INVESTIGATION OF NOVEL STATIC METHODS FOR THE

DETERMINATION OF VAPOR PRESSURES IN THE

PRESENCE OF INDIFFERENT GASES

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Bachelor of Science

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1953

Submitted to the faculty of the Graduate School of
the Oklahoma Agricultural and Mechanical College
in partial fulfillment of the requirements
for the degree of
MASTER OF SCIENCE
May, 1957

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ACKNOWLEDGMENT

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CHAPTER I

INTRODUCTION

Most of the work done in the field of chemistry is carried out with the substance(s) in the presence of some indifferent gas, usually air, it is therefore desirable for some applications to have the values of the vapor pressures which the substances exert under the same conditions so that the systems may be exactly considered from a thermodynamic standpoint.

The vapor pressure of a substance in the presence of an indifferent gas is usually obtained by measuring the partial pressure of its vapor. Nernst (1) has clearly pointed out the relationship of the partial pressure of a component's vapor in the presence of an indifferent gas to its vapor pressure in the following statement:

> If we bring a simple liquid into a vacuum, evaporation takes place, till the pressure of the gas formed has reached a definite maximal value, viz. the corresponding vapor pressure. In presence of another, but an indifferent gas, evaporation takes place till the partial pressure of the resulting vapor is equal to the vapor pressure.

The above statement is valid only for ideal systems, any interaction between the indifferent gas and the liquid and/or its vapor gives rise to deviations from Dalton's law of partial pressures. Consequently the partial pressure exerted by the liquid's vapor will differ from the vapor pressure it exerts _in vacuo_. Although deviations from ideality are usually small when the indifferent gas pressure is on the order of one atmosphere, any deviations may be determined by comparing the vapor pressure exerted in

a vacuum to the partial pressure exerted in the presence of an indifferent gas. (2).

The literature contains very many methods which are suitable for the determination of partial pressures in the presence of indifferent gases. A mention of only a few of the more important will be made, however. The method most often used is a modification of Regnault's (3) transpiration method. Regnault determined the vapor pressure of water by saturating a known volume of air by passing it through wet sponge and moist silk screens, absorbing the water in concentrated sulfuric acid and weighing it. Vapor pressures determined by Regnault in this manner were from 1 to 2 percent lower than those developed in vacuo. Later Shaw (4) repeated Regnault's experiments and confirmed his results.

Campbell (5) measured the partial pressure of several solvents in the presence of H_2, CO_2 and air. The principle of his method was that of allowing a liquid, previously saturated with an indifferent gas at a definite temperature and pressure, to evaporate into a space containing the same gas, under the same conditions. Campbell's results agreed with those of Regnault and Shaw in that he also found liquids exert a lower vapor pressure in the presence of an indifferent gas than when only in contact with their own vapor. He also proved that, in case of any one liquid, the vapor pressure lowering was proportional to the solubility of the gas, and conversely for any one gas the lowering was related to the properties of the solvent. It was pointed out by Campbell that in all cases the amount of gas dissolved was insufficient to account for the whole of the observed lowering and that the differences tended to disappear when the liquid was violently agitated.

Beare, McVicar and Ferguson (2) measured the partial pressure of

several organic solvents in the presence of dry air and CO_2 while agitating the liquid vigorously. The large discrepancies between the partial pressure and vapor pressure previously reported were not observed, however a lowering of less than 1 mm. Hg. was usually observed.

Dieterici (6) developed a differential static method, similar in principle to Campbell's absolute static method, that employed a sensitive gauge consisting of a metallic diaphram.

Lescoeur (7) proposed a method whereby the vapor pressure of a solution in the presence of an indifferent gas was calculated from the observed temperature at which the vapor condensed on a cooled metallic cylinder. Lescoeur's dew point method has been modified and improved by Cumming (8).

Purpose and Scope of Investigation

One of the advantages of determinimg vapor pressures in the presence of indifferent gases over that of determining vapor pressures in a vacuum is that degassing of the liquids, which is a time consuming process and leads to serious error if not done completely, is eliminated. (9). The purpose of this research was to develop a novel static method for the determination of partial pressures in the presence of an indifferent gas which would give high sensitivity in the vapor pressure range of 0 to 25 mm. Hg. and would require only a short time for the determination.

The procedure followed throughout this investigation was essentially that used by Campbell (5), that is, of allowing a liquid, previously saturated with an indifferent gas at a definite temperature and pressure, to

evaporate into a space containing the same gas, under the same conditions. Three pressure gauges were built and tested for their applicability to the determination of vapor pressures of solutions following this procedure.

The first pressure measuring device investigated was the single piston gauge, CHAPTER II, which was similar in principle to Melville's (10) direct reading manometer or the loaded piston manometer. (11). The direct reading manometer of Melville gave very high sensitivity, $\pm 10^{-3}$ cm. Hg., but was restricted in usefulness because of its limited range.

The second pressure measuring device investigated was the double piston gauge, CHAPTER III, which was similar in principle to the bell differential pressure element. (12) (13).

The properties of a displacement weight manometer were also investigated, CHAPTER IV. The principle of the displacement weight manometer is similar to that of the volume displacement manometer developed by Puddington (14) with the exception that the weight of manometric fluid displaced in one arm of a manometer is measured instead of its volume.

CHAPTER II

THE SINGLE PISTON METHOD

Construction of Apparatus

The null indicator used in this work was a Christian-Becker chain-
omatic analytical balance which was modified in order to weigh objects
outside of the balance case as shown in Fig. 1.

The piston gauge, equilibration flask and accessories were immersed
in an insulated constant-temperature bath. The bath consisted of a
cylindrical glass jar, 24 inches in height and 12 inches in diameter.
The jar was placed in a rectangular fiber board container, 14 x 14 x 24
inches, and the space between the jar and box was packed with shredded
asbestos. The bath was cooled by circulating water from a refrigeration
unit through 25 feet of 1/4 inch outside diameter copper tubing coiled
about the inner wall of the glass jar. The bath water was circulated
by a small submersible pump which drew water from the bottom of the bath
and discharged it at the top.

The temperature was regulated by a mercury thermoregulator that
consisted of a thin-wall-glass tube, 1.6 cm. in diameter and 50 cm. in
length, filled with 100 ml. of mercury. The mercury was forced to expand
into a 0.5 mm. capillary tube attached at the top of the mercury-filled
tube. The thermoregulator was used to actuate a Cenco-Gilson electronic
relay which in turn operated a 150 watt knife-blade immersion heater.

The bath temperature was controlled within a range of $\pm$ 0.01 degrees of

the desired temperature. The temperature of the bath was 25.00 ± 0.01° C. for all experiments and tests performed with this apparatus.

A 1000 ml. florence flask, joined to the piston gauge by a 24/40 standard-taper ground-glass joint and to the sample-holding apparatus by a 19/38 standard-taper ground-glass joint, served as the equilibration chamber. The design of the equilibration flask permitted the exposed surface of the liquid to be as large as practical and the diffusion path from the flask to the gauge to be short and of large cross sectional area.

The sample-holding apparatus, A Fig. 1, had a 100 ml. bulb for holding the liquid sample. The bulb was filled through a side arm that extended above the surface of the water in the bath. The filling tube was equipped with a 19/38 standard-taper ground-glass joint and was stoppered with a number 19 glass stopper. The 8 mm. O.D. by-pass tube allowed the sample-holding bulb to be vented from the system when the two lower stopcocks were opened and also permitted the system to be flushed with an indifferent gas through the uppermost stopcock.

The piston gauge was composed of three essential parts, the piston, the weight holder and weights, and the mercury cup and inlet tube.

The piston, B Fig. 1, was made of 1/25 inch stainless-steel tubing, sealed at the top and open at the bottom. A two inch brass rod was silver soldered to the center of the top. The top of the brass rod has female threads to receive a threaded hook. The lower half of the rod was 5/16 inch in diameter and the upper half was 1/4 inch in diameter, this provided a support for the weight holder.

Three cylindrical weights of lead, 20 gm. each, were molded to the 1/8 inch brass rods of the weight holder, C Fig. 1. The brass rods were spaced at 120 degrees of one another on the 3/16 x 1 1/4 inch brass disc.

The purpose of the weights was to lower the piston's center of graity so as to prevent the piston from tilting and making contact with the walls of the mercury cup and/or the inlet tube.

The mercury cup and inlet tube, $\underline{D}$ Fig. 1, were made of 1/25 inch stainless steel. The lower end of the inlet tube was fitted with a 24/40 standard-taper stainless-steel joint which fitted into the large ground-glass joint of the equilibration flask.

Principle of Operation

The operation of the piston gauge is based upon the principle that a change in force acting on the piston will be equal to the force required to counteract it. In our special case, the change of force acting on the piston will be due to the vapor pressure of the liquid and the force used to counteract it will be weight.

The apparatus is assembled as shown in Fig. 1, with the pointer of the analytical balance used as the null indicator, and by removing or adding weights on the balance pans the gauge can be nulled. Once the gauge is nulled, any change in pressure within the gauge will be proportional to the weight needed to counterbalance the pressure change.

$$W = KA \cdot \triangle P.$$

Where here and in the subsequent discussion:

$\underline{\triangle P}$ is the change in pressure within the gauge, cm. Hg.

$\underline{A}$ is the area of the piston, cm^2.

$\underline{W}$ is the change in weight, gm., required to nullify $\triangle P$.

$\underline{K}$ is a proportionality constant.

