GORDON

A Differential, Dynamic Method for the Accurate Determination of Relative Vapor-Pressure Lowering

Chemistry
Ph. D.
1912
A DIFFERENTIAL, DYNAMIC METHOD FOR THE ACCURATE DETERMINATION OF RELATIVE VAPOUR-PRESSURE LOWERING.

BY

HUGH BYRON GORDON
B. A. Miami University, 1908
M. S. University of Illinois, 1910

THESIS

Submitted in Partial Fulfillment of the Requirements for the
Degree of

DOCTOR OF PHILOSOPHY

IN CHEMISTRY

IN

THE GRADUATE SCHOOL

OF THE

UNIVERSITY OF ILLINOIS

1912
I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Hugh Byron Gordon

ENTITLED A Differential, Dynamic Method for the Accurate Determination of Relative Vapor-Pressure Lowering.

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE DEGREE OF Doctor of Philosophy

Recommendation concurred in:

Committee on Final Examination
The present investigation was undertaken in the fall of 1909 at the suggestion of Dr. E. W. Washburn, and has been carried on at the Chemical Laboratory of the University of Illinois during the academic years, 1909-10, 1910-11, and 1911-12.

I wish to thank Professor Washburn for his kindly interest and assistance during the progress of this work.
I. PURPOSE OF INVESTIGATION.

In the study of solutions to determine the molecular condition of the solute, any of the colligative properties, osmotic pressure, boiling point elevation, freezing-point depression, or vapor pressure lowering, may be employed. For this purpose the osmotic pressure is of very little assistance because satisfactory semi-permeable membranes have, as yet, been prepared for only one or two solutes.

The boiling-point raising is difficult to measure with sufficient accuracy because of its variation with changes in atmospheric pressure, and, in the case of aqueous solutions, because the molar boiling point elevation is small. It has the additional disadvantage that the temperature and concentration change at the same time.

The freezing-point depression can be measured with sufficient accuracy but like the boiling point raising, it is open to the objection that the temperature varies with the concentration. This objection does not apply to the vapor pressure lowering, since it can be measured at any desired concentration without changing the temperature. It possesses the further advantage that it can be used over a wide range of temperature, while the boiling point raising can be measured only above 100 degrees, and the freezing-point depression only below zero.

The vapor pressure lowering would therefore be the most desirable property to study if it could be determined with sufficient accuracy. The object of this investigation is to develop a method
II. REVIEW AND DISCUSSION OF PREVIOUS METHODS.

In the calculation of molecular weights/non-volatile solutes from the vapor pressure lowering, the Raoult-Van't Hoff formula,

\[ M = \frac{18 C p}{P_0 - P} \]

is used. Here \( C \) is the number of grams of the solute per hundred grams of water, \( P_0 \) is the vapor pressure of pure water at the temperature of the experiment, and \( P \) that of the solution. Berkeley and Hartley (Proc. Roy. Soc. Lon. 77-A, p. 156, 1906) used the vapor pressure method for determining osmotic pressure. The equation connecting the two has been shown (Washburn, Jour. Am. Chem. Soc., Vol. 52, p. 497) to contain the factor \( \frac{P_0 - P}{P_0} \). It will be seen that both this and the Raoult-Van't Hoff formula include as a factor the vapor pressure lowering, \( P_0 - P \). It is, therefore, the accuracy with which this quantity can be measured that determines the accuracy of the method. Let us assume that in order to be reasonably satisfactory, a method must enable us to measure \( \frac{P_0 - P}{P_0} \) with a probable error not much greater than one percent. In the study of "concentrated" solutions, it is important to be able to study the concentration range from say, one-half normal, up. For a half-normal solution of a uni-univalent salt, \( P_0 - P \) is about 0.35 mm. of mercury. Assuming the error in measuring \( P_0 \) itself to be
negligible, the error in $p_0 - p$ should not exceed one per cent of
$0.35 \text{ mm.}$, or $0.0055 \text{ mm.}$

Three chief methods for the measurement of vapor pressure
lowering have been used (Lincoln and Klein, Jour. Phys. Chem., 1907,
p. 518). These are:

(1) The Static Method which consists in introducing the
solution into a Torricellian vacuum and noting the depression of
the mercury column. This method has been shown by Landolt and
Kamlbaum (Carveth and Fowler, Jour. Phys. Chem. Vol. 4, 1904, p.313)
to be subject to errors which are very difficult to eliminate. A
very small amount of a gas dissolved in the solution will cause a
considerable error. It is further very difficult to obtain
equilibrium between the vapor and the solution, for a lowering of
the temperature will cause condensation upon the walls of the appa-
ratus and then the vapor pressure of pure water enters as a factor.
At best a very long time is required for the attainment of
equilibrium.

(2) The Indirect Method which consists in determining the
pressure under which the solution boils at a given temperature,
appears to be very simple, but the maintenance of constant
temperature and pressure and the accurate determination of these
for any given solution are attended by great difficulties.

(3) The Dynamic, or Air-Bubbling Method, by which the
vapor of a solution is carried away by a current of air. Either
the vapor is absorbed in a drying train and weighed, or the vessel
containing the solution is weighed and the weight of the solvent
evaporated found as the loss in weight of the solution. Usually the volume of air passed is measured and the vapor pressure of the solution calculated on the assumption that the vapor is a perfect gas. The vapor pressure lowering is then found by subtracting the value so found from that of pure water at the same temperature.

This method, as usually applied, is not very accurate, as will be readily understood from the following considerations. The formula used for the calculation of vapor pressures (Lincoln and Klein, l.c.) is

\[ P = \frac{B}{1 + V(1 + Kt')} \frac{Wd(B - p_0)}{m(1 + K't')}} \]

Where:
- \( t \) = the temperature at which the air is saturated,
- \( p \) = the vapor pressure of the liquid studied at \( t \) degrees,
- \( t' \) = the temperature of the aspirator,
- \( p_0 \) = the vapor pressure of water at \( t' \),
- \( B \) = the corrected barometer reading,
- \( K' \) = the coefficient of expansion of air = 0.003671,
- \( K \) = the coefficient of expansion of water (negligible)
- \( V \) = the volume of the aspirator at zero C.,
- \( W \) = the weight of one liter of air at zero C.,
- \( d \) = the theoretical density of water vapor,
- \( m \) = the weight of water absorbed.

