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AN APPARATUS FOR MEASURING THE VAPOR PRESSURE OF LIQUIDS BY THE GAS SATURATION METHOD

BY

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A THESIS

Submitted to the Faculty of The Creighton University in Partial Fulfillment of the Requirements for the Degree of Master of Science in the Department of Chemistry

OMAHA, 1937
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Chapter I

INTRODUCTION

In a projected study of acid and base equilibria in non-aqueous solvents, it was found desirable to determine the vapor pressures of weak bases from these solutions, for example, solutions of ammonia in benzene and ethyl alcohol. Since there are no data in the literature for these systems it was decided that an apparatus should be constructed which would give these values with a high degree of accuracy.

The vapor pressure of a liquid may be measured by either the static or dynamic method. The static methods are of three types; the direct, the indirect, and the differential. The direct method is one by which the vapor pressure of a liquid may be measured directly by placing a portion of it above the mercury in the vacuum of a barometer tube, heating to the desired temperature, and observing the depression of the mercury column. This method is open to the objection that the liquid causes too great depression of the mercury column. **(1) Another objection is**

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that there is no assurance that the concentration will remain constant throughout the solution. (2)
The indirect method, introduced by Ramsay and Young, determines the vapor pressure by the changes of boiling points with varying barometric pressures. (3) The objections to this method are: the concentration of the solution may change due to evaporation; the solute and solvent may be superheated; and the solute may decompose at high temperatures. (4) The differential method is one which gives directly the difference between the vapor pressure of a solvent and that of a solution. The objections to this method are: the apparatus is too complicated and inflexible; and the time required to make a determination renders it impractical for any but the most refined work. (5) The dynamic method, of which there have been several modifications, is a gas saturation method. Although this

3. Ibid., 231.
5. Pearce and Snow, op. cit., 231.
6. Ibid., 232.
method has several disadvantages, as will be discussed later, it is quite accurate and fairly rapid. (7)
For this reason the dynamic method was decided upon.

7. Derby, Daniels and Gutsche, Journal of the American Chemical Society, 36, 793.
Chapter II

THE GAS SATURATION METHOD

The dynamic, or gas saturation method of measuring vapor pressures, is carried out in the following way. A measured volume of an insoluble gas, sometimes air, is passed through the liquid whose vapor pressure is to be measured. The gas is in this way saturated by the vapor and the amount of vapor in the air measured by suitable methods. From the data thus derived the vapor pressure of the liquid may be calculated.

The first measurements of vapor pressure by the dynamic method were those reported by Regnault in 1845. He passed a measured volume of air through a sponge saturated with water and then through moistened silk screens. The vapor was absorbed from the air by passing it through sulfuric acid. Following Regnault were Walker and Ostwald who saturated the air using a Liebig saturating bottle. The Walker-

2. Ibid., 233.
Ostwald method was used, with minor modifications, until 1914 and 1915 when Derby, Daniels and Gutsche, (3) and Washburn and Heuse (4) designed apparatus which kept the liquid, whose vapor pressure was to be measured, constantly stirred by shaking either the saturation bottles or the entire apparatus. In these two methods, the greatest error in measuring vapor pressures which is due to the inability to measure accurately and conveniently the volume of displaced water, was largely eliminated. In the work of Derby, (5) Daniels and Gutsche, the volume of water displaced was measured accurately by drawing it into two calibrated 1135 cc. bulbs. The entire apparatus was immersed in the thermostat. Washburn and Heuse (6) used a constant level aspirator which was also kept in a constant temperature bath.

In 1927, Pearce and Snow (7) working at the

3. Derby, Daniels and Gutsche, loc. cit., 793.
5. Derby, Daniels and Gutsche, op. cit., 36, 793.
University of Iowa, designed an apparatus for use in measuring the vapor pressure of water and aqueous solutions. Their object was to simplify the apparatus and at the same time achieve more accurate results. For this purpose they used saturation tubes of the type (figure 1) designed by Bichowsky and Storch. The saturator is about 10 inches in length and 1 1/2 inches in diameter. The tubes (A) and (A') are of 5 mm. tubing. At the entrance of the tube (A) into the bottle, is a capillary tube (B) of 1 mm. diameter and at the bottom of the 5 mm. tube and behind the capillary opening is a small hole (C). The tubes are filled about half full in order that the central tube (D) will be filled with liquid. In operation, when air is drawn through, as the bubble issues from the capillary it is surrounded by the liquid in the tube. As the next bubble issues from the capillary, liquid is drawn through the hole and surrounds it. In this way each bubble that is formed, is surrounded by liquid as it travels down the tube. At the end of the tube (D) the bubbles break and before the gas can escape from the tube it must pass over the

surface of the liquid. In this way the gas comes in contact with the vapor above the liquid. There are several distinct advantages in using this saturation tube:

(a) It eliminates moving parts or stirring mechanisms as used by earlier investigators notably Derby, Daniels and Gutsche, and Washburn and Heuse;

(b) It allows ample time for complete saturation, and;

(c) It allows a more constant pressure during the course of the experiment.