Increase in pressure within the system causes an increase in the volume of the system owing to the mercury level within the gauge moving
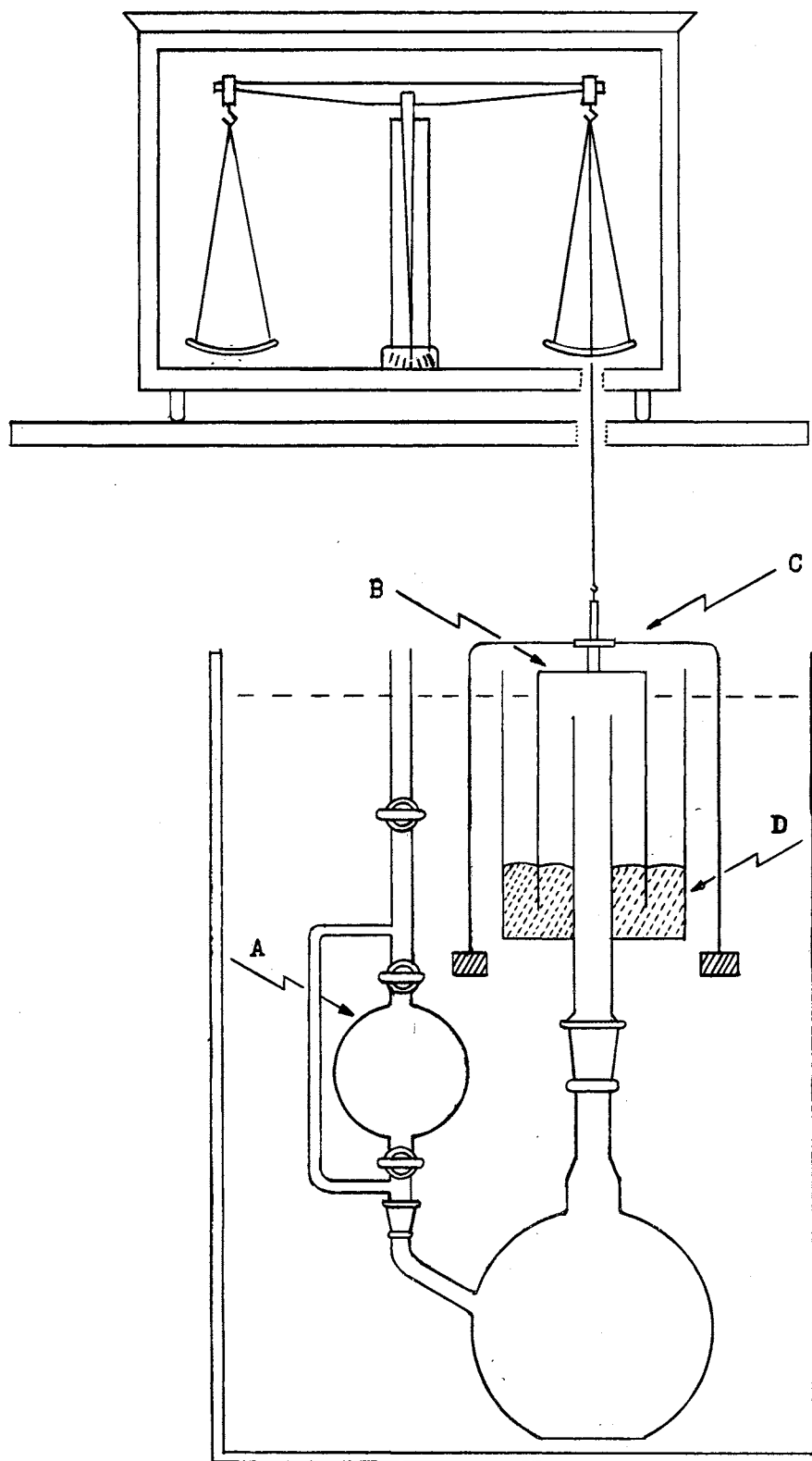
Fig. 1. Single Piston Gauge and Accessories.

downward, and therefore the increase in internal pressure will not be equal to an applied pressure such as the vapor pressure of a liquid. In order to determine the relation between the increased pressure and the actual applied pressure let:

P = the initial pressure within the system, cm. Hg.

V = the initial volume of the system.

N = the initial number of moles of gas in the system.

A = inner cross sectional area of the piston.

B = annular area between the inner wall of the mercury reservoir and the outer wall of the piston.

C = annular area between the inner wall of the piston and the outer wall of the inlet tube.

ΔH and ΔX = the change in height of the mercury levels inside and outside of the piston respectively.

Assuming that the gases behave ideally, we initially have, $PV = NRT$. Now we introduce an additional pressure, such as the vapor pressure of a liquid, and let it be represented as $\underline{P}'$, whence the final pressure $\underline{P}^*$ is equal to $(P + \Delta P)$ and

$$P + \Delta P = \frac{(N + N')RT}{V + \Delta V} .$$ (1)

Where N' is the number of moles of vapor introduced and $(V + \Delta V)$ is the final volume of the system.

Substituting $N' = P'(V + \Delta V)/RT$ and $N = PV/RT$ into equation (1) and rearranging we have:

$$P' = \Delta P + \frac{P\Delta V}{(V + \Delta V)} .$$ (2)

Since $\Delta V = C\Delta H = B\Delta X$ and $\Delta H + \Delta X = \Delta P$, then:

$$\Delta V = \frac{\Delta P}{(1/C + 1/B)} \cdot$$

Substituting the above expression for ΔV and W/KA for ΔP into equation (2) gives:

$$P' = \frac{W}{KA} + \frac{PW}{W + VKA(1/C + 1/B)} \cdot \tag{3}$$

A column of mercury with a 1 cm² cross section and 1 cm. in height exerts a force (W) of 13.59 gm. at 0° C. Substitution of these values into the equation $W = KAP$ gives a value of 13.59 gm./cm² cm. Hg. for the constant $\underline{K}$.

The following constants were evaluated by measuring the dimensions of the gauge with a micrometer.

      Cross sectional area of the piston; $A = 9.95$ cm².

      Outer annular area; $B = 7.25$ cm².

      Inner annular area; $C = 7.12$ cm².

The volume of the system was determined by measuring the volume of water required to fill it. This was 1320 cm³.

Substituting these values for the constants in equation (3) we have:

$$P' = \frac{W}{135} + \frac{PW}{(W + 49440)} \cdot \tag{4}$$

The advantage of the piston gauge is in its great sensitivity which is a function of the area of the piston. The weight required to null the balance when a force is applied within the gauge is proportional to the area of the piston and the applied pressure.

Weight (gm.) = Area of piston (cm².) · Pressure (gm./cm².).

Or: Weight (gm.) = Area of piston (cm².) · Pressure (cm. Hg.) · Constant. It follows from the above discussion that the constant is 13.59 gm./cm². cm. Hg.

Therefore: Weight (gm.) = 13.59 • Area of piston • Pressure.

Or: $\Delta W = 13.59 \cdot A \cdot \Delta P$

is the relationship between a change in pressure within the gauge and the weight required to balance it.

A piston of unit area would require 13.59 gm. of weight to counterbalance a change in pressure of 1 cm. Hg. If the sensitivity of the null indicator were only 1 part in 136, a change of pressure equal to 0.0074 cm. Hg. could be detected. The piston used in this investigation had a cross sectional area of 9.95 cm^2, substituting this value into the above equation gives: $\Delta W = 135 \Delta P$.

A change in weight of 0.1 gm. equals a change in pressure of 0.00074 cm. Hg. or 0.0074 mm. Hg.

Operating Procedure

The piston gauge, equilibration flask and simple holder were cleaned and then dried in a drying oven at 110° C. for one hour. After drying the apparatus was assembled as shown in Fig. 1, all joints and stopcocks were greased with Dow-Corning silicone lubricant. The assembled apparatus was clamped firmly to a ring stand, then immersed in the constant-temperature bath so that the water level was approximately one half inch from the top of the mercury cup. Although the weight holder arms extended over the mercury cup and into the water bath, stirring of the bath water was not vigorous enough to cause any lateral or vertical motion to the piston. The piston was connected to a hook soldered onto the bottom of the balance pan by a 10 inch piece of beaded chain, which allowed the piston to be rotated with the hand. The initial position of the piston was such that when the piston was centered over the inlet tube its top was level with the top

of the mercury cup. The same volume (70 ml.) of mercury was placed in the mercury cup for each run. In this way the mercury level was adjusted so that the weight of the piston and added weights was greater than the calculated weight required to balance the expected change in pressure. This assured that the piston always had negative buoyancy and that the change in pressure could be counterbalanced by removing weights from the pan on the left side of the balance.

The sample holder was filled with the sample through the filling tube which extended above the water line, (not shown in Fig. 1). The sample was then saturated with dry nitrogen gas by inserting a gas dispersion frit through the filling tube of the sample holder and slowly bubbling nitrogen through the sample for approximately one hour.

The nitrogen gas used was water-pumped tank nitrogen, which was dried in a drying train consisting of seven inch towers of concentrated sulfuric acid, activated alumina, and sodium hydroxide flakes.

The entire system was flushed with dry nitrogen by connecting the nitrogen supply to the extended tube of the sample holder, while the uppermost stopcock was open and the piston was raised slightly so as to allow the gas to escape around its lower rim. The system was flushed in this manner for thirty minutes, at the end of which time the piston was lowered to its orginal position and the stopcock on the sample holder was closed. The nitrogen supply tube was then replaced by a calcium chloride drying tube and the vent stopcock again opened. The pointer of the balance was brought to the null point by adjusting the necessary weights on the left pan of the balance. The vent stopcock was then closed.

The gas dispersion frit was removed from the sample holder and the filling tube stoppered with a greased glass stopper. The atmospheric

pressure was read and recorded as the initial pressure of the system.

The two lower stopcocks on the sample holder were opened and the sample allowed to drain down into the equilibration chamber in order to start the run.

