A SIMPLE METHOD OF VAPOR-PRESSURE MEASUREMENT FOR HIGH BOILING LIQUID SUBSTANCES

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Although there are many studies on the vapor pressure measurement of high-boiling liquids, relatively little work has been done on a simple way of measuring the vapor pressure at relatively high temperature. We have used a U-shaped barometer to develop a new, simple vapor-pressure measuring apparatus. This method is simple and it was used to measure the vapor pressure of esters, petroleum systems, silicone oil systems, diphenyl chloride system, alkylnaphthalene systems and polymonochlorotrifluoroethylene oil systems over a pressure range of from 0.5 to 20 mm Hg and at a temperature range of from 100°C to 300°C, with satisfactory result.

INTRODUCTION

Studies on the vapor pressure measurement for high-boiling liquids have been made for a long time. In a lower temperature region, the vapor pressure is low. In this range, dew point method[1], spring balance method[2] and others[3] have been used. In spite of its industrial importance, there is virtually no simple method available for measurement of vapor pressure in a range of from 0.5 to 20 mm Hg.

If, under equilibrium condition, a vapor phase can be handled as an ideal gas, there is following relationship, according to the law of thermodynamics, between the pressure P and the temperature T.

$$\frac{d \ln P}{dT} = \frac{\Delta H}{RT^2} \qquad (1)$$

Now, if ΔH is independent of temperature, then the equation will become a first order function of log P and T^{-1}. This, however, is not true in an actual case. In fact, ΔH changes in relation to a change in T. Therefore, it is not valid to make an extrapolation over a wide range. In order to obtain an accurate data for vapor pressure and heat of evaporation at a certain temperature, one has to determine such parameters at that particular temperature.

The principle of the device constructed by us is based on a direct measurement of vapor pressure by an U-shaped barometer. One of its characteristics is to use the liquid sample itself as the column fluid of the barometer.

Traditionally, barometer(or manometer) of this type which employs a liquid column has the following advantages : (i) The construction is simple and therefore, method of use and construction can be done easily. Moreover, since there is no movable part, the apparatus is relatively free of troubles. (ii) Pressure is measured directly from

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a difference of the heights of the heads of the liquid columns. Therefore, there is no need to make a sensitivity calibration. Measurement of an absolute value can be made, independently of molecular weight, as long as the specific gravity is known.

On the other hand, they have the following disadvantages: (i) the fluid itself may react with the sample vapor, (ii) the fluid may dissolve the vapor, or (iii) error may originate from the vapor pressure of the fluid itself, or (iv) temperature correction for the fluid column may be needed. By using the same substance for the sample and the column fluid, shortcomings (i),(ii), and (iii) were corrected.

The second characteristic is that a portion of the vapor is constantly released into vacuum which is usually higher than 10^{-3} mm Hg. By such mechanism, lower molecular weight impurities formed from thermal decomposition, even in extremely small quantities, are constantly removed, thus preventing them from being accumulated in the system. Since there is a hole, the initial "de-gassing" procedure can be carried out thoroughly. Even when the sample is made of a mixture, fractional distilling effect can be avoided because almost no condensation process takes place in the vapor chamber, and the released vapors are totally condensed and refluxed by the condensor. Thus, the composition of the sample within the boiler will remain unchanged. This latter aspect eliminate the biggest disadvantage of the distillation method. Thus, the present method can be most advantageously used on industrial products for which the measurement of the vapor pressure of a mixture is frequently important.

APPARATUS

The vapor pressure-measuring apparatus constructed by us was made totally of hard glass(Toshiba Telex). Outline of the apparatus is illustrated in Fig. 1.

