

A Simple Rapid Vapor Pressure Micromethod

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► A capillary tube method has been developed for measuring vapor pressure or phase changes. This method is simple, rapid, and suitable for high temperature and pressure measurements. It is inexpensive, and such a unit has been demonstrated to stand temperatures up to 400° C. and pressures up to 20 atm.

ALTHOUGH vapor pressure determinations for liquid substances are as frequent as melting point determinations for solids, there is no simple rapid vapor pressure method comparable to the capillary tube method for the melting point determination. The need for a rapid vapor pressure micromethod is reflected by the fact that commercial equipment was in production less than a year after the publication of a much improved method (3).

This paper describes an extremely simple but relatively precise method (accurate to $\pm 5\%$ in a single measurement), based on the change of position of a mercury plug acting as a free piston in a capillary tube, when the vapor pressure of the test substance, either solid or liquid, confined by the plug in the capillary tube is changed as described below.

DESCRIPTION OF APPARATUS

The arrangement of the equipment is shown in Figure 1. The thermometer, *A*, and a capillary tube, *B*, are immersed in an unsilvered Dewar flask. A capillary tube, 2.0 to 2.5 mm. in diameter, is large enough to facilitate insertion of the test sample to the bottom or sealed end. Larger diameters are undesirable because it is then difficult to retain the short suspended column of mercury, *E*. The diameter of the capillary tube should be uniform; thus a precision-bore tubing is preferred. However, for a 12-inch length of ordinary capillary tube, the diameter of the tube does not vary appreciably and can be used after calibration. The capillary tube should be long enough to be conveniently immersed in the bath. The temperature of the bath is conventionally controlled by a knife heater, *C*, and a variable autotransformer. Stirrer *D* keeps the temperature of the bath relatively uniform. A cathetometer (not shown) is used for measuring the change in position of the mercury.

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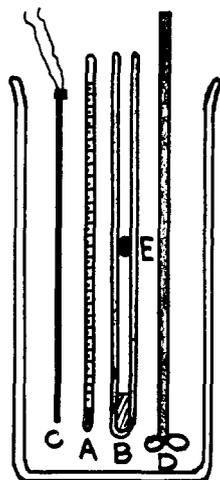


Figure 1. Assembly of apparatus for vapor pressure measurement



Figure 2. Sealed capillary tube

PROCEDURE

After the desired length of capillary tubing is cut and cleaned, using a conventional cleaning solution, the tube is dried and sealed at one end. If the uniformity of the tube diameter is not certain, as in the case of an ordinary capillary tube, this should be calibrated by determining the length of a known-weight mercury column with a cathetometer.

The tube diameter at any place should not vary more than $\pm 5\%$ from the average value over the entire length. The volume of the sealed tip can normally be estimated with sufficient accuracy by assuming that the tip is in the form of a hemisphere. If the geometric shape of the tip is irregular, the volume of the sealed tip can also be calibrated with a known-weight mercury. This volume of the sealed tip is needed in estimating the effective length of the capillary tube underneath the mercury plug when a solid is the test substance. For a liquid test substance, the effective length of the capillary tube is the distance from the surface of the liquid meniscus to the bottom surface of the mercury plug. The volume of the solid test sample is calculated from its known density and the weight of the sample.

The test sample is admitted into the test tube through a carefully drawn

thin-walled capillary tube inside the bore, so that no test sample adheres to the glass wall of the test tube. Usually a few milligrams of sample are adequate, because the amount of vapor space above the test sample is very small. If the test sample is a liquid mixture, such as petroleum fractions, the sample weight should be large enough so that the amount of liquid vaporized will not cause a significant change in the composition of the liquid phase. The mercury plug sufficient to form a 4-mm. seal is placed at about the middle of the tube by a dropper made from another drawn, thin-walled capillary tube. The test capillary tube should be tilted to about 45° when the mercury plug is placed. The test capillary tube, thermometer, and other accessories are arranged as shown in Figure 1, and the positions of the mercury plug and sample surface, if the sample is a liquid, are measured with a cathetometer.

