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The Vapor Pressure of Indium, Silver, Gallium, Copper, Tin, and Gold Between 0.1 and 3.0 Bar

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The vapor pressure of several liquid metals was measured using a method based on the gas-controlled heat pipe. Small samples of the test material were placed in a tungsten tube and heated to temperatures above 2900 K. The vapor pressure was measured using a gas-buffered pressure transducer and the vapor temperature was inferred from the tube surface temperature, which was measured with an optical pyrometer. Most of the tests were terminated by the failure of the containment tube. The measured pressures agree well with those calculated by thermodynamic methods from data at lower temperatures.

KEY WORDS: copper; gallium; gold; heat pipe; high temperature; indium; liquid metals; silver; tin; vapor pressure.

1. INTRODUCTION

Vapor pressure data for liquid metals at high temperature are sparse because accurate measurements are difficult to make. Available vapor pressure data, obtained by different investigators, may range over an order of magnitude at the same temperature. A measurement method based on the gas-controlled heat pipe has been developed relatively recently which offers improved accuracy over earlier methods. This new method, which may be described as a direct, dynamic measurement method using a gas-buffered pressure transducer, was first used by Bohdansky and co-workers at the Joint Research Centre at Ispra [1–4]. In the present paper, the

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extension of the heat-pipe method to temperatures in excess of 2900 K is described and new results are presented for the vapor pressures of In, Ag, Ga, Cu, Sn, and Au in the pressure range 0.1 to 3.0 bar.

2. METHOD

The heat-pipe apparatus used to measure vapor pressure is shown schematically in Fig. 1. A central, vertical, metal tube, the heat pipe, is lined on the inside with a capillary structure and filled with an inert gas at a certain pressure and with a small amount of the material to be investigated. The lower part of the heat pipe, called the evaporator, is heated and the upper part, the condenser, is cooled. Under steady-state operating conditions, a thin liquid layer, guided by the capillary structure, covers the wall of the heat pipe. Vapor, produced in the evaporator, flows up the center of the pipe to the condenser, where it is converted back into the liquid phase. The liquid returns to the evaporator along the wall of the tube, completing the test fluid circuit. The inert gas is swept to the top of

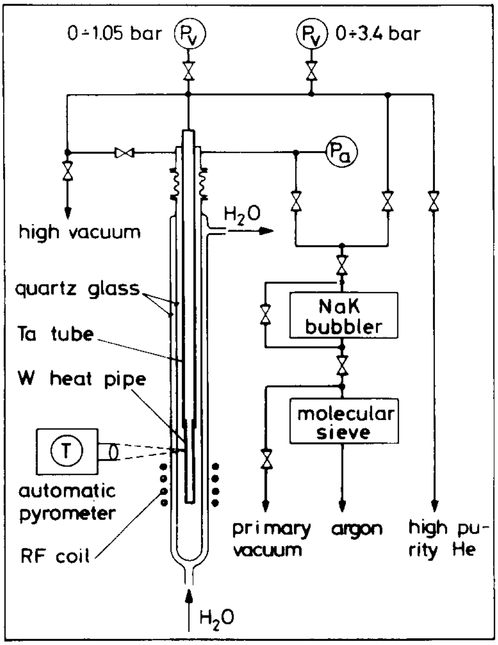

Fig. 1. Schematic experimental arrangement for vapor pressure measurements by the heat-pipe method at very high temperatures.

the condenser by the upward flowing vapor. This gas fills an extension tube which connects the heat pipe and the pressure transducer and blocks the flow of vapor. The heat transfer rate through this long gas plug and the surrounding thin-walled tube is low and the pressure transducer operates at room temperature.

The pressure drop in the vapor flow near the downstream end of the condenser is extremely small so that this section of the heat pipe operates under virtually isothermal conditions at the inner wall. The inert gas plug is in dynamic equilibrium with the vapor column beneath it. As long as the gas pressure is kept constant, the vapor pressure and, therefore, the temperature of the isothermal zone remain constant. A variation in the heat input causes a change in the length of the isothermal zone, increasing or decreasing the condenser area to maintain a heat balance, but does not influence the temperature. This provides a means for adjusting the length of the isothermal zone so that its temperature can be conveniently measured.