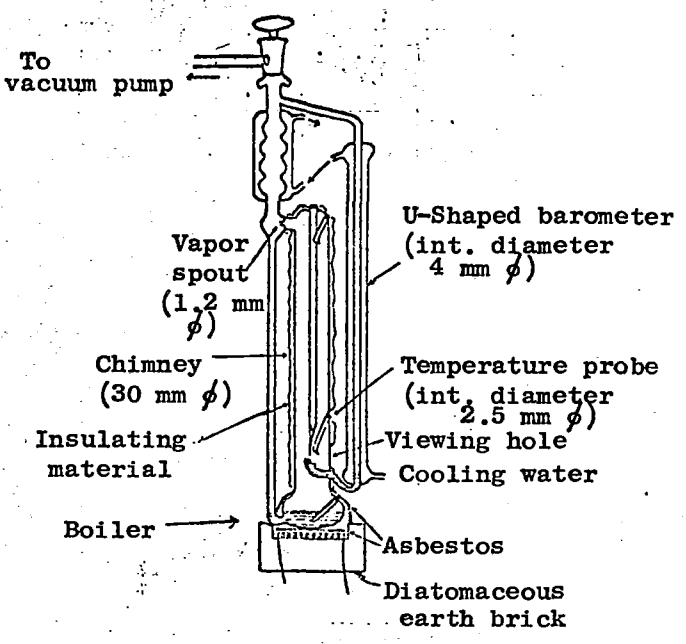

FIG. 1 Apparatus

Through the cock, the apparatus is connected to a vacuum pump to maintain a pressure of 10^{-3} mm Hg or lower. Inert gas is placed in the exhaust system, at a constant rate of flow, and its pressure is read by another mannometer, and adjusted accordingly. Thus, vapor pressure can be measured for a high vapor pressure range, without extending the fluid column portion.

Boiler and chimney portions are heated by a suitable means to maintain an uniform temperature throughout. A glass tube (internal diameter 2.5 mm ϕ) is attached to the middle and upper portion of the chimney, through which a thermocouple is inserted to measure the temperature. Temperature at these two areas has to be the same. The thermocouple and the tube attached to the boiler portion is used for measuring the temperature of the liquid phase. The thermocouple and the tube attached at the middle portion of the chimney extends near the opening of the U-shaped barometer within the chimney, and in this area the vapor pressure and the temperature are measured.

There is a hole(diameter 1.2 mm ϕ) on the top of the chimney, through which the

vapor is released into vacuum. The condensed liquid passes through the side tube and returns to the boiler.

The glass tube located at the center of the chimney has pointed tip, and its function is to supply liquid to the U-shaped barometer. With the rising temperature, condensed sample fluid will accumulate within the barometer. If one wants to resupply, one has only to blow an air from external sources into this center tube to forcibly cool down the system. It is, however, not advisable to force the system to cool too rapidly, because by such doing the temperature of the entire vapor phase tends to decline.

With this procedure, the temperature gradually elevates. After the height of the head of the liquid column protruding out of the U-shaped barometer has reached a sufficiently high level, the temperature is lowered slowly and the temperature and the pressure are measured. In such case, the shorter side of the U-tube being inserted into the chimney has always its fluid in the overflow state. In other words, one of the liquid column of the U-tube is fixed. The internal diameter of the U-shaped barometer is 4 mm ϕ, and its outside surface can be cooled with water. Therefore, the temperature can always be maintained constant.

The end of the U-tube located inside is open, and its meniscus may be horizontal, concave or convex. Accordingly, the reading of the head of the liquid column may change. In order to make the meniscus of the inner arm of U-tube to have the same shape of meniscus as that of the outer arm of the U-tube, a beak-shaped glass piece was attached. When the liquid is in overflow state, as illustrated in Fig. 2, one can not obtain a normal meniscus. Due to variation of the shape of the menisci of two arms of the U-tube, systematic errors always exist. In view of the magnitude of the data, however, this does not cause significant problem. But, rather, identical variations always reproduced, which reduces the distribution of data. Therefore, in our opinion, such a beak-like device should be attached.

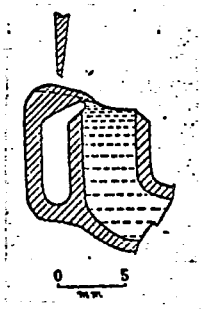

FIG. 2 Opening on the U-tube within the chimney

MEASUREMENTS AND RESULTS

An oil pump and a three-stage glass oil diffusion pump were used as the vacuum pump to obtain a vacuum of 10^{-5} mm Hg.

