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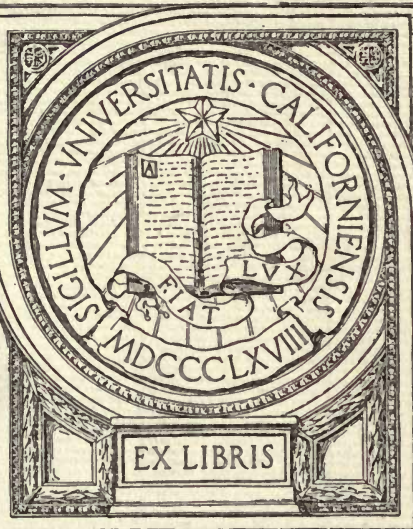
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Addition Compound Formation In  
Aqueous Solutions;  
Hydrates at the Boiling-Point.

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DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE RE-  
QUIREMENTS FOR THE DEGREE OF DOCTOR OF  
PHILOSOPHY IN THE FACULTY OF PURE  
SCIENCE OF COLUMBIA UNIVERSITY

BY

HORATIO WALES, Jr., A. B., M. A.



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Tri-County Press, Polo, Illinois

1921







UNIV. OF  
CALIFORNIA

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TO THE  
AUTHOR

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EXCHANGE

## ACKNOWLEDGEMENT

To Professor James Kendall, at whose suggestion this problem was undertaken, the author wishes to express his sincere gratitude for help and advice during the progress of the work.

The author also desires to extend his thanks to Professor Thos. B. Freas, for the many helpful suggestions made during Professor Kendall's absence.



## Addition Compound Formation In Aqueous Solutions; Hydrates at the Boiling Point.

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For many years a large number of chemists have believed that combination often occurs in a solution between the solvent and the solute. The methods used to show the existence of compound formation in solution are many and varied. The absorption spectra,<sup>1</sup> specific heat,<sup>2</sup> viscosity,<sup>3</sup> surface tension,<sup>4</sup> in fact the deviations which a large number of dissolved substances show from nearly every law of physics and physical chemistry have been used to uphold the solvate theory.<sup>5</sup>

This investigation was undertaken with the purpose of demonstrating the existence of hydrates by the boiling-point method. Very little work has been done along this line, four chemists having investigated non-aqueous solutions<sup>6</sup> and only one aqueous solutions.<sup>7</sup> As all of these workers have attempted to compute the amount of solvation by the "molecular rise of the

<sup>1</sup>Jones and Uhler, *Am. Chem. Jour.* **37**, 126, 207, 244, (1907); Jones and Anderson, *Ibid.* **41**, 163, 276, (1909); Jones and Strong, *Ibid.* **45**, 1, (1911); Moore, *Zeit. Phys. Chem.* **55**, 641, (1906); Lewis, *Ibid.* **56**, 223, (1906).

<sup>2</sup>Timofejew, *Chem. Cent.* **2**, 429, (1905); Bose, *Zeit. Phys. Chem.* **58**, 585, (1907); Muller and Fuchs, *Compt. Rend.* **140**, 1639, (1905); Dupre and Page, *Proc. Roy. Soc.* **20**, 336, (1872).

<sup>3</sup>Dunstan and Thole, *Trans. Chem. Soc.* **95**, 1556, (1909); Smith and Menzies, *Jour. Am. Chem. Soc.* **31**, 1191, (1909); Gaillaud and Bingham, *Am. Chem. Jour.* **35**, 195, (1906).

<sup>4</sup>Linebarger, *Jour. Am. Chem. Soc.* **22**, 5, (1900); Whatmough, *Zeit. Phys. Chem.* **39**, 129, (1901); Grunmach *Ann. Phys.* (4) **9**, 1261, (1902); Morgan, *Jour. Am. Chem. Soc.* **37**, 1416, (1915); *Ibid.* **39**, 2261, 2275, (1917).

<sup>5</sup>About twenty methods in all have been used. For a complete list of investigators and methods used see Bauer, *Ahrens Sammlung*, **8**, 466, (1903); Washburn, *Tech. Quart.* **21**, 363, (1908); Dhar, *Zeit. Elektrochem.* **20**, 57, (1914).

<sup>6</sup>Jones and Getman, *Am. Chem. Jour.* **32**, 338, (1904); Werner, *Zeit. Anorg. Chem.* **15**, 1, (1895); Biltz, *Zeit. Phys. Chem.* **40**, 185, (1902); Walden, *Ibid.* **55**, 321, (1906).