It will be seen that the chief sources of error are likely to occur in measuring the volume of gas aspirated, and in the
variation of the temperature of the thermostat. If a recording barometer is not used the error in measuring the atmospheric pressure may also be appreciable.

If the mean temperature of the thermostat varies as much as 0.01 degree from one experiment to another, the difference in vapor pressure of water at 25 degrees will be about 0.014 mm. (In Landolt and Bornstein's Tables the pressures given for water at 25 and 26 degrees are 23.546 and 24.891 mm. respectively).

As stated above the accuracy desired is 0.0035 mm., or about one-fourth of the above amount. If moreover, the mean temperature of the aspirator during the measurement of the volume of air passed through the system is known to not better than one-tenth degree, the fractional error in $p_0$ from this source will be approximately 0.00036. Since $p_0$ is about 23.6 mm. at 25 degrees, this amounts to about 0.0085 mm. It is hardly probable that the error in either of these temperatures will be as small as that assumed, but if it is, and if all other sources of error are negligible the probable error of $p_0$ and of $p$ will be $\sqrt{(0.0085)^2 + (0.014)^2} = 0.016$ mm. each. That of $p_0 - p$ will hence be $\sqrt{2(0.016)^2} = 0.023$ mm. For the ratio, $\frac{p_0 - p}{p_0}$, which for the sake of brevity we shall call $R$, the fractional error will be $\sqrt{(0.023)^2 + (0.016)^2} = 0.066$ or 6.6 per cent -- more than six times the allowable error of one per cent. The value 0.35 is that of $p_0 - p$ for a half normal solution and the value 24 is that of $p_0$ at 25 degrees. It is, therefore, evident that we may expect errors in $R$ of six or seven per cent when this method
is applied, in its usual form, to half normal solutions. The most accurate results hitherto obtained with the dynamic method are those of Lincoln and Klein (l.c.) and of Kahlenberg and Millard (Thesis/ Wisconsin, 1911). Their results on the vapor pressure of water are shown in Table I. In this and the succeeding tables $p_0$ stands for the vapor pressure of water, $p$ for that of a solution, $d$ for the deviation from the mean value of the series, $C$ for the concentration of a solution expressed in grams of solute per hundred grams of water, and $C$ for the concentration of a solution expressed in gram molecular weights of solute per thousand grams of water. It is evident from Table I that the results actually obtained are liable to even greater error than that assigned above, since the average deviation from the mean for the data of Lincoln and Klein is 0.052 mm. and of Kahlenberg and Millard 0.098 mm. Table II shows some of the data obtained on potassium nitrate by Lincoln and Klein and on sodium chloride by Kahlenberg and Millard. In the data obtained by Lincoln and Klein it will be seen that the average deviation from the mean is slightly greater than in the data obtained for pure water by the same observers. In the corresponding data obtained by Kahlenberg and Millard and average deviation from the mean is greater in the data obtained with pure water. In both cases the probable error is far greater than that which we have set as our limit.

The dynamic method has been used by Regnault (Ann. de ch. et de phys. (3), 15, P.158,1845) to measure the vapor pressure of water. Tammann [Wied. Ann. 33, p.322,1888] discussed Regnault's work
### TABLE I. VAPOR PRESSURE OF WATER AT 25°.

<table>
<thead>
<tr>
<th></th>
<th>Lincoln and Klein</th>
<th>Kahlenberg - Millard</th>
</tr>
</thead>
<tbody>
<tr>
<td>Po</td>
<td>d</td>
<td>Po</td>
</tr>
<tr>
<td>23.83</td>
<td>0.07</td>
<td>23.67</td>
</tr>
<tr>
<td>23.71</td>
<td>0.05</td>
<td>23.72</td>
</tr>
<tr>
<td>23.84</td>
<td>0.08</td>
<td>23.65</td>
</tr>
<tr>
<td>23.75</td>
<td>0.01</td>
<td>23.74</td>
</tr>
<tr>
<td>23.67</td>
<td>0.09</td>
<td>23.80</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Lincoln and Klein</th>
<th>Kahlenberg - Millard</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### TABLE II. VAPOR PRESSURE OF SOLUTIONS AT 25°.

<table>
<thead>
<tr>
<th>KNO₃: Lincoln and Klein</th>
<th>NaCl: Kahlenberg and Millard</th>
</tr>
</thead>
<tbody>
<tr>
<td>c₁</td>
<td>c₁</td>
</tr>
<tr>
<td>10.45</td>
<td>1.034</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>Mean</td>
<td>23.09</td>
</tr>
</tbody>
</table>
and applied the method to the determination of the aqueous tension of saturated solutions and of solid hydrates. His results are subject not only to the errors enumerated above as ordinarily applying to this method, but in addition, as he secured saturation by bubbling air through the solution, the volume of the air changed continually so that it was never fully saturated (Berkeley and Hartley, Nature, p. 222, 1905).

Ostwald (Phys. Chem. Measurements, Walker's translation, 1894, p. 188) passed dry air through the solution, then through water, then through sulphuric acid. The losses of weight in the solution and in the water respectively are proportional to the vapor pressure of the solution, and to its difference from that of water, respectively. The gain in weight of the sulphuric acid should equal the sum of these losses and thus acts as a check on the work. This method, like that of Tammann, has the objection that the bubbling prevents complete saturation. The quantity of solution to be weighed must also be very large to avoid concentration changes, and this makes accurate weighing difficult. In addition Tammann found that bubbling spattered the solution on the walls of the vessel, that these drops became concentrated by evaporation, and so the vapor pressure was reduced.