Boiler and chimney portions were heated separately, each using 0.5 mm ϕ nichrome wire and heated electrically. Heating is controlled by the use of sliducks which work independently. The heat lost by the vapor which is released from the small hole on the upper part of the chimney is only about 4 W, even when the vapor pressure within the chimney is as high as 20 mm Hg. Therefore, there will be no problem. The entire area may be enclosed in a copper block and heated externally, but in an actual practice, we have used the following mechanism.

In the boiler portion, nichrome wire wound around as a coil is embedded in a trench which has been formed spirally around a piece of a brick of diatomaceous earth. The entire body is wrapped with asbesto sheets to effect uniform heating and to maintain insulation. In chimney portion, it was wrapped with one layer of glass fiber tape. Nichrome wire is then wound over the glass fiber at a pich of about 1 cm. The wire layer is then covered and wrapped with asbesto layer and glass fiber tape to effect its insulation.

With this kind of insulation, it required about 100 W for the chimney portion and about 50 W for the boiler portion(room temperature 28°C), in order to heat them to 200°C.

To measure the temperature, a Cu-constantan thermocouple that has been temperature-corrected(measuring the melting point of lead and tin and boiling point of water) is inserted deeply into the side arm tube, and the voltage is read with a mV meter directly. The temperature of the center portion of the chimney portion was about 1°C higher than that of the upper portion of the chimney portion. Also, the liquid phase showed higher temperature(3°C) than the center portion of the chimney portion. Temperature of the vapor phase is the reading taken at the center portion when the temperature difference between the upper and center portions of the chimney portion is less than 1°C.

About 20 cc of the sample was charged in, and this amount was sufficient.

The specific gravity of the sample was measured with a float. A care was taken to keep the temperature of the water for cooling near 25°C, at which specific gravity measurement was taken.

Since the amount of liquid evaporated was extremely small, surface evaporation alone was sufficient. Even when the vapor pressure was high, there needs no concern for boiling. Unless the chimney portion is well insulated and the temperature is kept well, evaporation will be quite abrupt and boiling might take place.

It is timewise advantageous and also reliable to take the measurements, as the temperature is lowered. Although we did not see any delay in pressure reading due to reading of temperature, but we still paid attention in such a manner that the vapor pressure readings were taken after the temperature was lowered cautiously by 5°C. Ordinarily, it took about 60 minutes to take ten measurements at an interval of 5°C over a temperature range of 50°C.

Actual operation of the procedure is illustrated in Fig. 3. Results are illustrated in Fig. 4 and also in Table 1.

FIG. 3

DISCUSSION

Possible causes of errors are indicated below.

(1) Problem of overheating and problem of non-uniform temperature distribution within the gas phase.
(2) Pressure gradient caused by the vapor flow which accompanies the release of the vapor from the hole.
(3) Error due to temperature difference at both arms of the U-tube.

As far as (1) is concerned, since the vapor flows at a certain proper velocity through a large chimney and therefore it is little affected by the wall of the vessel, one may expect the temperature difference at various locations within the gas phase to be extremely small. In fact, in the chimney portion, the temperature difference between the upper and the middle portions was only about 1°C. And, in such case, the difference is not significant. Therefore, this will cause no significant problem.

With regard to (2), the amount of vapor released can be calculated from the equation which was originally derived in the fluid mechanics. And, the pressure gradient can be estimated from the resistance against

