdot 10^{-5}$	43,18
29	757	600	$5233 \cdot 10^{-6}$	$6,162 \cdot 10^{-6}$	$1,618 \cdot 10^{-4}$	43,66
						Avg. = 43,12 ± 0,27

temperature in °K; G is the effusion rate, calculated by the formula:

$$G = \frac{g}{\tau K \sigma},$$

where g is the amount of evaporated substance, τ is the exposure time; σ is the area of the effusion orifice, K is the Clausing coefficient.

The experimental results are given in Table 1. In order to check the effect of the radioactivity of the metal on the rate of its evaporation, experiments were carried out with inactive thallium (experiments 1–4). In this case the amount of evaporated substance was determined by the polarographic method ⁽⁹⁾. It turned out that thallium activity up to 2 mCi/g has practically no effect on the measurement results.

The data obtained both by the effusion method with various effusion orifices (experiments 1–19) and by the method of evaporation from an open surface (experiments 20–29) are, within the limits of experimental error, well described by the equation of a single straight line $\lg P = 8.0871 - 8899.4/T$, which was obtained by the method of least squares. This gives grounds to assume that the condensation coefficient of thallium in the liquid and solid states is close to unity.

The condensation coefficient depends on three principal factors—the composition of the gas phase, the energetic state of the surface, and the presence of oxide

and other films on the surface ⁽¹¹⁾. Equality of the condensation coefficient to unity indirectly shows that thallium vapor is monatomic.

The vapor pressure of Tl₂O considerably exceeds the vapor pressure of metallic thallium at the same temperatures ⁽¹⁰⁾. Before the experiments to determine the vapor pressure, thallium was subjected to prolonged heating in vacuum, as a result of which the surface of the metal was freed from oxide films and, consequently, the third factor could not affect the results.

The average heat of evaporation of thallium in the temperature interval 519–924°K is $\Delta H_T = 40.72$ kcal/mole.

On the basis of our experimental values of the vapor pressure and the Φ^* potentials of gaseous, solid, and liquid thallium, given in ⁽¹²⁾, by the formula

$$R \ln P = \Phi_p^* - \Phi_k^* - \frac{\Delta H_0^0}{T}, \quad (2)$$

values of ΔH_0^0 were calculated for each experiment (see Table 1). These quantities agree well with one another and do not show a systematic trend with changing temperature, which confirms the reliability of the results obtained by us. The mean value of ΔH_0^0 is 43.12 ± 0.27 kcal/mole. In addition, the heat of sublimation at 0°K, calculated for the middle of the temperature interval (700°K) by the formula

$$\Delta H_0^0 = \Delta H_T - \Delta (H_T - H_0^0)$$

and equal to 42.79 kcal/mole, agrees well with ΔH_0^0 calculated by formula (2).

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REFERENCES

1. W. Leitgeb, Zs. anorg. Chem., **202**, 305 (1931).
2. G. E. Gibson, cited in Landolt, **2**, 1332 (1923).
3. H. Wartenberg, Zs. Electrochem., **19**, 482 (1913).
4. F. F. Coleman, A. Egerton, Phill. Trans., A **234**, 177 (1934).

5. J. Fischer, Chem. Zs., **1**, 4208 (1937).
6. F. Muller, Helv. phys. Acta, **8**, 152 (1935).
7. Yu. A. Priselkov, A. V. Tseplyaeva, K. I. Smirnov, *An instrument for measuring saturated vapor pressure by the effusion method*, Izd. fil. VINITI, topic 39, No. P-58-95/6, 1958.
8. Yu. A. Priselkov, Yu. A. Sapozhnikov, A. V. Tseplyaeva, Izv. AN SSSR, OTN, No. 1, 106 (1959).
9. T. A. Kryukova, S. I. Sinyakova, T. V. Aref'eva, *Polarographic Analysis*, 1959, p. 269.
10. M. G. Shakhtakhtinskii, A. A. Kuliev, DAN, **123**, No. 6 (1958).
11. O. Knacke, I. N. Stranski, in: *Collected Papers. Advances in the Physics of Metals*, **3**, Moscow, 1960, p. 222.
12. L. V. Gurvich, ZhFKh, **34**, 217 (1960).

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