The heat pipes used for these tests were made from chemical vapor-deposited tungsten tubes. Each tube was 130 mm long, with a 12-mm outside diameter and an 8-mm inside diameter. The inner surface was lined with 30 axial grooves having a square cross section of 0.4 × 0.4 mm. These grooves formed the capillary structure. Each pipe was plugged on one end and electron-beam welded, on the other end, to a tantalum extension tube of approximately the same diameter, forming a 90-cm-long composite tube assembly. The tube assembly was suspended inside a double-walled quartz glass tube. The support flange for the tube assembly was water cooled; consequently, the exposed end of the assembly and the copper tubing connecting it to the pressure gauges and gas supply were at room temperature. Further details concerning the construction and cleaning of the heat pipes and the sample preparation are presented in Ref. 5. The specifications and sources of the metal samples used in these tests are summarized in Table I.

Table I. Test Material Specification and Source

Metal	Supplier	Purity (%)
Tin	Leytess Metal and Chemical Co., N.Y., U.S.A.	99.999
Gold	Degussa, Hanau, Germany	99.999
Silver	Leico Industries, Inc., N.Y., U.S.A.	99.999
Gallium	Leico	99.9999
Indium	Leytess	99.9999
Copper	Standard OFHC	99.95

During operation, argon, at a pressure of about 0.7 bar, fills the space surrounding the tube assembly to reduce tungsten evaporation and the mechanical load on the heat pipe wall. Cooling water flows through the annular space between the quartz tubes. The lower half of the heat pipe is heated using an R–F generator with a capacity of 30 kW. Heat is removed from the tube assembly by radiation and by convection of the surrounding argon gas. The heat input is adjusted so that the top of the isothermal zone is about 1 cm below the W–Ta joint. The outer wall temperature is measured above the heating coil, in the condenser region of the heat pipe, with an automatic precision pyrometer, corrected for the absorption in the quartz–water containment. The vapor temperature is determined by adding the calculated temperature drop through the heat pipe wall to the measured outer wall temperature. The vapor pressure is indicated on two precision pressure gauges. Provisions are made, as shown in Fig. 1, so that either helium or argon may be used as the buffer gas between the vapor and the pressure gauges.

Data taking in these tests began at a low temperature and pressure (generally at 0.1 bar) and continued, at progressively higher pressures, until either a vapor pressure of 3.4 bar was reached or the heat pipe failed. All of the heat pipes, except those containing In and Ag, failed due to penetration of the working fluid through the wall.

3. ACCURACY

The heat-pipe method for measuring vapor pressure has several features which enhance the accuracy in high-temperature applications compared with alternative methods [2]. Both the temperature and the pressure measurement can be made under most favorable conditions; the temperature of a large, isothermal surface and the pressure of an inert gas at room temperature are measured. Also, the vapor is produced by evaporation from the smooth surface of a thin layer of liquid without the formation of any bubles, and therefore, the deviations from thermodynamic equilibrium are small. Finally, there is a continuous distillation of the working fluid so that, if the temperature measurements are made in the condenser area, the effect of impurities is small.

Some precautions are necessary in order to realize the full potential of the method. The inert gas should be lighter than the metal vapor, otherwise the vapor–gas interface is unstable [6] and pressure fluctuations can occur [7, 8]. Furthermore, a lighter vapor will be carried high up into the gas by convective motions and may form a solid plug in the line to the gas control system.

The measured gas pressure and tube outer surface temperature may differ from the desired vapor pressure and temperature for a number of reasons. They are as follows:

dynamic pressure drop in the flowing vapor,
hydrostatic pressure of the vapor and the inert gas,
diffusion of the inert gas into the vapor,
mixing of the inert gas and the vapor by convective instabilities,
solution of impurities in the liquid,
deviation of the curvature of the liquid–vapor interface from the thermodynamic equilibrium situation (due to the finite flow resistance of the capillary structure),
incomplete thermodynamic equilibrium between vapor and liquid (due to finite evaporation and condensation rates), and
thermal resistance of the wall of the heat pipe.