TABLE 1

No.	Sample	Sp. Gr. d^{25}	Temp. range (°C)	Pressure range (mm Hg)	A*	B*	Heat of evaporation (kcal/mol)	Remark
E-1	Diethyl phthalate	1.118	110-170	1-18	9.14	3509	16.0	
E-2	Dibutyl phthalate	1.046	142-190	0.85-7	9.24	3876	17.7	
E-3	Di-2-ethylhexyl phthalate	0.983	195-245	1.2-11	10.31	4808	22.0	
E-4	Di-2-ethylhexyl azelate	0.914	208-265	1.1-15	10.42	4975	22.8	
E-5	Di-2-ethylhexyl sebacate	0.912	208-250	0.7-5	10.02	4878	22.3	
A-1	Alkylnaphthalene (side chain C=12)	0.932	168-220	1.2-15	10.24	4464	20.4	Lion Fat and Oil Co.
A-2	" (" C=16-18)	0.903	208-250	0.7-5	9.84	4785	21.9	"
H-1	Hydrocarbon oil (Insulation oil)	0.906	142-180	3-15	8.76	3436	15.7	Commercial insulation oil.
H-2	" (Lubrication oil)	0.844	132-186	1.8-12	6.39	2433	11.1	Matsumura Sekiyu W 50
H-3	" (Ejector pump oil A)	0.853	132-197	1.2-15	7.92	3175	14.5	" ME 250
H-4	" (" B)	0.872	171-242	0.8-14	8.95	4016	18.4	" ME 300
H-5	" (" C)	0.844	168-230	1.3-12	7.61	3289	15.0	Asahi Shinku DE oil
H-6	" (Diffusion pump oil A)	0.887	192-260	0.55-7.5	8.62	4132	18.9	Matsumura Sekiyu MD 350
H-7	" (" B)	0.878	225-300	0.5-8	8.52	4367	20.0	" MD 400
D-1	Diphenyl pentchloride	1.52	170-235	1.7-20	8.67	3731	17.0	Kanecrol 500, medium fraction
D-2	Diphenyl tetrachloride	1.454	145-192	1.2-9.6	8.60	3546	16.2	Kanecrol 400
D-3	Diphenyl trichloride	1.375	126-189	1.2-15.5	8.28	3279	15.0	Kanecrol 300
S-1	Silicone oil	1.027	161-210	2-18	9.50	4000	18.3	Dow-Corning DC-701, high frac.
F-1	Polymonochlorotrifluoroethylene oil	1.76	126-185	3.7-27	8.13	3145	14.4	Daifloil No. 10, medium frac.

* The contant when the points of measurements are expressed by an empirical formula

$$\log P = A - \left(\frac{B}{T}\right)$$ [where, P is in mm Hg, and T is an absolute temperature]

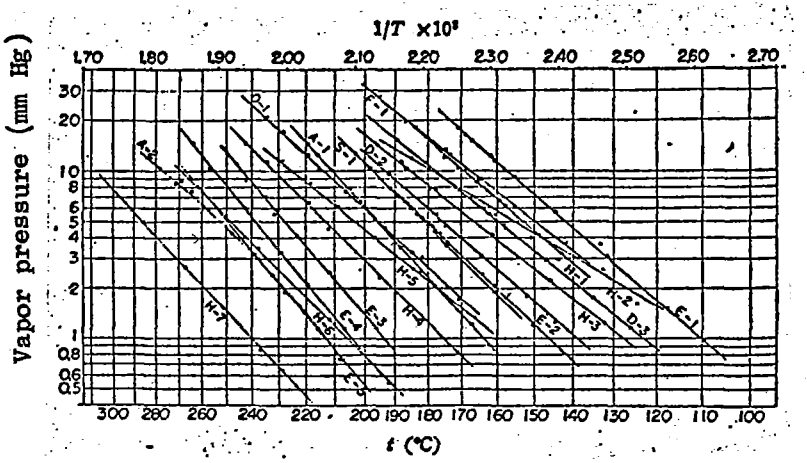

FIG. 4. Vapor pressure curves

the vapor flow within the chimney.

Let us assume a tank that is filled with a gas having a molecular weight M, having a pressure P_0(dyne/cm^2) at a temperature T_0(K^0). Let us also assume that the gas is constantly spouting out from a hole(cross sectional area S(cm^2)) into the vacuum. The amount of gas escaping into the vacuum during unit time (G (g/sec) can be expressed as follows[2].

$$G = SP_0\sqrt{\frac{M}{RT_0}}\cdot\sqrt{\frac{2\kappa}{\kappa+1}}\cdot\left(\frac{2}{\kappa+1}\right)^{\frac{1}{\kappa-1}} \qquad (2)$$

Where, R is gas constant, κ is the ratio (C_p/C_v) of the specific heat at constant pressure(C_p) to that at constant volume (C_v). In case of diethyl phthalate and at the highest chimney pressure (P_0 = 20 mm Hg), the pressure will correspond to an energy of 2.7 x 10^4 dyne/cm^2. If the temperature in this case is assumed roughly as 443^{0}K and the specific heat ratio κ is assumed as 1.02, M will be 222 and the cross-sectional area of the spout will be 1.13 x 10^{-2} cm^2. Therefore, G will be 1.4 x 10^{-2} g/sec. This will correspond to a vapor flow of about 88 cc per second.