Several other investigators have used the method with unsatisfactory results. Berkeley and Hartley (Proc. Roy. Soc. Lon. 1906, 77-A, p. 156) weighed their solution, which could not be done with great accuracy. They secured saturation by passing the air over the solution as suggested by Kahlenberg (Science, vol. 22,
July 1905) and thus avoided the incomplete saturation attendant upon air-bubbling. They secured an accuracy of about five per cent in their vapor pressure values.

Lincoln and Klein (l.c.) applied the method of Kahlenberg (l.c.) to the measurement of vapor pressure lowering of solutions of the nitrates of potassium, lithium, and sodium. Their work is subject to the usual errors of the dynamic method as described above.

As the history of vapor-pressure measurement has been carefully discussed by Lincoln and Klein (l.c.) and F. Henning (Ann. der Phys., 1907, 22, p. 609), it need not be further considered here.

III. OUTLINE OF THE METHOD OF THIS INVESTIGATION.

To avoid the sources of error described above the following plan was adopted: A current of air is made to pass over the solution under investigation, where it becomes saturated with water vapor in equilibrium with the solution. Then, after passing through a suitable drying train it passes over pure water in a saturator similar to that containing the solution and placed beside it. Here it becomes saturated with vapor in equilibrium with water. It next passes through another drying train and then to the aspirator. The gains in weight of the two drying systems - which will be referred to in future as the absorbers - give the water removed from the solution and from the pure water respectively. Correcting for the change in volume of the air in passing from one saturator to the other, we may assume that the weight of water absorbed is proportion-
al to the vapor pressure at which the air became saturated with it. The volume correction is kept small by making the pressure difference between the two saturators as small as possible. It may be objected that water vapor is not a perfect gas and so the weight absorbed will not be exactly proportional to the pressure, but using the data given in Landolt and Bornstein's tables for density of water-vapor, the calculated pressure at 25 degrees varies from the accepted value not more than do the results of various observers from one another. It cannot be stated definitely, therefore, that the vapor does not obey the gas laws, but even a large deviation from these laws would be of slight effect, since nearly the same error would occur in the case of the solution as of the water.

IV. CALCULATION OF THE RELATIVE LOWERING, R.

Under the assumptions given above, the weight of water, m, removed from a liquid by a given quantity of air is expressed by

\[ m = K p V, \]

where \( K \) is a proportionality factor, \( p \) is the aqueous tension of the liquid considered, and \( V \) is the volume occupied by the air. Under the conditions of these experiments, the same quantity of air is passed through both saturators. The volume passing through each saturator will therefore vary inversely as the partial pressure of the air in the saturator. Obviously this is in each case the atmospheric pressure diminished by the aqueous tension of the liquid with which the air is in equilibrium and by the difference between the total pressure within the saturator and the atmospheric pressure.
It therefore follows that

$$\frac{V_1}{V_2} = \frac{B-p_2-P_2}{B-p_1-P_1}$$

where the subscripts indicate whether the quantity is to be measured at the first or second saturator, $p$ refers to the aqueous tension, $P$ to the difference between the total pressure of the gas mixture and that of the atmosphere, $B$, and $V$ to the volume occupied by the gas mixture. From (1) it follows that the ratio of the weights of water which should be found in the two absorbers is given by

$$\frac{m_1}{m_2} = \frac{p_1 V_1}{p_2 V_2}, \text{ hence}$$

$$\frac{m_2-m_1}{m_2} = \frac{p_2-V_1}{V_2}, \text{ and}$$

$$\frac{p_2-p_1}{p_2} = \frac{m_2-m_1}{m_2} \frac{V_2}{V_1}$$

From (5) and (2) we obtain

$$\frac{p_2-p_1}{p_2} = \frac{m_2-m_1}{m_2} \frac{B-p_1-P_1}{B-p_2-P_2}$$

If both saturators contain pure water this obviously becomes

$$m_2 = m_1 \left( \frac{B-p_0-P_1}{B-p_0-P_2} \right),$$
where $p_0$ is the vapor pressure of pure water. For this series of experiments, made at 25°C, $p_0$ is taken as 23.546 mm. This is the value calculated from Regnault's data and given in Landolt and Bornstein's Tables.

Solving (3) for $p$ and substituting the value of $\frac{V_1}{V_2}$ obtained from (2), we obtain, for the case that the first saturator contains a solution and the second pure water,

$$\begin{align*}
(8) \quad p &= \frac{p_0 m (B-P_1)}{m_0 (B-p_0-P_2) + m p_0}.
\end{align*}$$

We may calculate $p$ by this formula, but since we wish $R$ instead of $p$, we may proceed as follows: Dividing both sides of equation (8) by $p_0$, subtracting each side from unity, expressing the result in fractional form, and collecting terms, we obtain

$$\begin{align*}
(9) \quad R &= \frac{p_0 - p}{p_0} = \frac{(m-m_0)p_0 + m_0 (B-P_2) - m (B-P_1)}{(m-m_0)p_0 + m_0 (B-P_2)}.
\end{align*}$$

For the sake of brevity the following abbreviations will be used:

$$\begin{align*}
R &= \frac{p_0 - p}{p_0}; \\
D_m &= m_0 - m; \\
D_p &= P_2 - P_1.
\end{align*}$$

Substituting these abbreviations in (9) gives

$$\begin{align*}
(9') \quad R &= \frac{m_0 (B-P_2) - D_m p_0 - m (B - P_1)}{m_0 (B-P_2) - D_m p_0}.
\end{align*}$$
Since $D_m$ can be determined more accurately than either $m$ or $m_0$, it is well to express the larger of these products in terms of it. By adding and subtracting $m_0(B-P_1)$ from the numerator of (9), and collecting terms, we obtain

\[
(10) \quad R = \frac{D_m(B-P_1 - P_0)}{m_0(B-P_2) - D_m P_0}.
\]