<sup>7</sup>Johnston, *Trans. Roy. Soc. Edin.* **45**, 193, (1906).

boiling-point," their results, as we shall show presently, are of little value.

The boiling-point method has also been used to determine molecular weights,<sup>1</sup> vapor pressure lowering,<sup>2</sup> heats of dilution,<sup>3</sup> and ionization.<sup>4</sup> With one exception<sup>5</sup> all investigators have used the van't Hoff equation<sup>6</sup> to compute their results.

In a number of communications recently appearing,<sup>7</sup> addition compounds of organic acids with organic substances containing oxygen have been described and compared. In a later paper<sup>8</sup> the results of this series of investigations were summed up and certain laws derived, which were then applied to aqueous solutions of a series of acids and their validity tested by means of freezing-point curves. As the results of these investigations are of great importance and have a direct application to this work, it seems advisable to repeat them here.

When an organic substance containing oxygen is added to an acid of the type HX, the existence of an addition compound in the liquid mixture can usually be demonstrated. In every case the formation of addition compounds becomes more evident both in the number and the stability of the compounds isolated, the more divergent the acidic strengths of the two components. With substances of similar acidic strengths no evidence of compound formation has been found.

In the system water-acid the conditions were shown to be exactly analogous to those for acids in pairs. With water func-

<sup>1</sup>q. v. Landolt-Bornstein, Tabellen.

<sup>2</sup>Raoult, Compt. Rend. **103**, 1125, (1887); Dieterici, Wied. Ann **62**, 616, (1897); Smits, Amsterdam, **2**, 469, (1910).

<sup>3</sup>Juttner Zeit. Phys. Chem. **38**, 112, (1901).

<sup>4</sup>Baroni, Gazz. Chim. Ital. **23**, [1], 263; [2], 249, (1893); Salvadori, Ibid, **26**, [1], 237, (1896); Schlamp, Zeit. Phys. Chem. **14**, 273, (1894).

<sup>5</sup>Juttner, loc. cit.

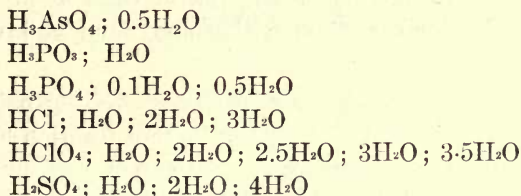
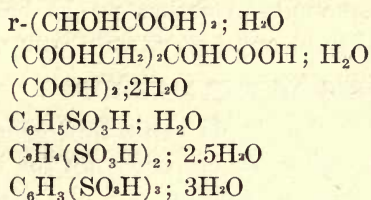
<sup>6</sup>The usual form of the van't Hoff equation for the elevation of the boiling-point is  $DT = Kc$ , where K is a constant determined by the solvent and c the weight concentration of the solvent.

<sup>7</sup>Kendall, Jour. Am. Chem. Soc. **36**, 1222, 1722, (1914); **38**, 1309, (1916); Kendall and Gibbons, Ibid, **37**, 149, (1915); Kendall and Carpenter, Ibid, **36**, 2498, (1914); Kendall and Booge, Ibid, **38**, 1712, (1916).

<sup>8</sup>Kendall, Booge and Andrews, Jour. Am. Chem. Soc. **39**, 2303, (1917).



tioning as an extremely weak acid, no evidence could be observed of hydrate formation with exceedingly weak acids. As the strength of the acid was increased, a regular increase could be seen in the extent of combination in the liquid state; the stronger the acid, the greater the amount of hydration. This need not be taken as the only proof that hydration increases with the acidic strength. The literature is filled with instances of hydrate formation. A few examples may well be cited here.<sup>1</sup>



These examples clearly illustrate that hydrate formation is the rule. In every case the number and complexity of the hydrates increases with the strength of the acid. These acids must exist in solutions largely combined with the solvent or their hydrates would not separate out as the solid phase. No hydrates of very weak acids, either organic or inorganic, have been isolated. If these acids as a class are combined with the solvent to any extent, some of their hydrates would surely be known. However, the failure to isolate a hydrate cannot be taken as proof of its non-existence. Compounds may be present in the solution and yet not be stable either at the temperatures used for evaporation or freezing.

The existence of hydrates in solution has already been indicated for a series of acids by means of freezing-point curves.<sup>2</sup> On account of the slight solubility very few acids are available

<sup>1</sup>Organic acids from Beilstein; inorganic from Landolt-Bornstein, Tabellen, (1912), p469-472.