As the vapor pressure of the liquid exerted an additional force on the piston, the weight that had to be removed to nullify this force was recorded at intervals until the system reached equilibrium. At equilibrium, the weights which had been removed during the run were proportional to the total change in pressure within the system. The vapor pressure of the liquid was then calculated using equation (4).

Correction for Variations in External Pressure

The single piston gauge suffers from the disadvantage of being affected by variations in atmospheric pressure. A correction must accordingly be made to the amount of weight at the end of the run if the atmospheric pressure at this time is different from the initial atmospheric pressure at the beginning of the run.

The change in weight on the left pan of the balance due to variations in atmospheric pressure is a function of both the atmospheric and internal pressures, since the internal pressure is also a function of the atmospheric pressure.

$$\Delta W \cong \left(\frac{\partial W}{\partial P_a}\right)\Delta P_a + \left(\frac{\partial W}{\partial P_i}\right)\Delta P_i \qquad (1)$$

Where: ΔP_a = change in atmospheric pressure.

ΔP_i = change in internal pressure.

ΔW = correction of weight required for a pressure change

of ΔP_a.

Since:

$$W = KA \cdot P_a \qquad \text{then} \qquad \frac{\partial W}{\partial P_a} = KA \qquad (2)$$

and $\qquad W = -KA \cdot P_i \qquad \text{then} \qquad \frac{\partial W}{\partial P_i} = -KA. \qquad (3)$

Increases in internal pressure require weight to be removed from the left balance pan; therefore, the sign is negative in equation (3).

$$P_i = \frac{NRT}{V} \qquad \text{therefore,} \qquad \Delta P_i \cong -\frac{NRT \cdot \Delta V}{V^2} = -\frac{P_i \cdot \Delta V}{V}.$$

Again we have, $\Delta V = C \Delta H = B \Delta X$ and $\Delta H + \Delta X = \Delta P_a$, it follows that:

$$\Delta V = -\frac{\Delta P_a}{(1/C + 1/B)}.$$

we then have:

$$\Delta P_i = \frac{P_i \Delta P_a}{V(1/C + 1/B)}. \qquad (4)$$

Sustituting equations (2, 3, and 4) into equation (1) we get:

$$\Delta W = KA \Delta P_a \left[1 - \frac{P_i}{V(1/C + 1/B)} \right]. \qquad (5)$$

Substituting the values for the constants into equation (5) gives:

$$W = (135 - 0.368 P_i) \Delta P_a. \qquad (6)$$

Using the above equation and plotting ΔW versus ΔP_a, a family of straight lines is obtained. Each line of the family passes through the orgin and has a slope of $(135 - 0.368 P_i)$.

Experimental

A series of experiments was run with the gauge filled with nitrogen, at a pressure of 74.29 cm. Hg., in order to determine the $\Delta W/\Delta P_a$ relationship experimentally so that the theoretical relationship of equation (6) in the preceding section could be checked. The experimental

and theoretical data are plotted in Fig. 2.

The inconsistancy of the experimental data shows the system responded very slowly to changes in atmospheric pressure, and indicates the poor sensitivity of the gauge during these experiments. Both of these effects were probably due to the piston rubbing against the walls of the inlet tube and/or mercury cup below the mercury level.

The gauge was also tested using C.P. reagent chlorobenzene in order to determine the approximate time required for a liquid of low vapor pressure to reach equilibrium. See Fig. 3.

In order to check the validity of the theoretical equation;

$$P' = \frac{W}{135} + \frac{PW}{(W + 49440)} \,$$

runs were made on 8.995 and 12.45 molal sulfuric acid solutions. The concentration of the acid solutions were determined by titrating the acid with standard sodium hydroxide solution using phenolphthalein as an indicator. The values of the solutions' vapor pressure were obtained from the literature. (15).

A 24 hour run was made on the 12.45 molal sulfuric acid solution, with changes in atmospheric pressure and the changes in weight being recorded throughout the run. Corrections for variations in atmospheric pressure were calculated using equation (6), p. 14. The results of these corrections are given in TABLE I, p. 18. Substitution of the value for the corrected weight after 24 hours and the initial pressure into the theoretical equation gave a value of 4.74 mm. Hg. for the vapor pressure of the 12.45 molal sulfuric acid solution. This experimental value deviates 22.7 per cent from the value 6.13 mm. Hg. obtained from the standard curve. (15).
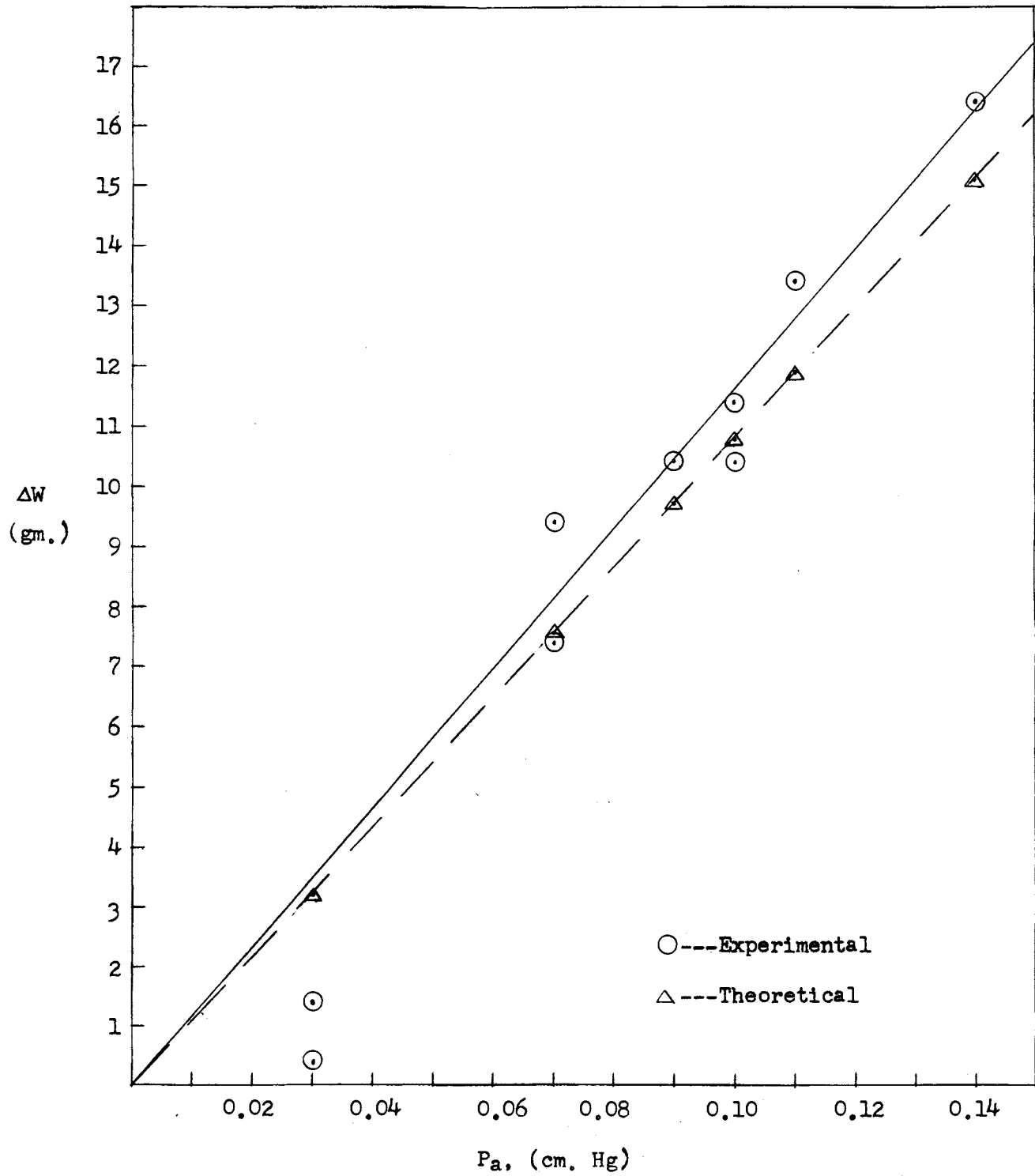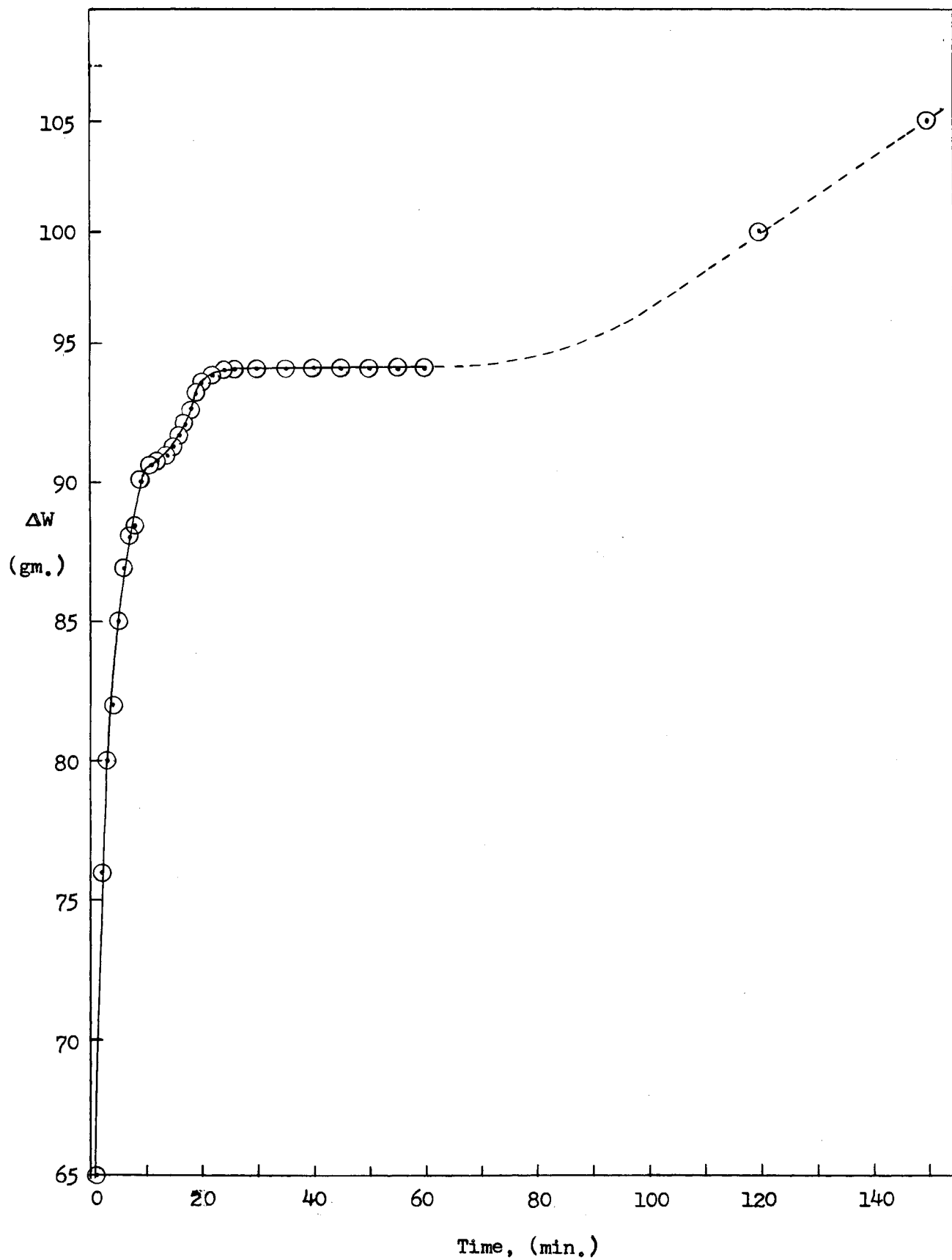
Fig. 2. Corrections for Changes in External Pressure