To decide upon the accuracy with which each quantity must be measured let us take an example of a half-normal solution, say experiment 11, table IV. Substituting the values there given equation (10) becomes,

\[
R = \frac{0.1653 \times (738-0.47-23.55) - 10.070 \times 0.86}{10.070 \times (738-1.33) - 0.1653 \times 23.55}
\]

\[
= \frac{118.0 - 8.7}{7420 - 4} = 0.01474.
\]

A glance at the denominator shows no appreciable error is to be feared in it. $D_m P_0$ is negligible while $m_0$ and $(B-P_2)$ can easily be measured with less than 0.1 per cent error. Hence the accuracy attainable in $R$ will be practically controlled by the accuracy attainable in the numerator. That is $118.0 - 8.7 = 7416R = 109.3$ and for an accuracy of one per cent in $R$ - the allowable error - the error in the numerator must not exceed 1.1 units. Hence the allowable error, $d$, in each term of the numerator as calculated from $\sqrt{2d^2} = 1.1$ is 0.8. The first term of the numerator must be known to $0.8/118$ or practically 0.7 per cent. This term consists of two factors,
the second of which, \((B-P_1-p_0)\), can without much difficulty be measured with an accuracy of 0.01 per cent. Consequently the accuracy in \(D_m\) need not be greater than 0.7 per cent or 0.001 g. The second term in the numerator must also be known to 0.8 units or to 0.8 units or to \(0.8 = 9.2\) per cent. The first factor of this term, \(m_0\), can easily be measured with an accuracy of 0.01 per cent hence accuracy in \(D_p\) need not be greater than 9.2 per cent of 0.86 which is 0.08 mm. — an accuracy which is easily obtainable.

It is evident from the foregoing considerations that if the saturators and absorbers are perfectly efficient any desired accuracy in \(R\) can be attained for a solution of any concentration if sufficient air is aspirated, for the accuracy in \(R\) increases with increase in \(D_m\) and this quantity in turn increases with increase in the concentration of the solution and with increase in the quantity of air aspirated.

The temperature coefficient of \(R\) is a function of the heat of dilution of the solution and since this is small for moderately concentrated solutions of salts, it is doubtful if it would cause an appreciable error in \(R\) if the mean temperature of the experiments should vary by as much as a degree.

V. DESCRIPTION OF THE APPARATUS.

Evidently the two important parts of the apparatus are the absorbers and the saturators. Several forms of saturator have been used and proven to be efficient. Kahlenberg (Sci. N.S. 22, p.74, 1905) proposes a shaking device for this purpose. This was used
by Lincoln and Klein and also by Kahlenberg and Millard, in their work referred to above. Berkeley and Hartley caused the air to pass through glass tubes containing the solution. The tubes were rocked back and forth so that a large surface was constantly wet with fresh solution and local concentration changes in the solution avoided. Frank C. Gutsche, (Thesis, Minnesota, 1910) describes an efficient apparatus for this purpose, consisting of large, rotating globes, containing glass beads and the solution studied.

In this investigation, a series of perpendicular tin boxes, containing frequent, transverse baffle-plates, over which the liquid was allowed to trickle, while the current of air ascended through the box were first tried. In the preliminary experiments with water in both saturators this system seemed to be effective, but the quantity of solution required was so great and the other apparatus required so complex, that it was abandoned before any experiments with solutions were made. The saturators finally used were a slightly modified form of the ones used by Berkeley and Hartley. Since they were not to be weighed, they were made much larger than the ones used by those investigators. The form is shown in Plate I. The main apparatus is made of glass tubing about 1.5 cm. in diameter and 38 cm. long. These straight, parallel tubes are connected in pairs by inverted U-tubes at their ends, and two pairs are connected at the middle by a similar U-tube. The small tubes attached to the larger ones at their middles are for the inlet and outlet of the air current. Those attached to the U-tubes at the end of the apparatus are used only in filling and cleaning
the apparatus. They are closed during an experiment. Two of these instruments are connected in series for one saturator. The air has thus to pass through eight tubes containing the solution before reaching the absorber. During an experiment the saturators, filled about half-full of the solution, are fastened in the thermostat upon a rocking platform. This platform makes four complete oscillations per minute. The angle of rocking is such that at their lowest position the ends of the tubes are completely filled with the liquid so that all the air passes through the upper end. At their highest position the ends are entirely empty. By this means a very large surface, constantly wet with fresh liquid, is obtained for saturating the air.

Two somewhat different forms of absorbers were found to be satisfactory. The form finally adopted is shown in Plate II and diagramatically in Plate II(a). The air enters the absorber through the flask, F, Plate II(a). This dips into a Dewar tube filled with chopped ice and water. Most of the moisture is condensed here and the rest is absorbed by the sulphuric acid which is contained in the tubes, A, and the phosphorus pentoxide contained in the flat-bottomed, double U-tube, P. The absorber is followed by a safety U-tube (not shown) also containing phosphorus pentoxide. The upright tube near the flask is closed by a ground-glass stopper, S, which is removed for cleaning and filling the apparatus. The other form of absorber found satisfactory had a flask and phosphorus pentoxide tubes similar to those shown but the tubes containing sulphuric acid were replaced by one or two large U-tubes filled with
Plate I.
Plate II.
pumice stone soaked in sulphuric acid. A small bulb blown at the bottom of the U-tube served as a receptacle for the excess of acid and water collected.