<sup>2</sup>Kendall, Booge, and Andrews, loc. cit.

for freezing-point determinations at high concentrations. At the boiling-point, however, the increased solubility allows a much wider choice of material. For this reason, and also since few solid hydrates are stable above ordinary temperatures, it was thought advisable to see if the relationships which have been demonstrated for solutions at low temperatures are also valid at the boiling-point. We would expect, however, since the most complex hydrates which have been isolated were formed at the lowest temperatures, that compound formation would be less extensive at the boiling-point than at any lower temperature.

### THEORETICAL BASIS OF THE METHOD

It is a well known fact that the simple van't Hoff equation for the elevation of the boiling-point can be used only for infinitely dilute solutions.<sup>1</sup> The true expression for the boiling point of a solution of a non-volatile substance, valid at all concentrations, is readily derived from a thermodynamical investigation of the problem.

If to a solution of a non-volatile solute at its boiling point  $T$  we add  $dN$  moles of solute, thus increasing its mol fraction by  $dy$  and decreasing that of the solvent by  $dx$ , the vapor pressure will vary as the mol fraction of the solvent in the solution,<sup>2</sup> and will be given by the expression:

$$(1) p=kx$$

differentiating, we obtain

$$(2) dp=kdx$$

and dividing 2 by 1 we find that the decrease in vapor pressure of the solvent is given by the expression;

$$(3) dp/p=dx/x$$

From the Clapeyron-Clausius equation we find that for small temperature intervals

<sup>1</sup>Even in very dilute solutions this formula cannot be considered as giving consistent results. Many investigators have attempted to determine molecular weights from boiling-point measurements, even though no two compounds nor two concentrations of the same compound give identical values for the "molecular elevation of the boiling-point." For example, different investigators have found values of this "constant" for aqueous solutions of KCl ranging from 463 to 621. (Johnston, loc. cit. p. 195.)

<sup>2</sup>Raoult, loc. cit. The mol fraction of the solvent is defined as the ratio of the mols of solvent to the total mols in the solution.



$$(4) dT = \frac{-RT^2 dp}{L p}$$

Substituting the value of  $dp/p$  in this equation we obtain:<sup>1</sup>

$$(5) dT = \frac{-RT^2 dx}{L x}$$

where  $x$  is the mol fraction of the **solvent** in the solution;  $T$  the absolute temperature of the boiling-point of the pure solvent;  $L$  the molar heat of vaporization of the pure solvent ( $537.5 \times 18.016$ ); and  $R$  the gas constant, 1.9885 calories.

In order to integrate this equation it is necessary first to express  $L$  as a function of  $\Delta T$  which can only be done approximately. We are fortunate, however, in having another solution of the problem. If  $L$  in a given case can be regarded as practically constant over the range covered by  $\Delta T$ , the integral becomes:

$$(6) \log_{10} x = \frac{-0.4343L}{RT} \frac{\Delta T}{T_B}$$

where  $T_B$  is the boiling-point of the solution. This equation may also be written:

$$(7) \log_e (1-y) = \frac{-L}{RT} \frac{\Delta T}{T_B}$$

where  $y$  is the mol fraction of solute. Expanding  $\log_e (1-y)$  by means of Taylors Theorem we obtain:

$$(8) \log_e (1-y) = \log_e 1 - y/1! + y^2/2! - y^3/3! + \dots$$

When the solution becomes very dilute  $y$  becomes very small and we may disregard all the higher powers. Equation 8 then becomes:

$$(9) \log_e (1-y) = -y$$

The temperature interval will also become so small that  $TT_B$  is nearly equal to  $T^2$ . Equation 7 may then be written:

$$(10) y = \frac{L}{RT^2} \Delta T$$

which is the usual form of the van't Hoff equation.<sup>2</sup> This equation represents the limit approached as the solution becomes more and more dilute. By no means can the use of a formula which only

<sup>1</sup>c. f. Washburn. Principles of Physical Chemistry. p. 164.

<sup>2</sup>c. f. Ikeda, Jour. Col. Sc. Tokyo, **29**, no. 10, p. 21, (1908).

holds for infinitely dilute solutions be justified for computing the hydrates formed in solutions of finite concentrations.

From equation 6 we see that if the boiling-point of a solution is abnormally raised it will mean that the value which was assigned to  $x$  is smaller than that calculated from the weights of the two components taken. If we have made the corrections required by the ionization and the change in  $L$ , the only explanation we are able to give at the present time is that some of the solvent has been removed by combination with the solute and thus caused its mol fraction to be lowered. The actual number of solvent molecules combining with each molecule of solute can be found by determining what value must be given to  $x$  to make the observed values of  $\Delta T$  fall on the ideal curve. The comparison of the variation in the boiling-point elevation of solutions of a series of compounds of varying strengths will, therefore, afford a means of indicating their relative degree of hydration in solution.