In addition it has been found that this saturation tube prevents spraying or fogging in solutions like those of ammonia in ethyl alcohol. In contrast to this, it was found that in an ordinary saturator when the bubble reaches the top of the liquid it breaks, thereby forming a fog which may easily be swept into the absorption bottle.

The third point mentioned is of importance in obtaining good results. The completeness of saturation of the gas depends upon the length of time that the bubble remains in contact with the liquid. If we

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9. Ibid., 2696.
consider a saturation tube of the conventional type, we find the length of time that the bubble remains in contact with the liquid depends upon the height of the column. However, as the length of the column increases, the hydrostatic pressure increases and as a result, the pressure on the bubble varies. This variation in pressure will cause a variation in the vapor pressure. In the Bichowsky and Storch tube, however, the length of time which the gas is in contact with the liquid can be regulated by the rate at which the gas is drawn down the tube or by lengthening the tube, or both.

The apparatus designed by Pearce and Snow consisted of an oxygen and hydrogen electrolysis cell. As these gases were produced they were led into a presaturator which was kept at a temperature slightly above that of the experiment. Complete saturation was then obtained by passing the gases into a battery of eight saturation tubes immersed in a thermostat at 25±0.002°. The water vapor was absorbed from the gases by a U tube containing glass beads covered with phosphorous pentoxide. The number of mols of hydro-

10. Ibid., 2695.
gen and oxygen was determined by a silver coulometer in series with the electrolysis cell, and from the weight of water, the number of mols of gas, and the pressure existing in the apparatus, the partial pressure of the water was determined. These investigators found the vapor pressure to be 23.752 mm. at 25° with the greatest deviation from the mean being .007 mm. This value is perhaps one of the most precise measurements yet made on the vapor pressure of water.

(12) Rodebush and Ewart in 1932, in measuring the vapor pressure of hydrogen chloride from glacial acetic acid solutions, modified this procedure by removing the hydrogen and oxygen generator and substituting for it suitable purifying tubes, while at the other end they placed an aspirator by which air could be drawn through the apparatus. The apparatus which is used in this work, and which is described below is essentially the same as that of Rodebush and Ewart.

Chapter III

APPARATUS AND PROCEDURE

The apparatus (figure 2) was so arranged that it could be placed in a 24 inch thermostat, whereas, those mentioned above required baths of a much larger size. In the figure, two purifying tubes at (A) contained 15 molar sodium hydroxide and 16 molar sulfuric acid. A rubber connection was made between these and the presaturator (B) which was kept at a temperature slightly above 25°.

The saturating tubes (C), the number of which had been reduced from eight to four due to the size of the water bath which was kept at a temperature of 25° ± .05°, made connection with the presaturator by a ground glass joint. These in turn were connected by a ground glass joint with the absorption tubes (D), which were of two types. The first type as shown in the figure consisted of two, of the type designed by Bichowsky and Storch. It was connected to the aspirator (E) by a glass joint. The second type used was a Fischer bottle, to which connection was made by another glass joint and mercury seal. Connection between this and the aspirator was by a piece of pressure tubing. The tube (F), containing potassium
hydroxide pellets, protected the absorption tubes from possible diffusion of water vapor from the aspirator. The manometer is designated by (G).

While Pearce and Snow used between 16 and 17 liters of gas, Rodebush and Ewart used only 1 liter of air as is done in this work. Since, as has already been explained, precise determinations of the vapor pressures cannot be made by the dynamic method, without an accurate measure of the volume of water displaced; and since, Rodebush and Ewart did not report the efficiency of the apparatus using 1 liter of gas, it was desirable to know what results could be expected. For this purpose it was decided to measure the vapor pressure of water at 25°.

Material

Water distilled from an alkaline solution of potassium permanganate in a pyrex all-glass still was used.

Experimental

The presaturator and four saturating tubes were filled to little over half full and placed in the water.

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bath where they were allowed to stand for about a half hour. The absorption tubes which had been previously weighed were then connected to the saturating bottles and lowered into the bath.