In a cylinder having a length of L(cm) and a diameter of D(cm), if the gas is flowing at a velocity of V(cc/sec) and the pressure difference between two ends of the cylinder is Δp(dyne/cm^2), then the pressure gradient can be written as following[6].

$$\frac{\Delta p}{L} = \frac{128\eta}{\pi}\frac{V}{D^4} \qquad (3)$$

In this equation, π is the viscosity coefficient of the gas, but its exact value is not known. Therefore, by assuming the molecular diameter as about 8 x 10^{-8} cm to calculate η as η = 130 x 10^{-6} poise, and substituting this value, along with V = 88 cc/sec and D = 3 cm, into the above equation, the pressure gradient will be 4 x 10^{-6} mm Hg/cm. This value is too small to be of any significance.

However, since the volume of the chimney is about 200 cc, it may be estimated that the vapor within the chimney is replenished anew every 3 seconds.

There needs a particular caution for the term (3). Since the volume expansion coefficient of ordinary organic liquid is in the order of magnitude of 1 x 10^{-3} or smaller, there will be 10 % error if the temperature difference between two arms of the U-tube is 100^{0}C. Further, since the height of the liquid column inside the chimney portion is about 8 mm, the error will amount to about 0.8 mm. But, the actual problem occurs when the difference of the liquid column heads is extremely small. Fortunately, in such case, the temperature is also low, and therefore the problem will not be serious. When two kinds of petroleum series oils were used to measure the pressure at 192^{0}C and at 224^{0}C (difference of liquid heads= 8 mm)' deviation from the vapor pressure curve was only less than 0.5 mm, in terms of liquid column. This means that the reading error is very small.

Usually a cooling water is circulated around the portion of the barometer that protrude outside to maintain a constant temperature. Even when the temperature differs by 5^{0}C, the change of specific gravity is only about 0.5 %. Therefore, the variation is not significant.

Even for the samples that tend to solidify or increase its viscosity at normal temperature, measurements can be taken. In such case, the U-tube portion of the apparatus has to be suitably heated.

Measurements were taken for dibutyl phthalate, di-2-ethylhexyl phthalate, and di-2-ethylhexyl sebacate and the results are compared with the data reported in literature.[7] The data seem to fall on a single curve, over a wide temperature range, as illustrated in Fig. 5.

Based on these results, we conclude that this simple vapor pressure-measuring apparatus has broad applicability.

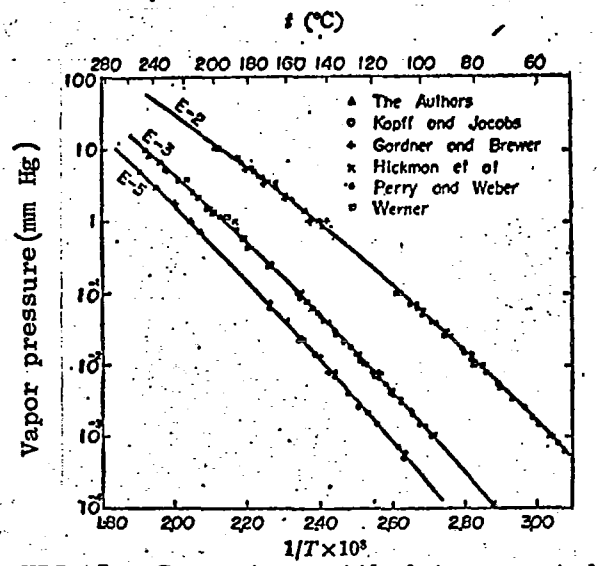

FIG. 5 Comparison with data reported in literature

Acknowledgement

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