THEORY AND METHOD OF CALCULATION

For vapor pressures lower than atmospheric, one end of the capillary tube may be left open. In this case, total pressure, P_T , inside the sealed chamber containing the test sample must be equal to the average atmospheric pressure, P , plus the pressure, E , exerted by the mercury plug, expressed in millimeters of mercury. After the temperature of the bath is brought up from initial T_1 to T_2 , expressed in absolute temperature, the vapor pressure of the substance accordingly changes from $(V_P)_1$ to $(V_P)_2$ and the height of the mercury plug changes from L_1 to L_2 measured from the surface of the test liquid sample with a cathetometer. The vapor pressure at T_2 , $(V_P)_2$, can then be calculated by the following equations:

$$P_T = P + E \quad (1)$$

$$(V_P)_1 = P_T - Pa \quad (2)$$

where Pa = partial pressure of air in the sealed chamber

$$(V_P)_2 = P_T - Pa \left[\frac{L_1 T_2}{L_2 T_1} \right] \quad (3)$$

$$= P_T - [P_T - (V_P)_1] \frac{L_1 T_2}{L_2 T_1} \quad (4)$$

To derive Equations 3 and 4, it is assumed that the diameter of the capillary tube is uniform, which is true for a precision-bore tube. It is desirable to simplify the calculations by using a very low starting temperature, so that the

initial vapor pressure of the test sample is substantially zero or $P_T = Pa$. In this case, Equation 3 can be expressed by

$$(V_P)_2 = P_T \left[1 - \left(\frac{L_1 T_2}{L_2 T_1} \right) \right] \quad (5)$$

For vapor pressure higher than atmospheric, the open end must be sealed after the sample and mercury plug have been inserted and the distance between the plug and sample surface of the test liquid has been accurately determined. This is done by using a small torch to heat the glass capillary tube at a considerable distance from the opening until the glass melts and seals together. Thus no water vapor from the torch will have a chance to enter the test capillary tube. The initial pressure in the sealed tube is then determined from the change of the plug position after sealing of the capillary tube (Figure 2). Because the friction between the mercury plug and the glass wall is small, the pressure above the plug will always be equal to the pressure below the plug, less the pressure due to the weight of the plug itself. From the pressure change in the upper end, the vapor pressure of the sample enclosed in the bottom of the capillary tube can be calculated by the equation derived below. Let

- L_1 = effective length between sample surface and bottom of the mercury seal at initial temperature T_1 (Figure 2)
- L_2 = effective length above mercury seal at initial temperature T_1
- E = length of mercury plug, mm.
- P_i = initial pressure inside upper portion of sealed tube—i.e., portion of tube not containing the sample.

If the pressure unit is expressed in millimeters of mercury,

$$P_i = (V_P)_1 + Pa - E$$

When the temperature is increased from T_1 to T_2 , L_1 changes to $L_1 + \Delta L$ and L_2 to $L_2 - \Delta L$.

So

$$P_i \left(\frac{L_2}{L_2 - \Delta L} \right) \left(\frac{T_2}{T_1} \right) = (V_P)_2 + (Pa) \left(\frac{L_1}{L_1 + \Delta L} \right) \left(\frac{T_2}{T_1} \right) + E$$

$$= (V_P)_2 + [P_i + E - (V_P)_1] \left(\frac{L_1}{L_1 + \Delta L} \right) \left(\frac{T_2}{T_1} \right) + E \quad (6a)$$

or

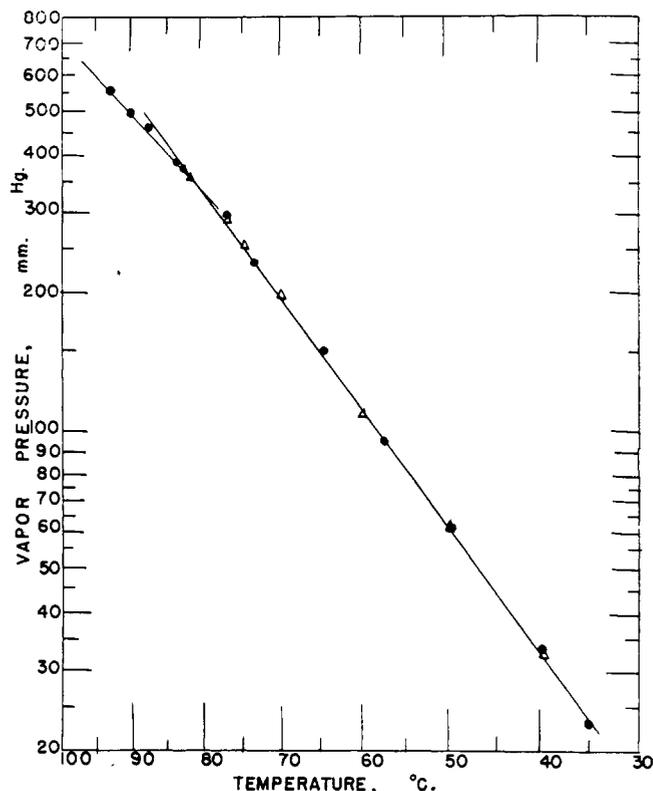
$$(V_P)_2 = P_i \left[\left(\frac{L_2}{L_2 - \Delta L} \right) \left(\frac{T_2}{T_1} \right) - \left(\frac{L_1}{L_1 + \Delta L} \right) \left(\frac{T_2}{T_1} \right) \right] + [(V_P)_1 - E] \left(\frac{L_1}{L_1 + \Delta L} \right) \left(\frac{T_2}{T_1} \right) - E \quad (6)$$