#### **APPLICATION OF THE THEORY TO THIS WORK**

The best methods that have been devised for determining the rise in boiling-point of a solvent, caused by the presence of a dissolved substance, are not free from many objections, both in theory and method. Some of these apparently cannot be eliminated, while others can be overcome to a greater or less degree. With an electrolyte as the solute our systems are far from ideal. The many disturbing factors influencing  $x$  and  $T$  must be taken into account. For the purpose of discussion these will be divided into three classes; those due to the solvent, those due to the solute, and those due to the method.

#### **FACTORS DUE TO THE SOLVENT**

Since water is an associated liquid, the use of the value  $H_2O=18.016$  in the calculations of the mol fractions will lead to values for  $x$  which are much too high. It would seem at first sight as though there is no solution to this difficulty. Fortunately, however, the variation in  $x$  with the molecular weight assumed for water is largely counterbalanced on the right hand side of the equation by the fact that  $L$ , the molar heat of vaporization is similarly affected. The actual differences in  $y$ , the mol frac-



tion of **solute**, and  $\Delta T$  as calculated for given concentrations of solute from equation 7 for two of the molecular forms of water are given in the following table:

Mols solute in 1000gms. water	(a) Water= <sup>**</sup> H <sub>2</sub> O		(b) Water=(H <sub>2</sub> O) <sub>2</sub>		Difference in $\Delta T$
	y	$\Delta T$	y	$\Delta T$	
0.5607	0.01	0.288	0.0199	0.288	0.000
1.1328	0.02	0.578	0.0392	0.572	0.006
2.3127	0.04	1.170	0.0769	1.155	0.015
3.5429	0.06	1.776	0.1132	1.724	0.042

It is apparent from these figures that the variation in the ideal curve with the association factor of water is beyond the ordinary experimental errors. At the boiling-point water is mostly dihydrol with a small amount of monohydrol.<sup>1</sup> Since the association factor of water also varies with the concentration of the solute, the water molecule becoming less complex in the more concentrated solutions, it is evident that basing the theoretical curve on the assumption that water=H<sub>2</sub>O would render all subsequent calculations, such as the estimation of the water of hydration, merely approximations, except in very dilute solutions.<sup>2</sup>

In our work the relative positions of the curves are all we can hope to establish and the mol fractions can all be expressed on the basis of water =H<sub>2</sub>O, since this will give a constant error throughout the range of concentrations studied.

In the integration of the above equation we assumed that the heat of vaporization of water remains constant over the range of temperatures studied (about three degrees). The fact that the heat of vaporization will change slightly with the temperature leads to a complication in the integrated equation.

We may express L as a function of the temperature by the equation:

$$(11) L=L_0 + (C_p - C)T$$

<sup>1</sup>The constitution of water. Tr, Farad. Soc. 6, 71, (1910).

<sup>2</sup>Previous workers have shown little hesitation on this point. Johnston (loc. cit. p. 873) calculates the hydration when  $\Delta T$  is 53°—and by the van't Hoff equation.

where  $L_0$  is the heat of vaporization at absolute zero.<sup>1</sup>

Substituting the numerical values for  $L_0$  (which is assumed to be constant) and the molar specific heats at 100°C, the fundamental equation becomes;

$$(12) \frac{dx}{x} = - \frac{13574 - 10.43T}{1.9885T^2} dt$$

Integrating this equation we obtain;

$$(13) \log_e x = 5.246 \log_e \frac{T_B}{T} - \frac{6826}{T} - \frac{\Delta T}{T_B}$$

From these two equations we then obtain the following theoretical values for the two highest concentrations studied.

	From 6	From 13
$\Delta T$	$x$	$x$
1.471	0.95000	0.95005
1.776	0.94000	0.94006

From these values it can be seen that the effect of correcting for the change in  $L$  with the temperature is infinitesimal.

The value of  $L$  also changes slightly with the pressure. The error due to this cause was entirely eliminated in this work by always using a pressure of 760 millimeters of mercury.

### ERRORS DUE TO SOLUTE

The total number of molecules in a solution of an electrolyte will be increased by ionization. If we know the ionization at any given concentration we can at once calculate the mol fraction of the solute. The exact estimation of ionization in solutions of the high concentrations examined here is subject to many errors. The conductance ratio in these cases cannot indicate the true degree of dissociation and a large viscosity correction is necessary<sup>2</sup> which at best will be only approximate. Moreover for strict accuracy, each solution requires conductivity and viscosity data

<sup>1</sup>Kendall (Meddel. fran K. Vets.-Akad. Nobel, Band 2, no. 26, (1913) ) has found that the heat of vaporization for one gram of water is more nearly expressed by the equation  $Q=83.06 (T_c-T)^{3/2}$ , where  $T_c$  is the critical temperature for water, 370°C. On account of the very complicated integral this equation gives, it could not be used.