These have been discussed in detail in Ref. 9. The effects of many of these mechanisms on measurement accuracy can be minimized by careful design of the experiment. For the present experiment, errors due to the above mechanisms have been estimated to be small compared to the uncertainty in the measurement of surface temperature and gas pressure. The error due to the thermal resistance of the wall has been minimized by applying a correction for the temperature drop, ΔT_w, between the inner and the outer walls of the heat pipe condenser. The correction is calculated from the known tube geometry, assuming the grooves to be completely filled with liquid metal, and the heat flux is estimated from the measured temperatures.

The pressure of the inert gas was measured using one of two pressure gauges with different ranges. Both were Model 61-050 Series 1500 gauges manufactured by Wallace and Tiernan–Chlorator GmbH with an accuracy of ±0.066% of full scale. The estimated uncertainty in the measured vapor pressure is ±0.7 mbar below a pressure of 1.05 bar and ±2.2 mbar above this pressure.

The heat-pipe condenser surface temperature was measured with a Leeds and Northrup high-precision automatic optical pyrometer, Model 8642, Mark II. This pyrometer was calibrated against a standard blackbody lamp viewed through the water-filled quartz tube. The uncertainty in the absolute vapor temperature, due chiefly to uncertainty in the tube surface emissivity, is 1.1%.

Table II. Vapor Pressure–Temperature Data

In			Ag			Ga			Cu			Sn			Au		
T (K)	ΔT_w (K)	P (bar)	T (K)	ΔT_w (K)	P (bar)	T (K)	ΔT_w (K)	P (bar)	T (K)	ΔT_w (K)	P (bar)	T (K)	ΔT_w (K)	P (bar)	T (K)	ΔT_w (K)	P (bar)
1952	6	0.100	2049	5	0.100	2109	9	0.100	2470	13	0.152	2463	14	0.150	2614	16	0.100
2011	7	0.150	2120	6	0.150	2174	10	0.150	2522	14	0.200	2516	15	0.200	2689	19	0.150
2040	8	0.200	2164	7	0.200	2240	12	0.200	2593	15	0.300	2605	18	0.300	2777	22	0.200
2093	8	0.300	2229	8	0.300	2284	13	0.300	2661	17	0.500	2662	20	0.400	2939	28	0.525
2138	9	0.400	2274	8	0.400	2329	14	0.400	2728	19	0.600	2705	21	0.500			
2174	10	0.500	2287	9	0.500	2371	15	0.500	2761	20	0.700	2741	22	0.600			
2205	11	0.600	2334	9	0.600	2408	16	0.600	2787	21	0.800	2775	24	0.700			
2230	12	0.700	2360	10	0.700	2429	17	0.700				2789	24	0.750			
2254	12	0.800	2400	11	0.800	2455	18	0.800				2804	25	0.800			
2273	13	0.900	2415	11	0.900	2480	19	0.900				2830	26	0.900			
2302	13	1.033	2427	11	1.033	2504	20	1.033				2860	27	1.033			
2327	14	1.200	2466	12	1.200	2533	21	1.200									
2353	15	1.400	2480	12	1.300	2570	22	1.400									
2385	15	1.600	2498	13	1.400	2600	23	1.600									
2409	16	1.800	2517	13	1.500												
2438	17	2.066	2529	14	1.600												
2452	18	2.200	2538	14	1.700												
2464	18	2.400	2548	14	1.800												
2486	19	2.600	2559	14	1.900												
2504	20	2.800	2574	15	2.066												
2523	20	3.000	2595	15	2.200												
2534	21	3.100	2614	16	2.400												
2543	21	3.200	2633	16	2.600												
2549	21	3.300	2649	17	2.800												
2561	22	3.400	2665	17	3.000												
			2678	18	3.200												
			2693	18	3.400												

4. RESULTS

The final, corrected data are presented in Table II, together with the applied wall temperature drop correction, ΔT_w. The data were fitted to the analytical form

$$\log P = A - \frac{B}{T} \tag{1}$$

with P in bar and T in K, using the least-squares method. The values for the constants A and B for each material as well as the boiling-point temperature and heat of vaporization, as calculated from the analytical expression using the Clausius–Clapeyron relation, are presented in Table III. The measured boiling-point temperature is also indicated (in parentheses) for those materials which were measured at atmospheric pressure.