Again, it is desirable to design the experiment in such a way that at the initial temperature, T_1 , the vapor pressure of the test substance is negligible. The small value E , normally less than 4 mm., may be neglected. Thus Equation 6 simplifies to

$$(V_P)_2 = P_i \left(\frac{T_2}{T_1} \right) \left[\left(\frac{L_2}{L_2 - \Delta L} \right) - \left(\frac{L_1}{L_1 + \Delta L} \right) \right] \quad (7)$$

Figure 3. Vapor pressure of $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ and its transition temperature

- \triangle (2)
- \bullet This study



RESULTS

The vapor pressure of laboratory distilled water was determined below 100°C . using an open capillary tube and above 100°C . using a closed tube. The results are given in Table I.

The change of the mercury plug position which results from heating water from 30° to 40°C . is about 0.7 cm., while the accuracy of reading the cathetometer is limited to about 0.01 cm., so that the error is considerably greater for small than for larger temperature changes. The vapor pressure approached equilibrium very fast, probably on the same order as that of the thermometer, reaching equilibrium temperature during the heating period. However, more than 15 minutes was required to attain equilibrium values upon cooling. The latter probably is

form. The decahydrate used in this study was recrystallized from reagent grade $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$, air-dried at room temperature, and crushed to powder in a mortar and pestle. Menzel and Sieg (2) accurately measured the transition temperature of the decahydrate to the anhydrous $\text{Na}_4\text{P}_2\text{O}_7$ by solubility data as 79.5°C ., but their vapor pressure measurements did not extend far beyond the transition temperature and could not be used to estimate the transition temperature. The vapor pressures of water above the $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ measured by the capillary tube method are given in Figure 3. The slope of the line ($\log p \sim 1/T$) above 80°C . changes, probably because the water vapor is in equilibrium with a saturated solution of anhydrous $\text{Na}_4\text{P}_2\text{O}_7$ above this temperature. The vapor pressures of $\text{Na}_4\text{P}_2\text{O}_7$ at temperatures below 80°C . agree very well with the data of Menzel and Sieg (2). The transition temperature determined by the intersection of these two lines is about 80°C ., which also agrees with the value determined by the solubility data.

DISCUSSIONS AND CONCLUSIONS

Sources of error other than measuring are:

THERMAL EXPANSION OF GLASS. The thermal expansion coefficient of glass is reported to be 0.033×10^{-4} (1), which would result in a lower pressure, about 0.5%, for the sealed tube tests at temperatures around 200°C .