The presaturator bath was kept at a temperature of 27°. After connections had been made, water was allowed to run from the syphon, whereupon air was pulled through the apparatus. When the first bubble of air left the last saturating tube the collection of water leaving the aspirator was begun. When one liter of water, measured into a volumetric flask had been collected, the flow of water was stopped, the tubes removed from the bath and the absorption tubes disconnected. After drying thoroughly these tubes were placed into a desiccator over concentrated sulfuric acid and allowed to stand for 40 minutes before weighing. Weighings were repeated until the bottles came to constant weight. From the weight of water, the number of mols was determined. Using the Fischer Bottle the procedure was similar to the above method. The bottle was weighed, attached to the saturators and the air drawn through. After disconnecting the bottles, about a half liter of dry air was drawn
through, the stop-cock closed and the bottle allowed to stand for 20 minutes. At the end of this time the stop-cock was opened momentarily and then closed again and the bottles weighed. Weighings were repeated until constant.

The volume of air used was calculated to standard conditions of temperature and pressure. From the mols of water and air and the pressure existing throughout the apparatus, the partial pressure of the water was determined. In Table I a series of results using the Bichowsky and Storch absorption tubes are given. The results obtained using the Fischer Bottle are given in Table II.
Table I

Vapor Pressure of Water at 25° using the Bichowsky and Storch type Absorption Tube

<table>
<thead>
<tr>
<th>Total Pressure in Aspirator (mm.)</th>
<th>Temp.(\text{H}_2\text{O}) (°C)</th>
<th>Mols Air (x 10^2)</th>
<th>Mols (\text{H}_2\text{O}) (x 10^3)</th>
<th>Partial Press. (\text{H}_2\text{O}) mm.</th>
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<tbody>
<tr>
<td>706.2</td>
<td>17.2</td>
<td>3.8213</td>
<td>1.355</td>
<td>23.58</td>
</tr>
<tr>
<td>705.7</td>
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<td>3.7300</td>
<td>1.305</td>
<td>23.30</td>
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<tr>
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<td>16.8</td>
<td>3.8591</td>
<td>1.313</td>
<td>23.64</td>
</tr>
<tr>
<td>705.4</td>
<td>17.0</td>
<td>3.8116</td>
<td>1.309</td>
<td>23.43</td>
</tr>
<tr>
<td>710.4</td>
<td>19.4</td>
<td>3.8017</td>
<td>1.350</td>
<td>23.81</td>
</tr>
<tr>
<td>709.6</td>
<td>20.2</td>
<td>3.8150</td>
<td>1.341</td>
<td>23.26</td>
</tr>
<tr>
<td>700.9</td>
<td>18.5</td>
<td>3.7663</td>
<td>1.289</td>
<td>23.20</td>
</tr>
</tbody>
</table>

Mean 23.6 ± 0.2 mm.

Table II

Vapor Pressure of Water at 25° using a Fischer Bottle Absorber

<table>
<thead>
<tr>
<th>Total Pressure in Aspirator (mm.)</th>
<th>Temp.(\text{H}_2\text{O}) (°C)</th>
<th>Mols Air (x 10^2)</th>
<th>Mols (\text{H}_2\text{O}) (x 10^3)</th>
<th>Partial Press. (\text{H}_2\text{O}) mm.</th>
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<tr>
<td>708.6</td>
<td>23.3</td>
<td>3.719</td>
<td>1.213</td>
<td>22.33</td>
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<tr>
<td>707.3</td>
<td>22.9</td>
<td>3.718</td>
<td>1.227</td>
<td>22.60</td>
</tr>
<tr>
<td>714.6</td>
<td>22.6</td>
<td>3.763</td>
<td>1.264</td>
<td>23.22</td>
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<td>22.6</td>
<td>3.738</td>
<td>1.243</td>
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<td>3.703</td>
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<tr>
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<td>713.3</td>
<td>25.0</td>
<td>3.731</td>
<td>1.210</td>
<td>22.50</td>
</tr>
</tbody>
</table>

Mean 22.75 ± 0.25 mm.
Chapter IV

DISCUSSION OF RESULTS

As may be seen in Table I the accuracy and the precision of the procedure is not of the degree desirable. The mean of the results shown is 23.6 mm. with a mean deviation of 0.2 mm. Some of the error of course can be accounted for by the use of sulfuric acid as the absorption agent, in place of more efficient agents such as phosphorous pentoxide or magnesium perchlorate.

From Table II it can be seen that the precision and accuracy are much poorer than in Table I. This can, perhaps, be accounted for by the inefficiency of potassium hydroxide as a drying agent as compared to sulfuric acid.

In the work as had been originally planned this problem of complete absorption should not be so difficult, since, the weak base is to be absorbed in a relatively concentrated solution of a strong acid and its amount determined by back titration. It should be possible to obtain values with accuracy of about 0.1 mm. which will be sufficient for the purpose for which the apparatus was constructed, and which seems to be the maximum efficiency of this apparatus.
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