5. DISCUSSION

The results are summarized in Fig. 2. The scatter of the data around the regression lines, Eq. (1), is seen to be small. The present data for each element are compared, in Figs. 3 through 8, with previous measurements and estimates summarized by Nesmeyanov [10]. The present data are represented, in these plots, by the regression lines indicated by the arrows.

Table III. Calculated Regression Constants, Boiling Point, and Heat of Vaporization

Metal	A	B	Boiling point (K)[a]	Heat of vaporization ($kJ \cdot mol^{-1}$)
In	5.4731	12581	2301 (2302)	241
Ag	5.4870	13342	2434 (2427)	255
Ga	5.5174	13798	2503 (2504)	264
Cu	5.5880	15821	2834	303
Sn	5.2171	14907	2860 (2860)	285
Au	5.3997	16773	3110	321

[a] Numbers in parentheses refer to measured values.

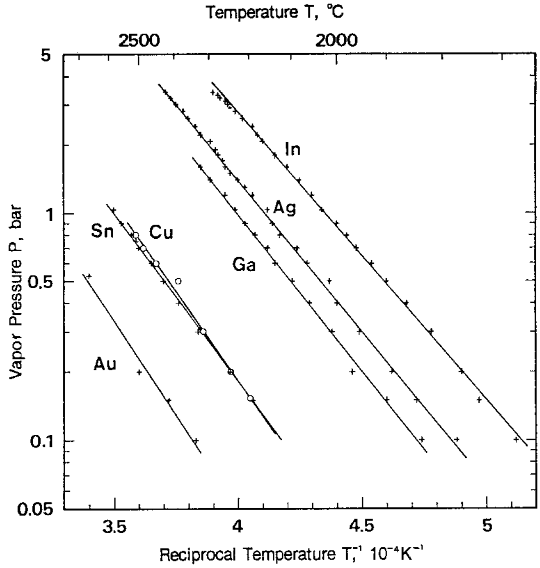

Fig. 2. Vapor pressure of In, Ag, Ga, Cu, Sn, and Au at high temperatures (heat-pipe method).

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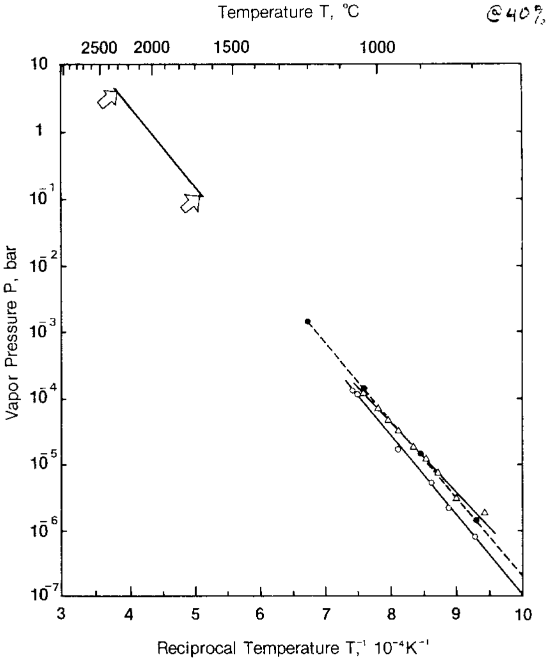

Fig. 3. Vapor pressure of indium.

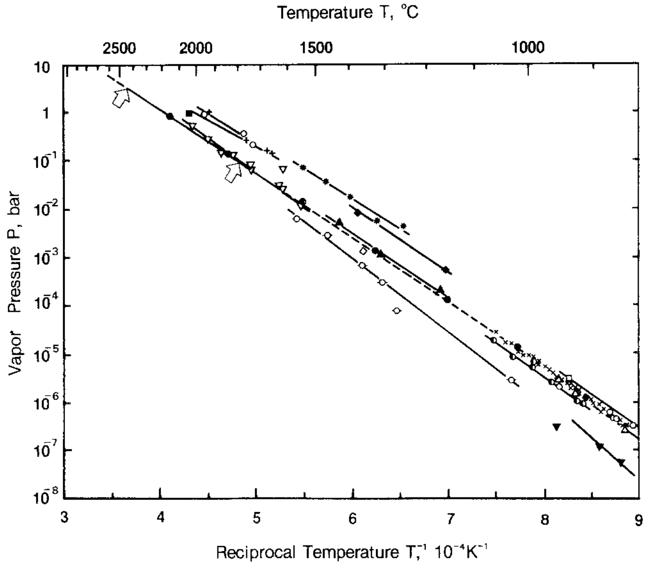

Fig. 4. Vapor pressure of silver.