REACTION BETWEEN MERCURY SEAL AND OXYGEN. At temperatures around

Table I. Water Vapor Pressure Determined by Capillary Tube Method

Temp., ° C.	Vapor Pressure, Mm. Hg			Difference, %	
	Measured values	Av. meas. value	Handbook value (1)	Based on sing. meas.	Based on av. value
Open Capillary Tube					
29.5	30.93, 30.97, 30.95	30.95	30.92	+1.62	+0.10
34.5	39.98, 40.37, 39.18	39.84	41.02	-4.48	-2.88
37.2	48.35, 47.51, 49.69	48.52	47.58	+4.43	+1.98
40.3	56.57, 54.55, 54.22	55.11	56.21	-3.54	-1.96
41.1	59.63, 58.81, 60.55	59.59	58.65	+3.24	+2.28
44.5	69.75, 69.83, 69.20	69.59	70.05	-1.21	-0.66
44.7	70.11, 70.85, 70.67	70.34	70.77	-0.93	-0.61
48.4	85.57, 85.40, 86.19	85.71	85.42	+0.90	+0.34
50.0	92.01, 92.27, 91.50	91.93	92.51	-1.09	-0.63
Sealed Capillary Tube, Air Filled					
146.0	2900	...	3203.4	-9.45	...
192.0	8600	...	9831.4	-12.52	...
214.0	12750	...	15488.0	-17.68	...
Sealed Capillary Tube, Nitrogen Filled					
153.3	3780	...	3897.9	-3.03	...
162.8	4750	...	4975.4	-4.52	...
215.7	15200	...	16074.2	-5.44	...

200° C., mercury reacts with oxygen to form mercuric oxide. For the sealed tube measurements, red mercuric oxide was noted on top of the mercury seal. This apparently introduced some error because, in runs as given in Table I, when nitrogen instead of air was used inside the capillary tube, the water vapor pressure measured at high temperatures was closer to the handbook value and the difference reduced to less than 6%.

CREEPING OF LIQUID WATER ABOVE MERCURY SEAL. If water vapor has condensed on the mercury seal, the water film could creep above the seal. For a sealed tube this can introduce a serious error due to vapor pressure

change with temperature in the upper sealed chamber. This can be checked by cooling the tube and determining if the seal returns to the original position or if any water droplets are visible in the upper chamber.

CREEPING OF GLASS CAPILLARY TUBE. Under moderate temperature and pressure, the glass tubing may elongate, which also will cause a lower measured water vapor pressure. This effect, however, was also assumed to be small, because there was very little change in measured vapor pressure at 192° C. after immersion in a hot fused salt bath for 42 hours.

DEVIATION FROM PERFECT GAS LAW. The measured water vapor pressure at

high temperatures will not change very much, if corrections are made for the deviation from perfect gas law.

It can be concluded that the capillary tube vapor pressure method is simple and, with open-end capillaries, gives reproducible results within $\pm 5\%$ of the true value. At high temperatures, however, where sealed tubes must be used, the measured vapor pressure values will be low. In the latter case, use of a capillary tube made of low thermal expansion Vycor glass and an inert gas blanket to avoid reaction between the mercury seal and oxygen will reduce the error considerably. This device has been demonstrated to stand temperatures up to 400° C. and pressures up to 20 atm.

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LITERATURE CITED

- (1) "Handbook of Chemistry and Physics," 36th ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1954.
- (2) Menzel, H., Sieg, L., *Z. Elektrochem.* **38**, 283 (1932).
- (3) Mottlau, A. Y., *ANAL. CHEM.* **29**, 1196 (1957).

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Vapor Phase Separation of Methyl- or Ethylmercury Compounds and Metallic Mercury

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► A method for the capture of ethylmercury and methylmercury compounds in the presence of mercury vapor was needed in a study of organic mercurial fungicide decomposition in soil. The method developed can be used to trap 10 γ or more of the alkyl mercury compound in a cubic meter of air. Where the organic and metallic mercury vapors occur together, this method offers means of quantitative separation.

DURING an investigation of organic mercurial fungicide decomposition in soil, it was necessary to measure the

loss of mercury into the atmosphere. From biological experiments, Boer (1) postulated a mechanism for the decomposition of organic mercurials in soil. He assumed at one point that the intact organic mercury vapor of the alkyl mercuric compounds of lower molecular weight, such as ethylmercury chloride, would be given off from the soil along with the metallic mercury vapor. Preliminary tests here appear to substantiate this. Thus a method to be used for mercury recovery in such a soil experiment must quantitatively capture both the organic and metallic mercury vapors.

The literature revealed numerous methods for capturing mercury vapor. Chemical absorption methods use potassium iodide-iodine solution (8), potassium permanganate-sulfuric acid solution (2-4), bromine and chlorine solutions (7), or iodized active carbon and mineral wool (11).

None of these methods is applicable to the capture of methyl- or ethylmercury chloride in the presence of metallic mercury vapor. The method described can be used to capture and determine by modified existing methods (5, 9, 10) either methyl- or ethylmercury compounds in the range of 10