<sup>2</sup>Kraus and Bray, Jour. Am. Chem. Soc. 35, 1315, (1913.)



for its own particular temperature of ebullition, whereas, all conductivity measurements were made at 100°C.

At high concentrations these errors become large, but since the ionization in these cases is extremely small, their actual effect is minimized, and their total influence on  $x$  is inconsiderable. For weak acids the ionization  $\alpha$  may be calculated directly from the equation:<sup>1</sup>

$$\frac{c \alpha^2}{1 - \alpha} = k$$

where  $c$  is the weight concentration of the solute and  $k$ , the ionization constant. For stronger acids, such as phosphoric and oxalic,  $\alpha$  is more nearly represented by the equation:<sup>2</sup>

$$\frac{c \alpha^2}{1 - \alpha} = k + k' \frac{(1 - \alpha)}{\alpha}$$

where  $k$  and  $k'$  are constants depending on the electrolyte.

Another possible disturbing factor is the association of the solute in solution. This would tend to place the value of the mol fraction of the solute below that calculated on the assumption of simple molecules. Except in a few rare cases association has only been found to exist in very concentrated solutions and here it is known to decrease with a rise in temperature.<sup>3</sup> As the mol fraction of the solute in this work was always small, extensive association is not to be expected and errors due to this cause may be neglected at the boiling temperatures.

In the integration of the fundamental equation it was assumed that  $L$  is independent of the concentration. This is true only if the heat of dilution is zero throughout the entire range. As this is not the case the corrections necessary in the integrated equation must be taken into account.

To evaporate one gram-molecule of water at 100°C,  $L$  cal-

<sup>1</sup>This equation has been shown to hold exactly for concentrations up to weight normal. Kendall, Jour. Am. Chem. Soc. **36**, 1083 (1914).

<sup>2</sup>Kendall, loc. cit.

<sup>3</sup>Peddle and Turner (Jour. Chem. Soc. **99**, 690, (1911)) from investigations on the boiling and freezing-points of solutions of a large number of organic substances in water, have found that the only class of substances which show no evidence of association is the aliphatic amines. Marked association was shown only by the aromatic compounds.

ories are necessary. If, however, to one mole of water we add  $n$  moles of some acid,  $\Delta Q$  calories will be given off or absorbed. The work to separate the solvent from this solution will then become equal to  $L + \Delta Q$  calories, where  $\Delta Q$  is either positive or negative.

Sufficient data is not available at the present time to calculate this correction.<sup>1</sup> However, by using a series of compounds which have heats of solution of the same order of magnitude, we will introduce a constant error in our work and the curves may be used to show relative hydration, although no comparison can be made between the lowest curve and the theoretical curve.

In view of the above errors it becomes apparent that the limitations of the method are of such a magnitude that, although with proper choice of materials we can show the **relative** hydration of a series of compounds, it would be utterly absurd to attempt to calculate the actual **amount** of combination between the solvent and the solute.

### ERRORS DUE TO THE METHOD

The boiling-point method is not capable of that degree of accuracy to which the freezing-point method has been developed. The difference between the temperature of the liquid and the surrounding objects is much greater than in the freezing-point method and correspondingly greater precautions are necessary to protect the solution and the thermometer from changes in the temperature of external objects.

A slight change in pressure will cause a large change in the boiling-point of a solution while its effect on the freezing-point is noticed only in the fourth place of decimals. Part of the solvent is continually separating as vapor and is returned as liquid at a temperature much lower than that of the boiling solution.

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<sup>1</sup>Abegg (Zeit. Phys. Chem. 15, 247, )1894) has found that "the corrections for the heat of dilution of acetic, formic, and tartaric acids, for depressions up to  $15^{\circ}$  are at the utmost of the same order of magnitude as the experimental errors in the freezing-point determinations." When we consider the magnitudes of the experimental errors of the freezing and boiling point methods, and recall that an elevation of  $0.52^{\circ}$  in the boiling-point is equivalent to a depression of  $1.86^{\circ}$  in the freezing-point, it becomes at once apparent that the corrections due to the heat of dilution for these acids at the boiling-point cannot be otherwise than negligible.