Fig. 3. Chlorobenzene

TABLE I

VAPOR PRESSURES OF SULFURIC ACID SOLUTIONS

Molality H_2SO_4	Time of Run	Weight	Experimental Vapor Press.	Literature Vapor Press.	Per Cent Deviation
8.995	80 min.	81.8 gm.	7.28 mm. Hg.	10.08 mm. Hg.	27.8
8.995	80	94.2	8.39	10.08	16.8
8.995	190	99.5	8.86	10.08	12.1
12.45	24 hrs.	53.2*	4.74	6.13	22.7

* Corrected for changes in external pressure.

Calculation of Results

The change in weight (W) due to the pressure exerted by the chloro-benzene was found to be 94.1 gm. with an initial pressure of 74.60 cm. Hg. Substituting these values into the theoretical equation,

$$P' = \frac{W}{135} + \frac{PW}{(W + 49440)}$$

gives: $P' = 0.697 + 0.142 = 8.37$ mm. Hg.

This experimental value of 8.37 mm. Hg. at 25° C. deviates 33.0 per cent from the literature value of 12.53 mm. Hg. (16).

The first run using 8.995 molal sulfuric acid solution produced a change in weight of 81.8 gm. at the end of 80 minutes. When this value and the value of the initial pressure (74.02 cm. Hg.) are subst-ituted into the theoretical equation a value of 7.28 mm. Hg. is obtained for the vapor pressure at 25° C. This experimental value deviates 27.8 per cent from the value of 10.08 mm. Hg. taken from the standard curve.

The second run using the 8.995 molal sulfuric solution produced a

change in weight of 94.2 gm. at the end of 80 minutes and a change of 99.5 gm. at the end of 190 minutes. Calculations gave a vapor pressure of 8.39 mm. Hg. at the end of 80 minutes and a vapor pressure of 8.86 mm. Hg. at the end of 190 minutes. The latter value deviates 12.1 per cent from the value taken as standard.

Conclusions

Determinations of the vapor pressures of the sulfuric acid solutions and chlorobenzene showed that the single piston gauge gave very poor precision. Although a theoretical correction can be made for variations in external pressures, considerable error is still introduced because the system reacts slowly to these variations. In deriving the equation for the correction for variations in external pressures it was assumed that the partial pressure due to the vapor pressure of the liquid was constant. This assumption is valid only when the vapor is in equilibrium with the liquid. Variations in external pressures cause variations in the volume of the system. This change in volume temporarily disturbs the vapor-liquid equilibrium within the system, and this results in a change in the partial pressure of the vapor. If the external pressure remains constant long enough for the vapor and liquid to attain equilibrium once again, then the correction for the change in external pressure can be applied. However, if the external pressure continues to vary then the vapor-liquid equilibrium will continue to be disturbed and it is impossible to make a precise measurement.

Other possible errors were failure to remove all water vapor from the system before the sulfuric acid solutions were introduced and fail-

ure to saturate the liquid sample with nitrogen. Supersaturating is a possible though not highly probable source of error also.

The indeterminable error due to changes in external pressure makes the single piston gauge an unsuitable instrument for determining vapor pressures in the presence of an indifferent gas in spite of its high theoretical sensitivity. Better design of the gauge might avoid some of the difficulties such as its sluggishness of response resulting from its mass and mechanical friction; however, the slowness of attainment of equilibrium in its use appears to be the critical factor which limits its usefulness.

CHAPTER III

THE DIFFERENTIAL PISTON METHOD

Construction of Apparatus

The null indicator used with the differential piston gauge was the same Christian-Becker chainomatic analytical balance that was used with the single piston gauge. For this work the balance was modified so that a piston could be suspended from the left as well as the right balance pan.

The differential piston gauge and its accessories was immersed in a insulated constant-temperature water bath. The bath consisted of a galvanized iron tank, 3 ft. long, 2 ft. wide, and 2 ft. deep. The tank was insulated on all sides and the bottom with 1 inch thick Celotex board. The bath was cooled by circulating water from a refrigeration unit through 25 ft. of 1/4 inch O.D. copper tubing coiled about the bottom of the tank. The bath water was circulated by a stainless steel, four-bladed, propeller-type stirrer. A 1/12 horsepower, split-phase electric motor, coupled to the stirrer by a "V" belt, was used to drive the stirrer.

The temperature was regulated by the same mercury thermoregulator used with the single piston gauge. The thermoregulator actuated a Cenco-Gilson electronic relay which operated a 300 watt immersion heater. The bath temperature was regulated to $25.000 \pm 0.005°$ C. for all work done with the differential piston gauge.

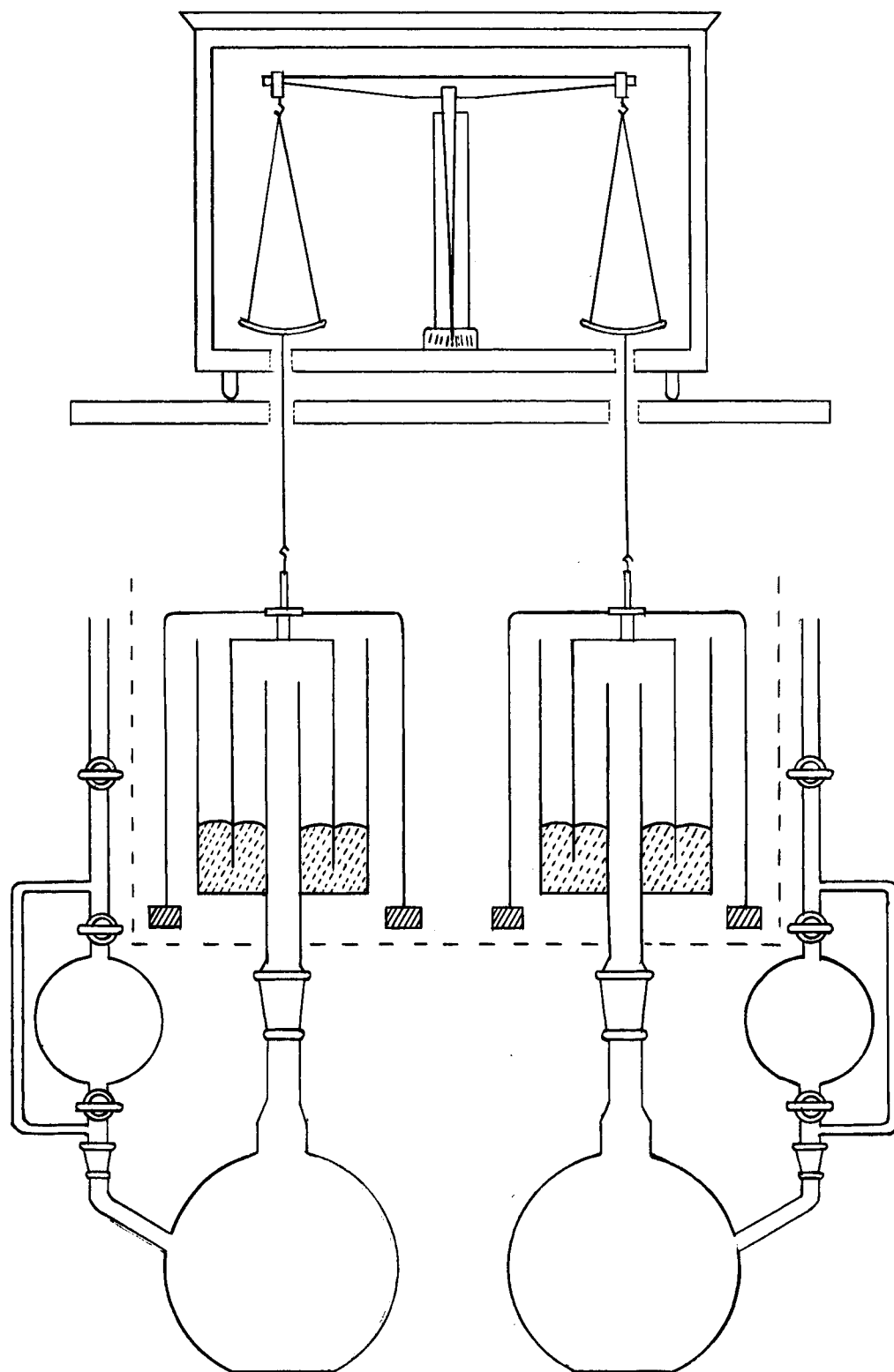The differential piston gauge, Fig. 4, consisted of the single piston