The thermostat was both heated and regulated by electricity. It was a box three feet square and three and one-half feet deep. The water was thoroughly stirred by means of a large turbine stirrer and another stirrer having five sets of four paddles each. Both stirrers were driven at the rate of 400 R.P.M. The power was derived from a one-sixth horse-power electric motor. The same shafting which drove the stirrers rocked the platform on which the saturators were placed. A worm gear reduced the velocity from 400 to 4 R.P.M. The large quantity of water demanded a great deal of heat to maintain it at 25° - the temperature of the experiments. This was supplied by an alternating current of about 10 amperes or 1100 watts. This high current often caused the carbon tips of the current interrupter to cling together so that the heating current was not broken when it should have been. Several efforts were made to overcome this difficulty but none was entirely successful. As a result the temperature of the thermostat often varied several tenths of a degree during an experiment. As was shown above, a moderate temperature change which affects both saturators alike, should cause no appreciable error in the results. With water in both saturators - as in the preliminary experiments - the temperature variation is without effect if the water is thoroughly stirred so that both saturators are affected alike. In the first experiment with a solution the regulator worked fairly well.
In the later ones an effort was made to make the temperature changes below 25° equal those above that temperature.

To measure the difference in pressure between the system and the atmosphere open water manometers were used. In the final form an inclined manometer on whose scale one centimeter was equivalent to 0.0062 cm. mercury was attached to the system between the second saturator and absorber. Its reading was recorded as $P_2$. Then the open end of the manometer was connected to the system between the first saturator and absorber. The reading of the manometer now indicated the difference in pressure between the two saturators, and, subtracted from $P_2$ gave $P_1$, the difference of the pressure within the first saturator from that of the atmosphere. These pressure differences were apparently determined with an accuracy of two or three hundredths of a millimeter of mercury. Except when the pressures were being read the manometer was cut off from the saturators by stop-cocks.

The air was drawn through the system by means of a water pump. The pressure was kept tolerably constant by attaching the pump at the bottom of a tube in which the water was kept at a nearly constant level. The rate of flow of air through the system was regulated by means of screw-cocks on the rubber tube connecting the second absorber to the pump.

The absorbers were placed on brackets attached to the outside of the thermostat near its top. Since the temperature of the thermostat was higher than that of the room it was necessary to heat the saturated air as it came from the saturator to the
absorber. This was accomplished by wrapping the tube through which the air passed with wire through which an electric current flowed.

In connecting the various parts of the apparatus a good grade of rubber tubing was used. The joints which were made under water were coated with a mixture of rosin and bees' wax. Outside of the thermostat, wherever there was danger of leakage, the joints were coated with paraffin. From time to time the system was tested for leaks, using a pressure difference from ten to fifty times that to which it would be subjected during an experiment. These rubber joints were found entirely satisfactory.

A diagram of the entire system is given in Plate III, where 0 is the overflow to maintain a constant level over the suction pump, P. T is the tube by which water from the top enters the reservoir, R; CC are screw-cocks for adjusting the rate of flow of air; U₁ and U₂ are safety tubes containing phosphorus pentoxide; A₂ and A₁ are the absorbers; S₂ and S₁ the saturators, and S₂ and S₁ the presaturators. L is a U-tube filled with soda-lime to remove carbon dioxide from the air aspirated; M is the manometer, outside the thermostat, and C₁ and C₂ are the stop-cocks by which it is cut off from the main system when not in use. K is the thermostat.

VI. MATERIALS USED.

All the water used in the experiments was a good grade of conductivity water prepared by distilling ordinary distilled water from an alkaline solution of potassium permanganate.
A special still with a block tin condenser was used for this purpose.

The potassium chloride used in the investigation was Kahlbaum's best grade twice recrystallized from conductivity water. By spectroscopic test it was found free from sodium. The solution was made up by fusing the salt in a weighed platinum crucible, weighing, dissolving in water in a weighed flask, and adding enough water to bring the total weight to that desired. The weighings were made with calibrated weights and were reduced to vacuo. To prepare the more dilute solutions a weighed quantity of the first solution was diluted with the desired weight of water.

VII. DETAILS OF MANIPULATION.

In carrying out an experiment the procedure was as follows: The absorbers and saturators were cleaned with a mixture of potassium dichromate and sulphuric acid, rinsed thoroughly with water, and dried. The double U-tube of the absorber was then filled with phosphorus pentoxide and glass beads, a plug of glass wool was placed in the arm from which the air left the absorber, and 20 c.c. of sulphuric acid was placed in the absorber through the upright tube, C, Plate II(a). The apparatus was then carefully tilted back and forth until the acid was properly distributed among the different tubes, then all stop-cocks were closed, and the entire outside of the absorber was thoroughly rinsed with water and wiped nearly dry. The two absorbers which were to be used in the experiment, after being treated as described above, were next placed upon the opposite pans of a large Bueprecht balance (in a
constant temperature room) capable of weighing them to a tenth of a milligram and the weights adjusted for equilibrium. A few hours later the weights were again adjusted for equilibrium. If the temperature of the balance case changed more than a tenth of a degree, as shown by two thermometers graduated in tenths of a degree and hung in the balance case, the absorbers were opened to the air to equalize the pressure and closed again before the weights were readjusted. The weights were adjusted at intervals of several hours until the readjustment required was only a few tenths of a milligram. Then the point of rest and sensitiveness of the balance were observed, the lighter absorber, which had been placed on the right balance pan, was removed and the heavier weighed accurately. The latter was then removed and the zero point of the balance observed. The weight of the heavier absorber and their difference were then recorded. The weights used were calibrated but it was found that the corrections were negligible. The weights were not corrected to vacuum, for as was seen in the calculations above, except for a small volume-correction-factor, the weights of the water absorbed enter in the calculation of \( R = \frac{m_0 - m}{m_0} \), so that this correction would cancel. It was found that after weighing, the absorbers could be washed and reweighed with such accuracy that the difference in their weights checked the value previously determined to 0.0002 g.