Although the loss due to this cause cannot be determined accurately, the following illustration will show that it is negligible.

The volume of the vapor above the liquid was about 100cc. Let us assume that the concentration of the solute is 5%—calculated on the basis of no loss of vapor—and that the weight of water lost is 0.1 gm., a value which is much too high. Now, since we started with thirty-five grams of water in each case, we would have in this solution 0.1023 gram-molecules of solute. Correcting for the loss of vapor we would have 34.9 gms. of water acting as the solvent, which would make the concentration of the solute equal to 5.01% molar. We have purposely chosen a case where the error due to this cause would be at a maximum and have magnified this error. As this concentration represents the upper limit of the curve and the errors in all other cases will be smaller, we may safely neglect this factor entirely.

At the boiling-point the solution must be in equilibrium with the vapor of the pure solvent. To obtain this the vapor and the solution must be intimately mixed, regular boiling must be insured, and the heat exchange with the surrounding objects must be at a minimum; otherwise, the temperature observed will not be the temperature of the solution. The first condition is secured when the solution is boiling briskly and is continually agitated and always in contact with the bubbles of vapor passing upwards. The second condition is accomplished as nearly as possible by the form of the apparatus used, the details of which will be given later.

### METHOD

Previous investigators have found that when water is used as the solvent, the boiling point results were not satisfactory and in nearly every case the data thus obtained has been used to compute molecular weights.<sup>1</sup> A study of the results obtained shows that in no case have two compounds nor two concentrations of the same compound given identical values for the "molecular rise of the boiling-point."<sup>2</sup>

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<sup>1</sup>Landolt-Bornstein, Tabellen, loc. cit.

<sup>2</sup>Johnston (loc. cit.) finds that the results of different investigators vary by as much as 20% and thinks that this may be due to errors in the determination of the boiling-point of water. The magnitude of the error makes this explanation very improbable.

It would seem that the aqueous solutions have presented a special difficulty and in order to obtain uniform results, nearly every investigator has designed a special form of apparatus, a rule to which we are no exception.

The boiling-point of a liquid is defined<sup>1</sup> as the lowest temperature at which a liquid can remain **steadily** boiling at any given pressure. However, it has been found by several investigators<sup>2</sup> that for the attainment of exact temperature adjustment it is necessary to maintain an extremely energetic boiling. Although this may lead to a possible source of error (due to superheating), it may be minimized by supplying the heat to the solution at a constant rate during the boiling (which would tend to keep the amount of superheating constant). This is practically impossible to accomplish if we are to use the usual method of heating with a bunsen burner.

To overcome this difficulty somewhat, we used as our source of energy a cylindrical resistance heater, into which the tubes were placed. The tubes were at first separated from the heater by an air space, but later an asbestos cylinder was placed inside the heater as it was thought that the sudden changes observed in the thermometer readings were caused by heat being radiated into the bulb. Whether this is the true explanation or not, no further trouble was experienced along this line.

It was also noticed that a change of 30 watts (corresponding to a change in current of one ampere) in the power supplied to the heater would cause a change in the thermometer readings of about 0.°02; the temperature remaining constant in either case. In this work the power supplied to the heater was kept constant at all times, thus ensuring a constant rate of boiling in all the determinations.

The boiling-point tubes used in this investigation were a modification of the usual Beckmann type, being slightly larger and with the arms placed near the top in order to give as small a vapor space as possible. Previous investigators have used garnets in the boiling point tubes to secure a uniform ebullition. We found that these were appreciably soluble in the boiling solu-

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<sup>1</sup>Nernst, *Theoretical Chemistry*.

<sup>2</sup>Biltz, *Zeit. Phys. Chem.* **40**, 207, (1902).



tions of the stronger acids used, such as oxalic and phosphoric acids, and substituted small quartz crystals with good results. The same weight, thirty grams, of quartz was always used in order to keep their volume constant.