Fig. 4. Double Piston Gauge and Accessories

gauge described in CHAPTER II and another single piston gauge made to the same specifications. The two single piston gauges were fixed rigidly in a small galvanized tank, 5 x 10 x 9 inches, represented by the short-dash lines in Fig. 4. A distance of 6 1/4 inches was left between the centers of the inlet tubes and a 24/40 standard-taper joint on the bottom of the inlet tube was extended through the bottom of the small tank. The bottom of the tank was perforated with 1/4 inch holes so that the tank would be filled with water when immersed in the constant-temperature bath. The differential piston gauge and accessories were clamped rigidly to a latticework, consisting of 1/2-inch metal rods and two 36-inch ringstands, and immersed in the constant-temperature bath so that the water level was 1/2 inch from the top of the mercury cup.

Both equilibration chambers and sample-holding apparatus were made to the same specifications as those described in CHAPTER II.

Principle of Operation

The differential piston method for determining vapor pressures involves measuring the difference between the vapor pressure of a standard solution and that of a liquid of unknown vapor pressure. Its operating principle is the same as that of the single piston method, with the exception that now the difference in the changes in pressures within the two systems is measured by the weight required to null the balance when both systems are in a state of equilibrium.

In order to facilitate the discussion of the differential piston method we shall let the following symbols represent their respective quantities.

ΔP_S = the change in pressure within the system containing the liquid of standard vapor pressure, cm. Hg.

ΔP_X = the change in pressure within the system containing the liquid of unknown vapor pressure, cm. Hg.

ΔP^* = the difference in the pressure changes of the two systems, $\Delta P_S - \Delta P_X$, cm. Hg.

P_S' = the vapor pressure of the liquid taken as the standard, cm. Hg.

P_X' = the vapor pressure of the liquid of unknown vapor pressure, cm. Hg.

W = the weight required to nullify ΔP^*, gm.

P_S and P_X are the initial pressures of the system containing the liquids of standard and unknown vapor pressures respectively, cm. Hg.

V_S and V_X are the initial volumes of the system containing the liquid of standard and unknown vapor pressures respectively, cm^3.

ΔV_S and ΔV_X are the change in volume of the system containing the liquid of standard and unknown vapor pressures respectively, cm^3.

From equation (2), p. 9 we have for the system containing the liquid of standard vapor pressure,

$$\Delta P_S = P_S' - \frac{P_S \Delta V_S}{(V_S + \Delta V_S)} \tag{1}$$

and

$$\Delta P_X = P_X' - \frac{P_X \Delta V_X}{(V_X + \Delta V_X)} \tag{2}$$

for the system containing the liquid of unknown vapor pressure. Subtraction of equation (2) from equation (1) gives:

$$\Delta P^* = P_S' - P_X' - \left(\frac{P_S \Delta V_S}{(V_S + \Delta V_S)} - \frac{P_X \Delta V_X}{(V_X + \Delta V_X)} \right).$$

Letting P_S and P_X be represented by P_i and neglecting the change in volume of each system with respect to its initial volume we have;

$$\Delta P^* = P_S' - P_X' - \left(\frac{\Delta V_S - \Delta V_X}{V} \right) P_i. \tag{3}$$

Where $\underline{V}$ represents the initial volumes of the systems, V_S and V_X. The weight $\underline{W_S}$ required to nullify a change in pressure of ΔP_S is,

$$W_S = KA_S \cdot \Delta P_S ,$$

and the weight $\underline{W_X}$ required to nullify a change in pressure of ΔP_X is,

$$W_X = KA_X \cdot \Delta P_X.$$

Where A_S and A_X are the cross sectional areas of the pistons. Since the systems oppose one another and the areas of the pistons are equal we have:

$$W = W_S - W_X = KA(\Delta P_S - \Delta P_X) ,$$

or;
$$W = KA \cdot \Delta P^*. \tag{4}$$

Where $\underline{A}$ represents the cross sectional areas of the pistons. Substitution of equation (3) into equation (4) gives:

$$W = KA \left[P_S' - P_X' - \left(\frac{\Delta V_S - \Delta V_X}{V} \right) P_i \right]. \tag{5}$$

Solving for P_X' we get:

$$P_X' = P_S' - \frac{W}{KA} - \left(\frac{\Delta V_S - \Delta V_X}{V} \right) P_i. \tag{6}$$

The change in volume ΔV_j is related to the change in pressure ΔP_j by the equation given on p. 10;

$$\Delta V_j = \frac{\Delta P_j}{(1/C + 1/B)}.$$

Where $\underline{B}$ is the annular area between the inner wall of the mercury reservoir and the outer wall of the piston and $\underline{C}$ is the annular area between

the inner wall of the piston and the outer wall of the inlet tube.
Therefore we have:

$$\Delta V_s = \frac{\Delta P_s}{(1/C + 1/B)_s} \quad \text{and} \quad \Delta V_x = \frac{\Delta P_x}{(1/C + 1/B)_x}.$$

If both gauges are made to the same specifications the denominators
of the two above equations are equal.

It then follows that:

$$\Delta V_s - \Delta V_x = \frac{\Delta P_s - \Delta P_x}{(1/C + 1/B)} = \frac{\Delta P^*}{(1/C + 1/B)}. \tag{7}$$

Substitution of W/KA for ΔP^* of eq. (4) into eq. (7) gives:

$$\Delta V_s - \Delta V_x = \frac{W}{KA(1/C + 1/B)}. \tag{8}$$

Substituting eq. (8) into eq. (6) we get:

$$P_x' = P_s' - \frac{W}{KA}\left[1 + \frac{P_1}{V(1/C + 1/B)}\right]. \tag{9}$$

Substituting the values for the constants, as given in CHAPTER II,
into eq. (9) we have:

$$P_x' = P_s' - \frac{W}{135}\left[1 + (0.00274)P_1\right]. \tag{10}$$

Effect of Variations in External Pressure

The relation between the change in weight, arising from changes
in atmospheric pressure, and the change in atmospheric pressure for a
single piston gauge was given by eq. (5), p. 14.

$$\Delta W = KA \cdot \Delta P_a \left[1 - \frac{P_1}{V(1/C + 1/B)}\right].$$

Where ΔP_a is the change in atmospheric pressure and ΔW is the change
in weight due to ΔP_a. Applying this equation to each of the single

piston gauges of the double piston gauge we have:

$$\Delta W_S = KA \cdot \Delta P_a \left[1 - \frac{P_i}{V_S(1/C + 1/B)_S} \right], \qquad (1)$$

for the system containing the liquid of standard vapor pressure, and

$$\Delta W_x = KA \cdot \Delta P_x \left[1 - \frac{P_i}{V_x(1/C + 1/B)_x} \right], \qquad (2)$$

for the system containing the liquid of unknown vapor pressure. If the double piston gauge is to be independent of changes in atmospheric pressure then ΔW_S must equal ΔW_x. Equating eqs. (1) and (2) and canceling like quantities, such as the inital pressure and the dimensions of the gauges gives:

$$V_S = V_x$$

as a condition which must be satisfied in order for ΔW_S to equal ΔW_x.

The double piston gauge used in this investigation met the above requirements well within experimental error. For all practical purposes the dimensions of the two piston gauges were the same and the volumes of the systems were found to differ by less than 0.1 per cent.

Operating Procedure

The procedure for operating the single piston gauge, as described in CHAPTER II was applied simultaneously to both of the systems of the double piston gauge, with the exception that the balance was always nulled by adding weight to the side of the apparatus having the higher vapor pressure. The unknown vapor pressure was then calculated using equation (10), p. 26.

Experimental

Test with the gauge demonstrated that the device was free of effects
caused by variations in atmospheric pressure. The gauge failed, however,
to show the expected sensitivity when mercury was used as the manometric
liquid. It appeared that mercury had a high frictional drag on the mov-
ing pistons, thus accounting for the loss in sensitivity. When di-n-butyl
phthalate was used as the manometric liquid the sensitivity increased by
a factor of ten. Although di-n-butyl phthalate had the disadvantage of
wetting the walls of the pistons to a variable extent and thereby causing
erratic results, experiments were conducted using it as a manometric liq-
uid in order to investigate the practicableness of the apparatus.

Two runs were made using 8.995 molal sulfuric acid solution as the
liquid of standard vapor pressure and 12.45 molal sulfuric acid solution
as the liquid of unknown vapor pressure. The first run required 7.68 gm.
to nullify the difference in pressures of the two systems after 40.5 hours.
The run was continued for another 4.5 hours without any noticeable change
in weight. The second run required 7.48 gm. to null the apparatus after
27 hours; continuation of the run gave erratic readings which were be-
lieved to result from water leaking into the system containing the standard.