While the absorbers were coming to constant weight, the saturators were half filled, one with water, the other with the
solution under investigation. They were then placed in the thermostat on the rocking platform and loosely tied to it by means of insulated copper wire. The connections were made as shown in Plate III, except for the absence of the absorbers, and the rubber connections daubed with the rosin and bees'-wax mixture. Next the thermostat was filled with water and its temperature raised to 25 degrees by means of live steam from a pipe arranged for that purpose. The final adjustment of temperature was made with the electric heating and regulating system. A current was then passed through the coils which heated the air as it came out of the saturators and the system was tested to see if it was air tight. This was done by connecting the system through a gas wash bottle to a suction pump that would cause from ten to fifty times the pressure difference to which the apparatus would be subjected during an experiment, closing the air-passage at the first safety-U-tube or at the soda-lime tube, L, Plate III - depending on which half of the apparatus was being tested - and noting whether any air bubbled through the wash-bottle. If bubbling did not quickly cease a leak in the system was indicated. This was promptly discovered and stopped. Each half of the system was tested separately in the same way. Before being filled each absorber was tested in this way and each stop-cock was tested both in the open and closed positions.

When all parts of the apparatus were found to be tight, gas wash bottles were placed in the system instead of the absorbers and air aspirated as during an experiment for an hour or
two. By this means the air-passages were brought into equilibrium with the moist air from the saturators. Then the aspiration was stopped, the wash-bottles were removed, and the absorbers, which had been weighed as described above, were put into their places. All the stop-cocks were next opened and the aspiration begun. The rate of aspiration was measured approximately by means of a gas-meter and was adjusted as desired by means of the screw-cocks, CC, Plate III.

After a short time $P_2$ was measured by connecting the open manometer, $M$, as shown in Plate III, but without the connection to the first absorber. If the meniscus was unsteady, its mean position was noted and the stop-cock, $C_2$, was closed when the meniscus was near this point. The manometer was immediately read, connection was made to the first absorber, and both stop-cocks opened. The pressure then given by the manometer reading - taken in the same manner as $P_2$ - was $P_2 - P_1$. This was subtracted from $P_2$ and recorded together with that quantity, the time of day, and the barometer reading. The pressures were recorded as above at intervals whose frequency varied according to the constancy of the readings.

When sufficient time had elapsed the stop-cocks of the absorbers were closed and the aspiration pump stopped. The absorbers were then replaced by others which had been cleaned, filled, and weighed in the same manner as the first pair, and a second experiment commenced immediately. The first pair of absorbers was wiped well with a damp cloth, then with a dry one, and were weighed in the manner described above.
As an example of the course of a typical run, the following data for experiment 7, Table IV, are given:

<table>
<thead>
<tr>
<th>Time</th>
<th>B</th>
<th>P₁</th>
<th>P₂ - P₁</th>
<th>P₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>4/20/12 6:30</td>
<td>741.0</td>
<td>0.44</td>
<td>1.27</td>
<td>1.71</td>
</tr>
<tr>
<td>7:30</td>
<td>742.0</td>
<td>0.33</td>
<td>1.20</td>
<td>1.53</td>
</tr>
<tr>
<td>8:30</td>
<td>743.0</td>
<td>0.35</td>
<td>1.06</td>
<td>1.41</td>
</tr>
<tr>
<td>9:30</td>
<td>743.5</td>
<td>0.37</td>
<td>1.02</td>
<td>1.39</td>
</tr>
<tr>
<td>10:30</td>
<td>743.5</td>
<td>0.38</td>
<td>1.02</td>
<td>1.40</td>
</tr>
<tr>
<td>11:30</td>
<td>742.5</td>
<td>0.42</td>
<td>0.95</td>
<td>1.37</td>
</tr>
<tr>
<td>12:30</td>
<td>742.0</td>
<td>0.33</td>
<td>1.21</td>
<td>1.54</td>
</tr>
<tr>
<td>Mean</td>
<td>742.5</td>
<td>0.37</td>
<td>1.11</td>
<td>1.48</td>
</tr>
</tbody>
</table>

The pressures are all expressed in millimeters of mercury. Absorbers A and B were used. The rate of flow of air was about 39 liters per hour.

Weights before the run; Weights after the run;
Absorber A = Absorber B + 2.7555 g. Absorber A = B + 2.6347 g.
Absorber A = 318.2505 g. Absorber A = 323.2851 g.

hence m₂ - m₁ = 2.7555 - 2.6347 = 0.1208 g.,
and m₁ = 323.2851 - 318.2505 = 5.0346 g.

Excluding the first three experiments of Table III which were made with absorbers having a small bore and hence a high resistance to the air current, (P₂ - P₁) varied, as shown by the figures in Tables III and IV, between 0.24 mm, and 1.50 mm.
according to the rate of aspiration.

The Beckmann thermometer used in the thermostat was standardized by comparison with a thermometer standardized at the National Bureau of Standards.

To ascertain whether any appreciable concentration change occurred in the solution during the experiments, determinations were made of the conductivities of samples of the half-normal solution taken from the first part and from the latter part of the saturator respectively after the series of experiments. The bridge readings for these samples and for the original solution were as follows:

<table>
<thead>
<tr>
<th></th>
<th>Original</th>
<th>630.0</th>
<th>1st</th>
<th>635.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution</td>
<td>630.2</td>
<td>2nd</td>
<td>630.3</td>
<td></td>
</tr>
</tbody>
</table>

The difference in the conductances of the original solution and the sample from the latter part of the saturator is hardly above the limit of experimental error. It may have been caused by slight changes in the temperature of the thermostat. Since the bridge-reading increased with the conductance it is evident that the second solution was about two per cent more concentrated than the first. These results show that equilibrium was practically completely attained before the air entered the latter part of the saturator.

**VIII. THE EXPERIMENTAL DATA**

To test the efficiency of the method pure water was first used in both of the saturators. The results thus obtained
are shown in Table III. In the first three experiments the air was moistened by bubbling through water before entering the first saturator, but the dry air from the first absorber was led directly into the second saturator. Under these conditions if the saturation is incomplete, there will be less water found in the second absorber than is calculated from that in the first and the pressure difference.