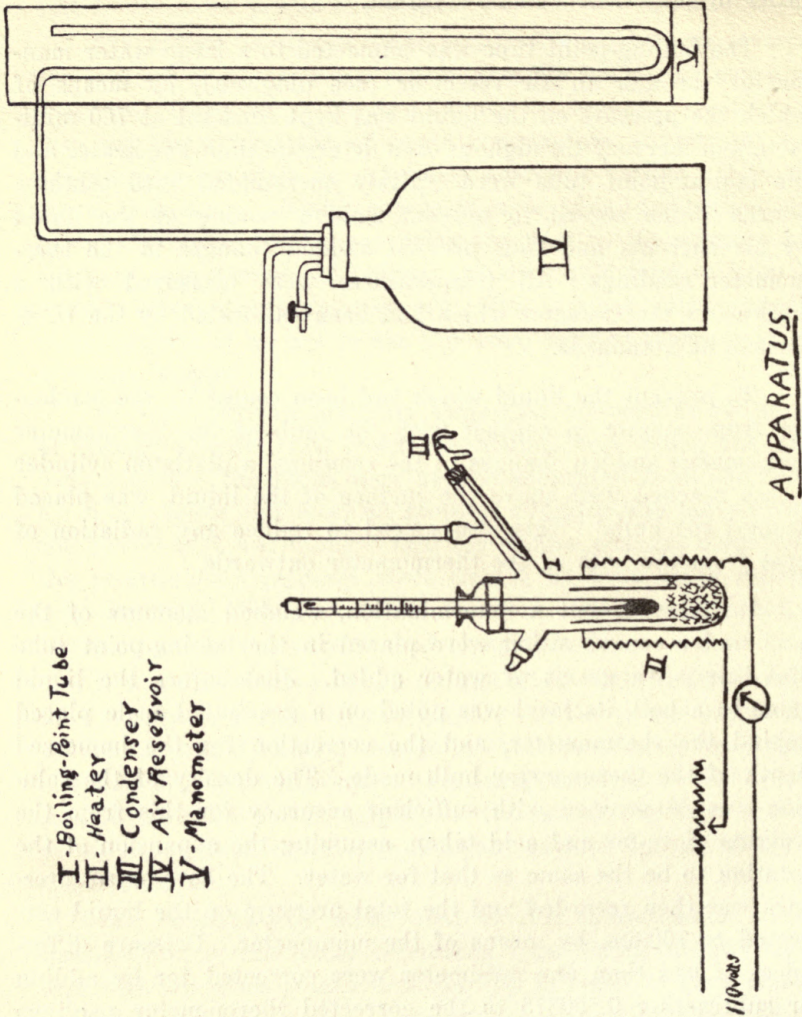
The boiling-point tube was connected to a large water manometer through an air reservoir (see diagram), by means of which the pressure on the liquid was kept constant at 760 millimeters of mercury throughout each determination. The heater and the boiling-point tube were entirely surrounded with asbestos boards which served to prevent sudden cooling of the liquid by air currents and thus prevent sudden changes in the thermometer readings. All temperatures were measured with a Beckmann thermometer which had been calibrated by the U. S. Bureau of Standards.

To prevent the liquid which had been cooled by the condenser from coming in contact with the bulb of the thermometer and causing sudden changes in the readings, a platinum cylinder which reached well above the surface of the liquid, was placed around the bulb.<sup>1</sup> This also served to reduce any radiation of heat from the bulb of the thermometer outwards.

In carrying out a determination, weighed amounts of the acid under consideration were placed in the boiling-point tube and thirty-five grams of water added. Just before the liquid came to a boil, its level was noted on a graduated scale placed behind the thermometer, and the correction for the immersed depth of the thermometer bulb made. The density of the solution was determined with sufficient accuracy for this from the weights of water and acid taken, assuming the expansion of the solution to be the same as that for water. The barometric pressure was then recorded and the total pressure on the liquid corrected to 760mm. by means of the manometer. Pressure differences of less than one millimeter were corrected for by adding or subtracting 0.°00375 to the corrected thermometer readings

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<sup>1</sup>Jones, Am. Chem. Jour. **19**, 584, (1897).





for each tenth millimeter of mercury differing from 760.<sup>1</sup> Thermometer readings were taken at intervals of thirty seconds over a period of four or five minutes and their average recorded. By working only on days when the barometer was fairly constant, we were able to obtain temperatures which did not vary by more than 0.°01 during the period of observation. All experiments were repeated at least twice before the final results were plotted. About fifty points were determined for the curve of each acid. The method of computing the results was as follows:

Weight acid used (Succinic) -----	2.3433	gms
Weight water -----	35.00	gms
Gram molecules succinic acid -----	0.0198	
Gram molecules water -----	1.9444	
Molar per cent acid -----	1.01%	
Barometer height (corrected) -----	755.13	mm.
Correction due to immersed depth of thermometer <sup>2</sup> -----	2.65	mm.

The 2.22 mm required to bring the pressure to 760mm were added by means of the manometer.