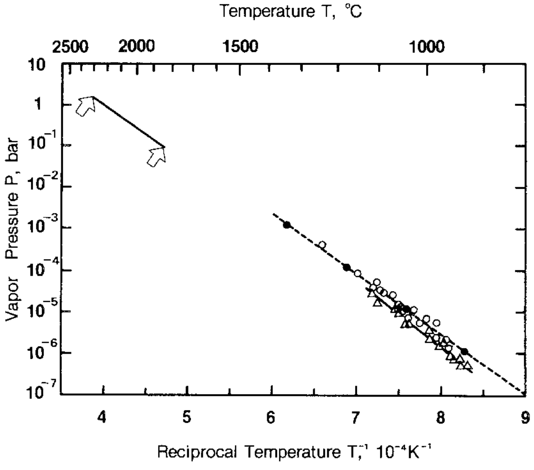

Fig. 5. Vapor pressure of gallium.

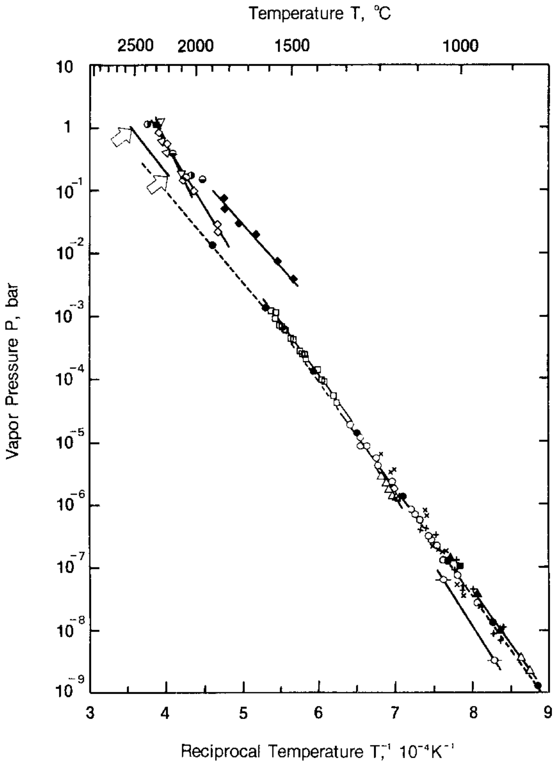

Fig. 6. Vapor pressure of copper.

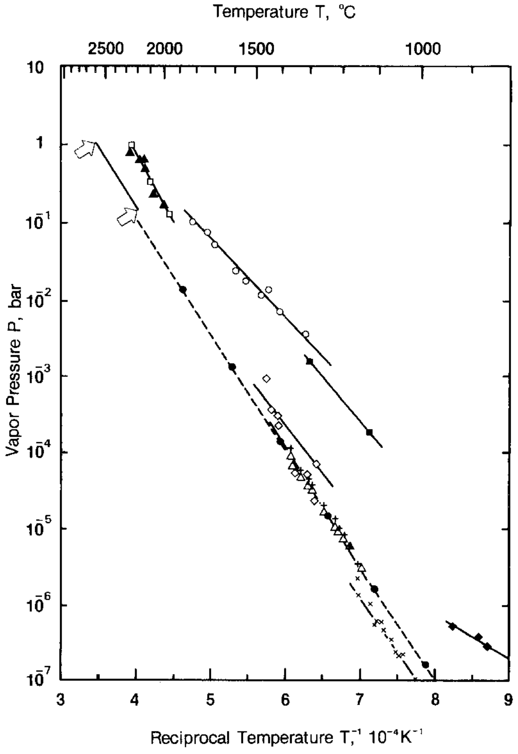

Fig. 7. Vapor pressure of tin.