The letters at the heads of the columns in Table III have the following meaning: T is the approximate duration of the experiment expressed in hours; \( m_1 \) the weight of water absorbed in the first absorber; \( m_2 \) that found in the second absorber, and \( m_2' \) that calculated from \( m_1 \) and the other data by means of equation (7). \( V \) is the approximate rate of flow of the air expressed in liters per hour. \( B, P_1, \) and \( P_2 \) have the same significance as in the formulas developed above.

from the table

It will be seen that complete saturation was obtained even when the air was not moistened before entering the saturator, but to prevent undue evaporation of the liquid in the saturator the air was moistened before entering both saturators in all the experiments after the third recorded in Table III, and in all those recorded in Table IV. It will be further seen from Table III that the accuracy of the method is independent of the rate of aspiration of air for rates not exceeding 50 liters per hour, since the results are equally good when the rate is 50 and 14 liters per hour. It should be mentioned that in the first experiment recorded in Table III, \( m_2 \) was weighed instead of \( m_1 \). Their positions in the table are therefore reversed. Experiment 5, Table IV, is disregarded since its value for \( R \) has more than 4 times the average deviation.
TABLE III. PURE WATER IN BOTH SATURATORS.

<table>
<thead>
<tr>
<th>I</th>
<th>m₁</th>
<th>V</th>
<th>B</th>
<th>P₂-P₁</th>
<th>P₁</th>
<th>P₂</th>
<th>m₂</th>
<th>m₂</th>
<th>m₄-m₄</th>
<th>m₄/m₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6</td>
<td>5.407</td>
<td>41</td>
<td>750.</td>
<td>4.48</td>
<td>--</td>
<td>--</td>
<td>5.376</td>
<td>5.3137</td>
<td>-0.0628</td>
</tr>
<tr>
<td>2</td>
<td>22</td>
<td>24.514</td>
<td>51</td>
<td>750.</td>
<td>2.95</td>
<td>--</td>
<td>--</td>
<td>24.621</td>
<td>24.613</td>
<td>+0.0089</td>
</tr>
<tr>
<td>3</td>
<td>19.5</td>
<td>21.814</td>
<td>51</td>
<td>750.</td>
<td>2.91</td>
<td>--</td>
<td>--</td>
<td>21.895</td>
<td>21.902</td>
<td>-0.0092</td>
</tr>
<tr>
<td>4</td>
<td>9</td>
<td>3.634</td>
<td>18</td>
<td>735.5</td>
<td>--</td>
<td>0.17</td>
<td>0.50</td>
<td>3.6350</td>
<td>3.6358</td>
<td>-0.0018</td>
</tr>
<tr>
<td>5</td>
<td>8.5</td>
<td>2.739</td>
<td>15</td>
<td>744.</td>
<td>--</td>
<td>0.16</td>
<td>0.57</td>
<td>2.7404</td>
<td>2.7405</td>
<td>-0.0009</td>
</tr>
<tr>
<td>6</td>
<td>24.5</td>
<td>10.121</td>
<td>19</td>
<td>738.5</td>
<td>--</td>
<td>0.22</td>
<td>1.20</td>
<td>10.1391</td>
<td>10.1349</td>
<td>+0.0042</td>
</tr>
<tr>
<td>7</td>
<td>23</td>
<td>7.090</td>
<td>14</td>
<td>750.</td>
<td>--</td>
<td>0.15</td>
<td>0.49</td>
<td>7.0947</td>
<td>7.0933</td>
<td>+0.0014</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Mean</td>
<td>0.00026</td>
</tr>
</tbody>
</table>

TABLE IV. DATA ON KCl.  
Temp. = 25°.  
Molecular Weight = 74.56

<table>
<thead>
<tr>
<th>C</th>
<th>m₁</th>
<th>m₀</th>
<th>B</th>
<th>P₁</th>
<th>P₂</th>
<th>100R</th>
<th>d</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.290</td>
<td>4.3073</td>
<td>4.494</td>
<td>742.</td>
<td>0.22</td>
<td>0.50</td>
<td>3.992</td>
</tr>
<tr>
<td>2</td>
<td>&quot;</td>
<td>3.9730</td>
<td>4.143</td>
<td>737.</td>
<td>0.19</td>
<td>0.44</td>
<td>3.947</td>
</tr>
<tr>
<td>3</td>
<td>&quot;</td>
<td>3.957</td>
<td>4.1258</td>
<td>735.5</td>
<td>0.17</td>
<td>0.46</td>
<td>4.041</td>
</tr>
<tr>
<td>4</td>
<td>&quot;</td>
<td>2.773</td>
<td>2.8980</td>
<td>737.5</td>
<td>0.12</td>
<td>0.36</td>
<td>3.960</td>
</tr>
<tr>
<td>5</td>
<td>&quot;</td>
<td>6.417</td>
<td>6.7144</td>
<td>734.</td>
<td>0.59</td>
<td>1.97</td>
<td>(4.112)</td>
</tr>
</tbody>
</table>

Mean 3.990 0.026  
Mean 2.100 0.025  
Mean 2.125 0.000  
Mean 2.150 0.025  
Mean 2.125 0.017  
Mean 1.470 0.018
The formula used in experiments 4 to 7, Table III, was equation (7) above. This should have been employed also in experiments 1 to 3, but in these cases \( p_1 \) and \( p_2 \) were not themselves measured, but only their difference, and the formula used was

\[
m_2 = m_1 \frac{(B - p_0)}{B - p_0 - (p_2 - p_1)},
\]

which is approximately the same as (7). To show this the value of \( m_2 \) for experiment 4 was calculated by this formula and found to be 3.6357 g. instead of 3.6358 g. as calculated by equation (7). The difference is below the limit of experimental error.

In considering the relative accuracies of the method developed in this investigation and the dynamic method as usually applied, we may compare the results of Lincoln and Klein and of Kahlenberg and Millard shown in Tables I and II with those in Table IV.