. When di-n-butyl phthalate was used as the manometric liquid the vol-
ume change in each of the systems was 13.0 times greater than when mercury
was used; therefore, it was necessary to correct for this in the theoret-
ical calculations, eq. (10), p. 26. The theoretical equation then became:

$$P_x' = P_s' - \frac{W}{135}\left[1 + (0.0354)P_i\right].$$

Substitution of the weight (7.68 gm.) and the initial pressure
(74.49 cm. Hg.) into the above equation gave a value of 2.07 mm. Hg. for

the difference in vapor pressures of the two acid solutions. This value deviates 48 per cent from the value obtained from the standard curve (3.95 mm. Hg.).

A value of 2.01 mm. Hg. was found for the difference in vapor pressures of the two acid solutions in a second experiment. The counterweight was 7.48 gm. and the initial pressure was 74.35 cm. Hg. Although this value deviated 49 per cent from the literature value of 3.95 mm. Hg., it deviated only 3 per cent from the experimental value calculated from the first run.

Conclusions

The double piston gauge proved to be independent of variations in atmospheric pressure. When mercury was used as a manometric liquid the gauge failed to show the expected sensitivity. This is believed to be due to the mercury having a high frictional drag on the moving piston. When di-n-butyl phthalate was used as the manometric liquid the sensitivity was increased by a factor to ten. However, di-n-butyl phthalate has three characteristics that make it unsuitable as a manometric liquid, these are as follows:

(1) It wets the walls of the piston to a variable extent and thereby introduces erratic errors into the results.

(2) It has a low density (1.0418 at 25° C.) and therefore cannot be used for any systems but those having a very low vapor pressure.

(3) In general, organic vapors are soluble in di-n-butyl phthalate.

It was concluded that the double piston gauge used in this work was

too massive and had too many mechanical difficulties associated with it

for it to be a generally practicable device for the measurement of vapor

pressures.

CHAPTER IV

THE DISPLACEMENT WEIGHT MANOMETER

Description of Apparatus

The displacement weight manometer, Fig. 5, was mounted on a 1 1/2 inch thick board with four wooden clamps which were carved to fit the contours of the manometer. The mounting for the manometer was fastened in a like manner to the 1/2 inch diameter rods of a welded vacuum rack. This permament type of mounting assured that the relative positions of the manometer arms remained unchanged throughout the investigation.

Reference to Fig. 5 will be made throughout the following discussion of the displacement weight manometer. The two three-way stopcocks (SC 2 and SC 3) consisted of high vacuum stopcock barrels with Teflon plugs having a 2 mm. bore. Teflon plugs were used in order to eliminate the use of a lubricant which would adhere to the walls of the manometer tubes and surface of the mercury. The manometer tubes T_1 and T_4 had an inside diameter of 1.5 cm. and a length of 33 cm. and 35 cm. respectively. Manometer tube T_2 had an inside diameter of 1.3 cm. and a length of 38 cm. as measured from the top of SC 3 to the bottom of the 19/38 standard-taper joint. The side arm leading from T_2 to the equilibration chamber had an inside diameter of 1.3 cm. and an overall length of 65 cm., 38 cm. from T_2 to the 19/38 standard-taper joint and 37 cm. from the top of the joint to the top of the equilibration chamber. Manometer tube T_3 joining the bottom of T_4 to the bottom of the Teflon stop-

To Vacuum Pump and

Dry Air Supply

SC 5

SC 4

500 ml.

$T1$

$T2$

250 ml.

MR

A

SC2

B

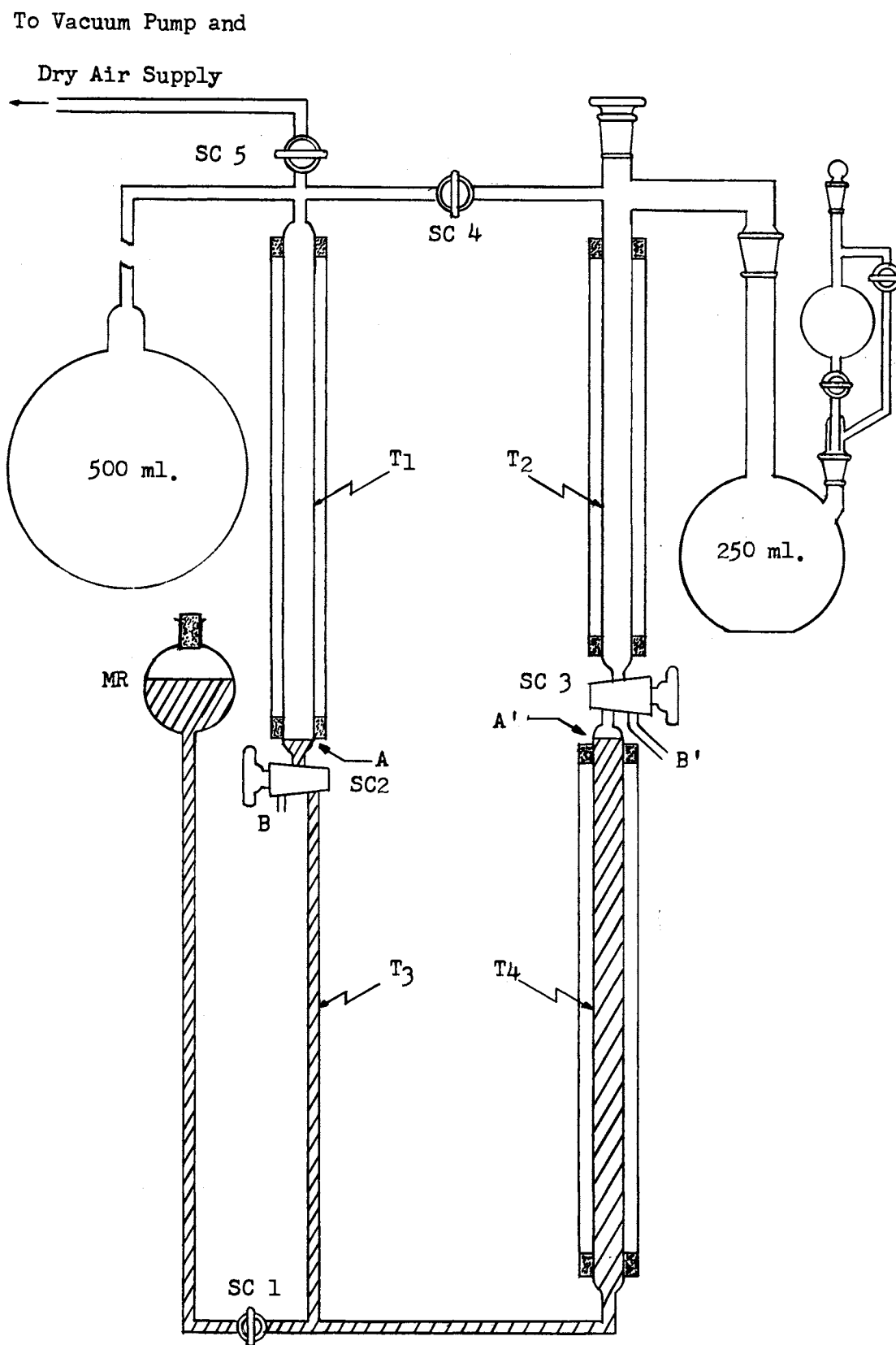SC 3

A'

B'

$T3$

$T4$

SC 1

Fig. 5. Displacement Weight Manometer

cock (SC 2) was made of 1 cm. O.D. heavy-wall glass tubing. The stop-cock at the bottom of T_3 (SC 1) had a standard-taper barrel with a Teflon plug, which had a 2 mm. bore. An all-glass stopcock (SC 4), having a bore of 3 mm., was joined to the two arms of the manometer by 8 mm. O.D. glass tubing. A 2 mm. bore standard-taper stopcock (SC 5) connected the manometer to the vacuum pump and dry air supply. The 500 ml. flask was attached to the manometer at the top of T_1 by 76 cm. of 1 cm. O.D. glass tubing. A 200 ml. leveling bulb joined to the Teflon stopcock (SC 1) with 1/4 inch I.D. Tygon tubing served as the mercury resevoir, MR. The equilibration chamber was a 250 ml. flask to which was sealed a 1 cm. O.D. side arm equipped with a 12/30 standard-taper female joint to receive the sample-holding apparatus. The 50 ml. bulb of the sample-holding appa-ratus was filled through the 10/30 standard-taper joint which was stop-pered with a glass stopper. Micro stopcocks were used on the 6 mm. O.D. vent and drain tubes of the sample-holding apparatus.

The manometer was themostated by circulating water from the 90 gal-lon constant-temperature bath through the 3.5 cm. O.D. water jackets about T_1, T_2, and T_4. The water jackets were sealed at the ends with rubber stoppers and had their inlet and outlet tubes extending through the 1 1/2 inch thick mounting board. The 500 ml. flask was immersed to a depth of approximately 50 cm. in the constant-temperature bath. The 250 ml. equil-ibration chamber and sample-holding apparatus were also immersed in the constant-temperature bath.

The constant-temperature bath used in this work was the same as that used with the differential piston method. The thermoregulator was a thin-wall glass tube filled with 200 ml. of toluene working against a head of mercury, which in turn completed the control circuit of the relay.

The relay was a high-current electronic relay employing a thyratron vacuum tube, No. 5559. (17). The bath was heated with a 300 watt immersion heater operated at 150 watts by the relay. The bath temperature was regulated to $25.000° \pm .002°$ C. for all work done with the displacement manometer.

Principle of Operation

The displacement weight manometer is a differential manometer containing a definite volume of mercury. Vapor pressure measurements are made by weighing, on an analytical balance, the amount of mercury forced up one side of the manometer tube. In order to facilitate the discussion we shall let the following symbols represent their respective quantities as given below.

P^o = the initial pressure of the right and left sides of the manometer, cm. Hg.

V_r and V_l = the initial volumes of the right and left systems respectively, cm^3.