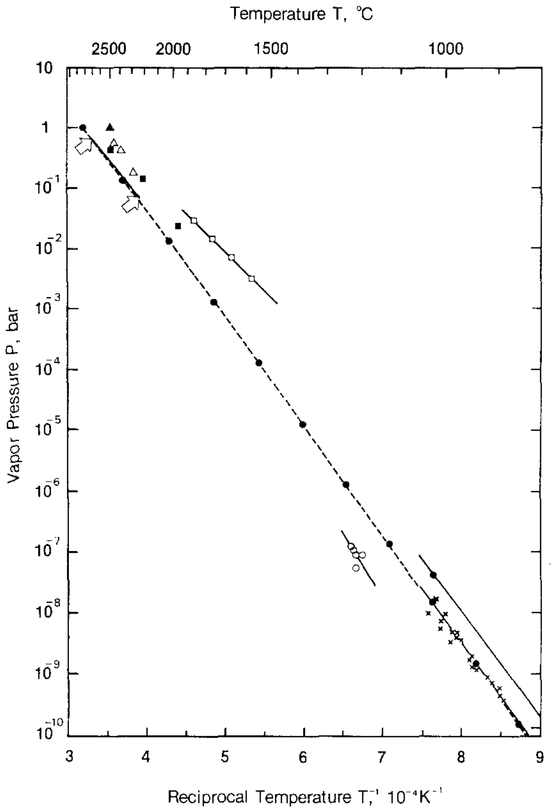

Fig. 8. Vapor pressure of gold.

In the cases of In and Ga (Figs. 3 and 5), no data or estimates are presented in Ref. 10 in the temperature range investigated here. The results for Ag (Fig. 4) agree remarkably well with the estimate of Nesmeyanov. The present results for Au (Fig. 8) are also in good agreement with his estimate. The data for Sn (Fig. 7) fall just beyond the range of the estimate provided in Ref. 10 but are consistent with the low-temperature data on which the estimate was based. The largest deviation between the present results and the estimate of Nesmeyanov is for Cu (Fig. 6). Here again, the estimate was based on an extrapolation of low-temperature data.

The boiling points of these metals have also been estimated by Hultgreen et al. [11] from data taken at lower temperature. These boiling points are as follows: In, 2346 K; Ag, 2436 K; Ga, 2478 K; Cu, 2836 K; Sn, 2876 K; and Au, 3130 K. These values agree well with the data presented here.

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REFERENCES

1. J. Bohdansky and H. E. J. Schins, *J. Appl. Phys.* **36**:3683 (1965).
2. J. Bohdansky and H. E. J. Schins, *J. Phys. Chem.* **71**:215 (1967).
3. J. Bohdansky and H. E. J. Schins, *J. Less-Common Metals* **13**:248 (1967).
4. H. E. J. Schins, R. W. M. van Wijk, and B. Dorpema, *Z. Metal.* **62**:330 (1971).
5. F. Geiger and D. Quataert, Corrosion Studies of Tungsten Heat Pipes at Temperatures up to 2650°C, Second Int. Heat Pipe Conf., Report ESA SP-112, Vol. 1, p. 347 (1976).
6. M. Bader, The Gas-Controlled Heat Pipe as a Tool for Wetting Studies, Second Int. Heat Pipe Conf., Report ESA SP-112, Vol. 1, p. 327 (1976).
7. C. Bassani and C. A. Busse, A Pressure Controlled Precision Thermostat, Second Int. Heat Pipe Conf., Report ESA SP-112, Vol. 1, p. 537 (1976).
8. C. Bassani and J. Loens, Precision Temperature Control with Gas Buffered Water Heat Pipes, Third Int. Heat Pipe Conf., AIAA Publ. CP-784, p. 162 (1978).
9. C. A. Busse, J. P. Labrande, and C. Bassani, in *Temperature Measurement, 1975*, B. P. Billing and T. J. Quin, eds., Inst. Phys. Conf. Ser. No. 26, p. 428 (1975).
10. A. N. Nesmeyanov, *Vapor Pressure of the Chemical Elements* (Elsevier, Amsterdam, 1963).
11. R. Hultgreen et al., *Selected Values of the Thermodynamic Properties of the Elements* (American Society for Metals, Metals Park, Ohio, 1973).