In the case of the data of Lincoln and Klein for a normal solution of potassium nitrate, the probable error in \((p_0 - p) = \sqrt{(0.052)^2 + (0.062)^2} = 0.081\) mm. The fractional error is

\[
\frac{0.081}{p_0 - p} = \frac{0.081}{0.057} = 0.12 \text{ or } 12 \text{ per cent.}
\]

Since the error in \( p_0 \) itself is negligible in calculating the probable error in \( R \), the latter is also 12 per cent.

In the case of the data of Kahlenberg and Millard for a 3.42 normal solution of sodium chloride, the probable error in

\[
(p_0 - p) = \sqrt{(0.03)^2 + (0.098)^2} = 0.102 \text{ mm.}
\]

The fractional error in \((p_0 - p)\) and in \( R \) is, therefore, \( \frac{0.102}{p_0 - p} = 0.102 = 0.036 \) or 3.6 per cent.
For a solution of the same concentration as the example from the data of Lincoln and Klein, the per cent error caused by an absolute error of 0.102 mm. would be about 15.

From the data in Table IV it is seen that the average deviation from the mean in the values of \( R \) is 1.2 per cent for a half-normal solution, 0.8 per cent for a 0.75 normal, and 0.6 per cent for a 1.3 normal solution. It is evident from these figures that the data obtained in this investigation are about 20 times as accurate as the best values heretofore obtained for similar solutions, and it is very probable that with a few modifications of the apparatus and thermostat, the relative pressure lowering of a normal salt solution could be measured with an accuracy of at least 0.25 per cent.

**IX. IMPROVEMENT IN THE METHOD.**

In some of the experiments the solution formed films which sometimes passed with the air current up over the inverted U-tube and into the horizontal tube following. This occurred at the end of the saturator which was rising just as the last part of the solution was flowing away and resulted in uneven distribution of the solution and erratic pressure differences. This could be remedied by making the inverted U-tube higher and blowing a bulb in the arm farthest from the absorber, large enough to break the film in passing through it.

Another improvement would be to arrange the saturators and absorbers on superimposed platforms. By placing one saturator containing water on the lowest platform, a second saturator
containing the solution on the next platform - say, nine inches above the first - a third saturator containing water on a third platform at the same height above the second platform, and the three absorbers corresponding to the three saturators on a fourth platform high enough above the others that it would be well above the surface of the water. The weights of water absorbed by the first and third absorbers would check each other and thus two experiments could be carried on at the same time. This arrangement would have the added advantage that as all the platforms would rock together no flexible joints would be necessary - except in the connections to the manometer - so that no rubber joints would be needed. The tubes of the absorbers would, of course, extend at right angles to those of the saturators, so that the rocking motion would not cause the sulphuric acid to clog the former.

The platforms should be firmly attached to a portable stand which could be raised out of the thermostat to permit the removal or replacement of the saturators. Besides making it more convenient to adjust the saturators in place, this arrangement would avoid the delay incident to the emptying and refilling of the thermostat whenever the saturators need to be removed or adjusted for any purpose.

By using a steam coil instead of live steam for heating the water, it would be possible to use distilled water in the thermostat, thus enabling one to observe the apparatus during an experiment. The heating coils should moreover be evenly distributed around the thermostat. Thus if a coil were placed at each corner of the
thermostat, the effects on all sides of the saturators would be very nearly alike. More thorough stirring would, of course, be beneficial in the same way. By having several heating coils of rather high resistance in series it should be possible to obtain sufficient heat to maintain the thermostat at the desired temperature without the excessive current used heretofore, and the consequent failure of the relay to break the circuit at the proper time.

**X. SUMMARY.**

1. Of the various methods available for the measurement of the vapor pressure lowering, the dynamic method is the only one capable of sufficient accuracy to be useful in studying molecular weights in solution. This method, as heretofore applied, is subject to large errors chiefly from two sources; first, from the measurement of the volume of air aspirated, and second, from the variation in the mean temperature of the thermostat in two successive experiments.

2. A differential modification of the dynamic method has been worked out and tested in this investigation, with the result that the two sources of error mentioned above have been practically completely eliminated.

3. The method is briefly the aspiration of the same quantity of air through two saturators placed beside each other in the same thermostat. One of these saturators contains pure water and the other, the solution to be investigated. Immediately after leaving
each saturator the air passes through a suitable absorber which removes all of the water vapor from it. The volume of the air is not measured and the temperature of the thermostat need not be very carefully regulated, since as long as it is uniform small variations do not affect the results.

4. The accuracy of the method has been tested by the measurement of the vapor pressure lowerings of a series of potassium chloride solutions. The results obtained were about twenty times as accurate as the best previous work with similar solutions.

5. The apparatus and best method of procedure for carrying out the differential, dynamic method are described. The results obtained in this investigation indicate that the method is easily capable of giving the relative vapor pressure lowering of a normal salt solution with an accuracy of 0.25 per cent.
BIOGRAPHICAL.

The writer received his early education in the public schools of Brown Co., Ohio. During the winters of 1902-03 and 1903-04 he taught public school in this county. In the spring and summer of 1904 he attended Miami University as a special student. During the winter of 1904-05 he taught school in Champaign Co., Ohio. In the spring of 1905 he resumed his study at Miami University at which institution he continued, both during the academic years and the summer sessions, until June, 1908, when he was graduated with the degree of Bachelor of Arts (cum laude). In the fall of 1908 he entered the University of Illinois as a scholar in Chemistry. The following year he continued his studies in this institution as a fellow in chemistry and in the spring of 1910 received the degree of Master of Science in Chemistry. During the academic years 1910-11 and 1911-12 he was a graduate assistant in chemistry at the University of Illinois.

He was engaged in technical chemical work in Chicago, Illinois, during the summer of 1910, and in Cleveland, Ohio, during the summer of 1911.

He is a member of the American Chemical Society, The Illinois State Academy of Science and Phi Lambda Upsilon.