ΔV = the change in volume of the right and left systems, cm^3.

ΔP_r and ΔP_l = the change in pressure within the right and left systems respectively, cm. Hg.

P_r^* and P_l^* = the final pressures in the right and left systems respectively, cm. Hg.

ΔP = the difference in pressures of the two systems, cm. Hg.

Assuming that the gases behave ideally we initially have:

$$P_r^o = \frac{N_r RT}{V_r} \; ; \; P_l^o = \frac{N_l RT}{V_l} \text{ and } P_r^o = P_l^o.$$

Where N_r and N_l are the number of moles of gas, dry air, in the right and left system respectively. Introducing N_x moles of gas, such as the

vapor of a liquid into the system on the right expands the right system by a volume of ΔV and compresses the left system by the same amount. When the vapor is in equilibrium with its liquid we have:

$$P^*_r = \frac{(N_r + N_x)RT}{V_r + \Delta V}, \quad \text{and} \quad P^*_l = \frac{N_l RT}{V_l - \Delta V}.$$

Subtracting P^*_l from P^*_r we get:

$$\Delta P = \left[\frac{N_r + N_x}{V_r + \Delta V} - \frac{N_l}{V_l - \Delta V} \right] RT. \tag{1}$$

Substituting $P^\circ V_r/RT$ for N_r, $P^\circ V_l/RT$ for N_l, and $P_x(V_r + \Delta V)/RT$ for N_x into equation (1) gives:

$$\Delta P = P_x + \left[\frac{V_r}{V_r + \Delta V} - \frac{V_l}{V_l - \Delta V} \right] P^\circ. \tag{2}$$

Where P_x represents the vapor pressure of the liquid. The change in volume of the system is the amount of mercury forced down in the right manometer arm and the amount of mercury forced up in the left manometer arm.

$$\Delta V = \frac{\text{weight of mercury, gm.}}{\text{density of Hg. at } 25^\circ C.} = \frac{W}{d} \tag{3}$$

The difference in pressure is related to the change in volume by the equation,

$$\Delta P = \Delta V(1/A_r + 1/A_l),$$

where A_r and A_l are the cross sectional areas of the right and left manometer arms respectively. The above equation is seen to be analogous to the one given in CHAPTER II, p. 10. Substituting W/d for ΔV into the above equation gives:

$$\Delta P = \frac{W(1/A_r + 1/A_l)}{d}. \tag{4}$$

Substituting equations (3) and (4) into equation (2) and rearranging we have finally:

$$P_x = \frac{W(1/A_r + 1/A_1)}{d} - \left[\frac{V_r}{V_r + W/d} - \frac{V_1}{V_1 - W/d} \right] P^o . \qquad (5)$$

Operating Procedure

The displacement weight manometer was cleaned by filling it with warm dichromate cleaning solution and allowing it to stand for approximately thirty minutes. After the cleaning solution had been drained from the manometer, it was rinsed several times with distilled water followed by a final rinsing with reagent acetone. The manometer was then evacuated for one hour to remove the acetone vapors. The equilibration chamber and sample-holding apparatus were cleaned in a similar manner and dried at 110° C. in a drying oven. Since the 500 ml. flask did not come in contact with any vapors and it could be isolated from the system while the manometer was being cleansed; its initial cleansing was all that was necessary.

Once the manometer and its accessories had been cleaned and dried and the sample-holding apparatus was filled with the liquid sample, the apparatus was assembled as shown in Fig. 5. All glass stopcocks, ground-glass joints and stoppers were greased with Dow-Corning silicone lubricant.

The mercury reservoir was now filled with freshly distilled mercury while the Teflon stopcock (SC 1) was in the closed position. The mercury in the reservoir (MR) was introduced into both limbs of the manometer until the levels were above the Teflon stopcocks (SC 2 and SC 3). These were then closed and the excess mercury drained off through B and B'. Stopcocks 2 and 3 were again opened and the mercury levels allowed to reach equilibrium. Since SC 3 was positioned above SC 2 the level in T_4 was below SC 3 while the level in T_1 was above SC 2 (at levels A' and A respectively).

The pressure above the manometer was adjusted to 740.0 mm. Hg. by admitting dried air into the manometer through SC 5. The air was dried by passing it through a drying train consisting of 7 inch towers of concentrated sulfuric acid, activated alumina, and sodium hydroxide flakes.

The initial pressure within the manometer (740.0 mm. Hg.) was determined with a small differential oil manometer. One arm of the oil manometer was connected to the displacement weight manometer while the other arm was joined to a 100 ml. bulb which was filled with air to a pressure of 740.0 mm. Hg. and immersed in the constant-temperature bath. Since the bath temperature was controlled to $\pm$ 0.002° C., the pressure within the 100 ml. bulb varied over a range of $\pm$ 0.005 mm. Hg.

After the manometer was filled with dried air at the prescribed pressure, stopcock 4 was closed and the two micro stopcocks on the sample-holding apparatus were opened to allow the liquid sample to drain down into the equilibration chamber. The liquid was allowed to come to equilibrium with its vapor while being stirred vigorously with an immersible magnetic stirrer. The increase in pressure in the manometer arm T_2 and T_4 corresponding to the vapor pressure being measured caused the mercury to rise in the left arm T_1. At equilibrium the mercury in T_1 was drained off through $\underline{B}$ and weighed on an analytical balance. The vapor pressure corresponding to the weight of mercury was then obtained from the calibration curve.

Calibration Procedure

The relation between the weight of mercury and the corresponding solution vapor pressure, given by equation (5), p. 36, is valid over a range of pressures only if the cross sectional areas of the manometer

tubes are constant. The manometer tubes used in this work were fabricated from buret barrels and did not have constant bores over the desired range, therefore it was necessary to calibrate the manometer carefully using a differential oil manometer.

The oil manometer was connected between the arms of the displacement weight manometer, Fig. 5, so that the difference in the pressures in the right and left systems could be determined. The displacement weight manometer was filled with mercury to levels A and A' and the apparatus filled with dried air at a pressure of 740.0 mm. Hg. by the same procedure given on p. 37. Stopcock 4 was then closed and dried air was introduced through a stopcock which had been added in place of the 19/38 ground-glass stopper at the top of T_2. The increase in pressure in the right manometer arm caused the mercury and oil levels to move upward in the displacement weight and oil manometer respectively. Thus the pressure in the left manometer arm was also increased. This pressure in the left system was reduced to 740.0 mm. Hg., as determined by the small oil manometer, p. 37, by allowing the excess pressure to escape through a capillary stopcock. The difference in height of the levels in the oil manometer was read with a cathetometer. The amount of mercury corresponding to this difference in pressure was drained from T_1 through B and weighed on an analytical balance.

In the following discussion of the relation between the difference in pressure as read on the oil manometer and the partial pressure of the dried air introduced into the right system we shall use the following symbols.

P^o = the initial pressures in the right and left systems, cm. Hg.

P_r^* and P_l^* = the final pressures in the right and left systems

respectively, cm. Hg.

ΔP = the difference in pressures of the two systems (the oil

manometer reading converted to cm. Hg.).

P_x = the partial pressure of the dried air introduced into the

right system, cm. Hg.

V_r = the initial volume of the right system, cm³.

ΔV = the change in volume of the right system, cm³.

N_x = the number of moles of dried air introduced into the

right system.

N_r = the number of moles initially present in the right system.

Assuming that the gases behave ideally we initially have:

$$P^0 = \frac{N_r RT}{V_r},$$

for the pressure in the right and left systems. After introducing N_x

moles of dried air into the right system and reducing the pressure in

the left system to its initial value of 740.0 mm. Hg. we have:

$$P_r^* = \frac{(N_r + N_x)RT}{V_r + \Delta V}, \quad \text{and} \quad P_l^* = P^0,$$

for the final pressures in the right and left systems respectively.

Subtracting P_l^* from P_r^* gives:

$$\Delta P = \frac{(N_r + N_x)RT}{V_r + \Delta V} - P^0. \tag{1}$$

Substituting $P^0 V_r/RT$ for N_r and $P_x(V_r + \Delta V)/RT$ for N_x into the above

equation and rearranging we get:

$$P_x = \Delta P + \frac{P^0 \Delta V}{V_r + \Delta V}. \tag{2}$$

as the relation between the oil manometer reading (cm. Hg.) and the

partial pressure of the introduced air or the vapor pressure of a liquid,

assuming that a mixture of the vapor and air initially present in the system also behave ideally.

The displacement weight manometer was calibrated over a range of pressures from 0 to 25 mm. Hg. The change in volume (ΔV) corresponding to a given P_x was determined by dividing the weight of mercury forced up in the manometer tube (T_1) by its density at 25° C. P° was 740.0 mm. Hg. for all determinations and the initial volume of the right system was found to be 410 cm? by measuring the volume of water required to fill the system. P_x corresponding to a given weight of mercury was evaluated using equation (2).

A calibration curve was obtained by plotting the vapor pressure (P_x) against the weight of mercury (W) and drawing a smooth curve through the best points. The curve was linear and had a slope of 1.205 over the pressure ranges of 0 to 3 mm. Hg. and 17 to 25 mm. Hg. The portion of the curve over the pressure range of 3 to 17 mm. Hg. was slightly concave downward with a maximum deviation of 0.38 mm. Hg., at P_x = 11 mm. Hg., from a straight line drawn between the two linear portions.

Experimental

In order to determine the precision of the manometer a series of experiments were made in which the vapor pressure of distilled water was measured. The water samples for the twenty-two measurements were all taken from the same distillation of water. The distilled water was kept, under an atmosphere of air, in a closed container which was thermostated in the constant-temperature bath.

The time of the runs ranged from 2 to 71 hours. Runs made in less than 18 hours indicated that sufficient time had not been allowed for

the systems to attain equilibrium. Runs made in 18 hours or more gave values ranging from 18.75 to 26.11 mm. Hg. for the vapor pressure of water.

Possible reasons for the lack of precision were considered to be:

1. Failure to remove all the water vapor from the system before the water samples were introduced.

2. Existence of small permanent leaks in the system and/or leaks developing through stopcocks or glass joints which were difficult to detect.

3. Failure to allow sufficient time for the system to attain equilibrium.

The first of the above possible sources of error was checked by evacuating the system for a considerably longer period of time, approximately two hours, then filling the system with air which had been passed through the original drying train and a trap containing activated charcoal at $-78°$ C. This procedure plus the repairing of two small leaks, however, added very little to the precision of the manometer.

At this point it was concluded that sufficient time had not been allowed for the system to come to equilibrium. In order to decrease the time required to reach equilibrium the system was modified so as to reduce the volume that had to be saturated with water vapor.

The volume of the modified system was the volume of the manometer tube T_2, Fig. 5, plus the volume of a side arm, 18 cm. long and 1.3 cm. in diameter. This volume was found to be 79 cm³ by measuring the volume of water required to fill it.

The water sample was sealed in a 4 ml. vial, the vial placed in the side arm, and the water vapor introduced into the system at the start

of the run by breaking the vial with a small magnet. The system was lined with strips of filter paper which distributed the water through the system by its absorptive action.

Three 24 hour runs were made with the modified system. The weight of mercury obtained from the first and second run was 15.73 gm. and 15.66 gm. respectively. The third run gave a low value of 14.97 gm. The corresponding vapor pressures for the first and second runs was 16.79 and 16.87 mm. Hg. respectively as found from the calibration curve. Although these values deviate considerably from the literature value of 23.76 mm. Hg. the precision was better than 0.5 per cent.

Conclusions

The displacement weight manometer and its associated system as used in this investigation is inadequate for the determination of vapor pressures. The lack of precision obtained with this apparatus was attributed largely to the failure of the liquid-vapor system to attain a state of equilibrium.

Consideration of the results of this investigation leads one to the conclusion that an apparatus of this kind capable of measuring vapor pressures in the presence of an indifferent gas at atmospheric pressure must have the following properties.

1. A short and large diameter path through which the vapor must diffuse in order to saturate the system.

2. Temperature control throughout in order to keep the initial volume of mercury constant and to prevent measurable change in the pressure of the indifferent gas with respect to changes in temperature.

3. Freedom from leaks with as few stopcocks and joints as possible

4. Large-bore manometer tubes to insure that the shape of the mer-
cury meniscus is the same for all determinations.

Displacement Weight Barometer

It is believed that a displacement weight barometer embodying above
desirable properties could be constructed. A sketch of a proposed app-
aratus is shown in Fig. 6. The barometer consists of a 25 mm. I.D. mer-
cury reservoir and a 1 mm. I.D. barometer tube. The upper end of the
barometer is sealed into a small glass chamber which can be evacuated
and drained of mercury through the stopcock (SC 2). The barometer tube
might be thermostated by circulating water from a constant-temperature
bath through the 35 mm. O.D. water jacket. The equilibration chamber
is a 1000 ml. flask equipped with a female glass joint to receive the
barometer tube. The liquid sample is sealed in a vial placed in the

equilibration chamber.

To operate the displacement weight barometer, the apparatus is
assembled as shown in Fig. 6, with the mercury reservoir full of mer-
and the vial containing the sample placed in the flask. The equilibra-
tion chamber is evacuated and filled with dried air through SC 1. The
pressure in the equilibration chamber is adjusted to 760 mm. Hg. by
admitting dried air through SC 1 until the mercury in the barometer tube
is level with the top of the drawn tip. Any mercury that happens to
spill over into the evacuated bulb is drained through SC 2 into an evac-
uated vial fitted to SC 2. The sample vial is then broken and the liquid
sample stirred with a magnetic stirrer during the run. The increased
pressure within the equilibration chamber causes the system to expand

Evacuated Bulb

Drawn tip

Water Inlet

SC 2

Barometer Tube

Water Jacket

760 mm.

To Vacuum Pump and

Dry Air Supply

Water Outlet
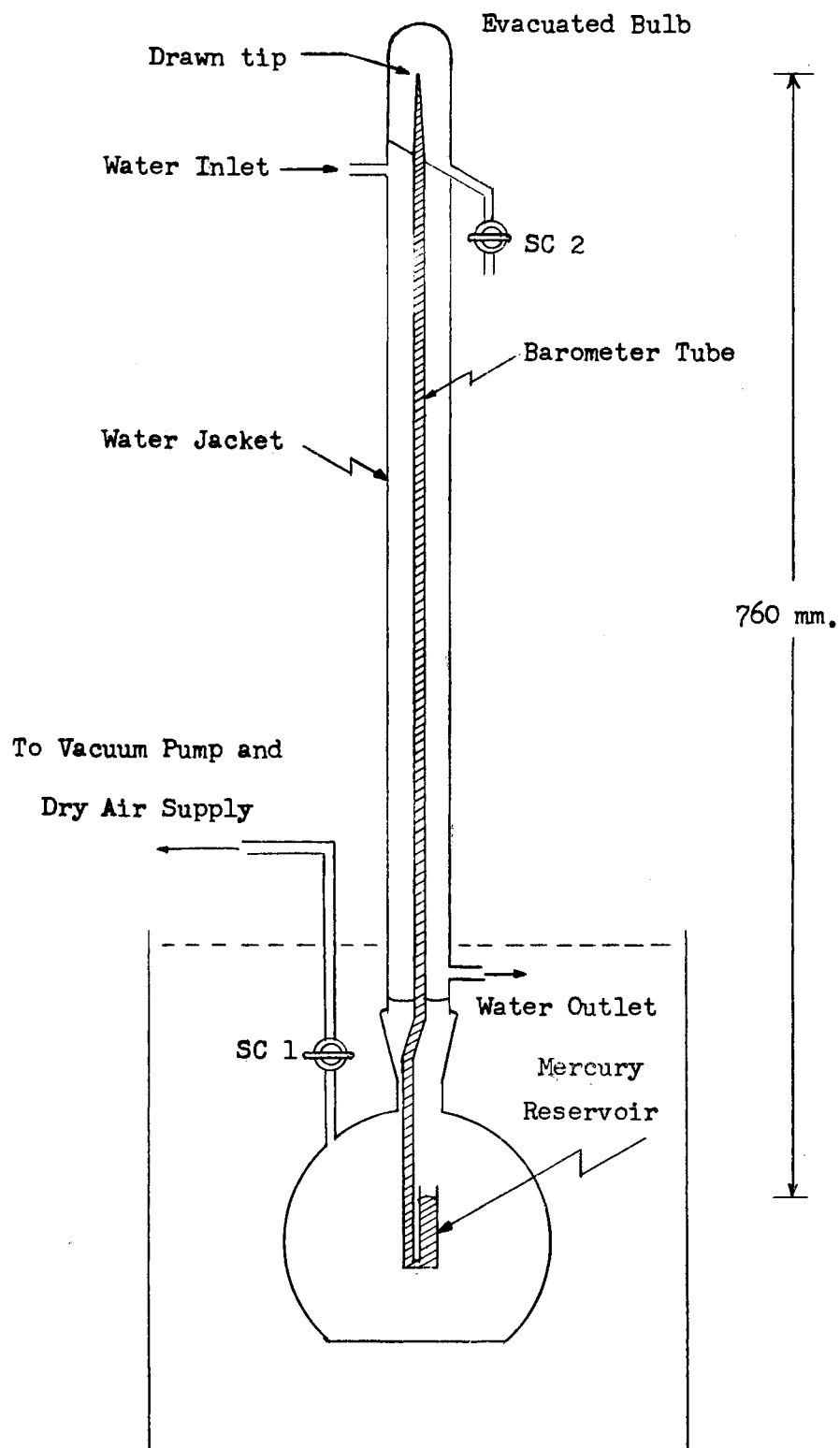
SC 1

Mercury
Reservoir

Fig. 6. Displacement Weight Barometer

by forcing the mercury through the barometer tube until the pressure is reduced to its initial value of 760 mm. Hg. This change in volume (ΔV) is the volume of mercury that is forced out the drawn tip of the barometer tube and into the evacuated chamber. This volume of mercury is drained from the apparatus at the end of the run and weighed on an analytical balance.

The increase in pressure within the equilibration chamber due to the vapor pressure of the liquid is given by the equation,

$$\Delta P = P_X - \frac{P^{\circ}\Delta V}{V + \Delta V},$$ (1)

where, ΔP = the increase in pressure within the equilibration

         chamber, cm. Hg.

         P_X = the vapor pressure of the liquid, cm. Hg.

         P° = the initial pressure within the system, 760 mm. Hg.

         ΔV = the change in volume within the system, cm^3.

         V = the initial volume of the system, cm^3.

Rearranging eq. (1) and substituting W/d for ΔV and W/Ad for ΔP we get,

$$P_X = \frac{W}{Ad} - \frac{P^{\circ}W}{Vd + W};$$ (2)

where,   W = the weight of mercury displaced, gm.

         d = the density of mercury at 25° C.

         A = The cross sectional area of the mercury reservoir, cm^2.

The vapor pressures of liquids can be calculated using equation (2) when the area of the mercury reservoir A is constant over the pressure range. When A is not constant the apparatus must be calibrated over the desired pressure range in order to obtain the relation between the vapor pressure and the weight of mercury displaced.

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THESIS TITLE: INVESTIGATION OF NOVEL STATIC METHODS FOR THE
               DETERMINATION OF VAPOR PRESSURES IN THE PRESENCE
               OF INDIFFERENT GASES

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