Observed boiling-point (average of ten readings taken at thirty second intervals) -----	1.°115
Stem temperature 30°.	
Calibration correction -----	— .004
	1. 111

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<sup>1</sup>This correction although approximate is well within the experimental error for the pressure differences used. Berkeley and Appleby, working with saturated salt solutions found that the effect of changes in the barometric pressure on the temperature of equilibrium were greater than with pure water. (Proc. Roy. Soc. **85A**, 492, (1911) ) The magnitude of the coefficient depends upon the solubility of the salt and also upon the temperature coefficient of the solubility. Thus for Na<sub>2</sub>SO<sub>4</sub> which is only moderately soluble and does not vary in solubility with the temperature, the coefficient is 0.°00052C per millimeter of mercury, while for KNO<sub>3</sub> which has both a high solubility and a large temperature coefficient of solubility, the coefficient is 0.°0217C per millimeter, or about forty times as large. This plainly shows that the method of actually measuring the temperature difference between the boiling-points of the solution and pure solvent, regardless of the pressure, cannot possibly give correct results unless the pressure is 760 millimeters on both liquids.

<sup>2</sup>Smith and Menzies, Jour. Am. Chem. Soc. **32**, 901, (1910).

Reading corrected for calibration -----	1. 111
Setting factor ( $1^\circ=1.0186$ ) -----	. 020
	<hr/>
	1. 131
100° corresponds on Beckmann thermometer to--	. 904
	<hr/>
	0. 227
Exposed stem correction -----	. 018
	<hr/>
Boiling-point elevation -----	0. 245

### CONDUCTIVITY MEASUREMENTS

The conductivity measurements were made with a Freas cell having electrodes approximately one centimeter square and one centimeter apart. The resistance was measured with a Leeds Northrup bridge and the current produced with a Leeds Northrup Constant High Speed Generator which gave a current of an approximately sine wave form and a frequency of 1000 cycles. Temperature regulation was obtained by placing the conductivity cell in a steam bath, allowing about one half hour in each case for the solution to reach the temperature of the steam. Although the temperature of boiling water may vary widely, as has been mentioned, the vapor above it will always have the same temperature; this temperature being determined by the barometric pressure. Except in extreme cases this temperature will not vary from 100°C by more than 0.°2.

In computing the volume occupied by the solution at 100° it was assumed that the thermal expansion coefficients of the solutions were the same as that for water. Although this is not strictly true it is within the experimental error for the small volumes worked with. In every case two solutions of widely different concentrations were prepared and the dilutions made on both in order to minimize any errors due to volume measurements.

The cell was standardized by determining the conductivity of a solution containing ten milli-equivalents of potassium chloride per liter. The specific conductivity of a solution of this strength at 100° is  $7.54 \times 10^{-3}$  mhos.<sup>1</sup> All solutions were prepared from triply distilled conductivity water which gave a conductiv-

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<sup>1</sup>Noyes. Conductivity of Aqueous Solutions, p47.



ity of  $3.9 \times 10^{-5}$  at  $100^\circ\text{C}$ . The values for  $\Lambda_\infty$  were taken from the literature whenever it was possible. No corrections were made for viscosity.

v (liters)	Oxalic Acid. $(\text{COOH})_2^*$ Specific conductivity	$\Lambda_\infty = 857^1$		mol fraction acid
		$\Lambda$	$\alpha$	
0.328	0.06920	23.7	0.027	0.0615
0.656	0.05915	38.9	0.045	0.0296
1.312	0.05564	73.0	0.085	0.0145
2.624	0.04005	105.1	0.122	0.0072
5.248	0.02854	150.8	0.176	0.0035
Phosphoric Acid. $\text{H}_3\text{PO}_4$		$\Lambda_\infty = 730^2$		
0.203	0.1256	25.5	0.035	0.0844
0.504	0.07242	36.5	0.050	0.0395
1.008	0.04920	49.6	0.068	0.0191
2.016	0.03402	68.6	0.094	0.0094
3.028	0.02813	85.2	0.116	0.0059
Citric Acid. $(\text{CH}_2\text{COOH})_2\text{COHCOOH}$		$\Lambda_\infty = 858^3$		
0.514	0.01248	5.9	0.006	0.0455
1.028	0.01177	12.1	0.014	0.0202
2.057	0.01001	20.6	0.024	0.0095
4.114	0.007705	31.7	0.037	0.0046
8.228	0.005710	47.7	0.055	0.0022
d-Tartaric Acid. $(\text{CHOHCOOH})_2$		$\Lambda_\infty = 860$		
0.433	0.1709	7.4	0.008	0.0570
0.866	0.1593	13.8	0.016	0.0245
1.732	0.1149	19.9	0.023	0.0114
3.464	0.08253	28.6	0.033	0.0055
6.928	0.05946	41.2	0.047	0.0027

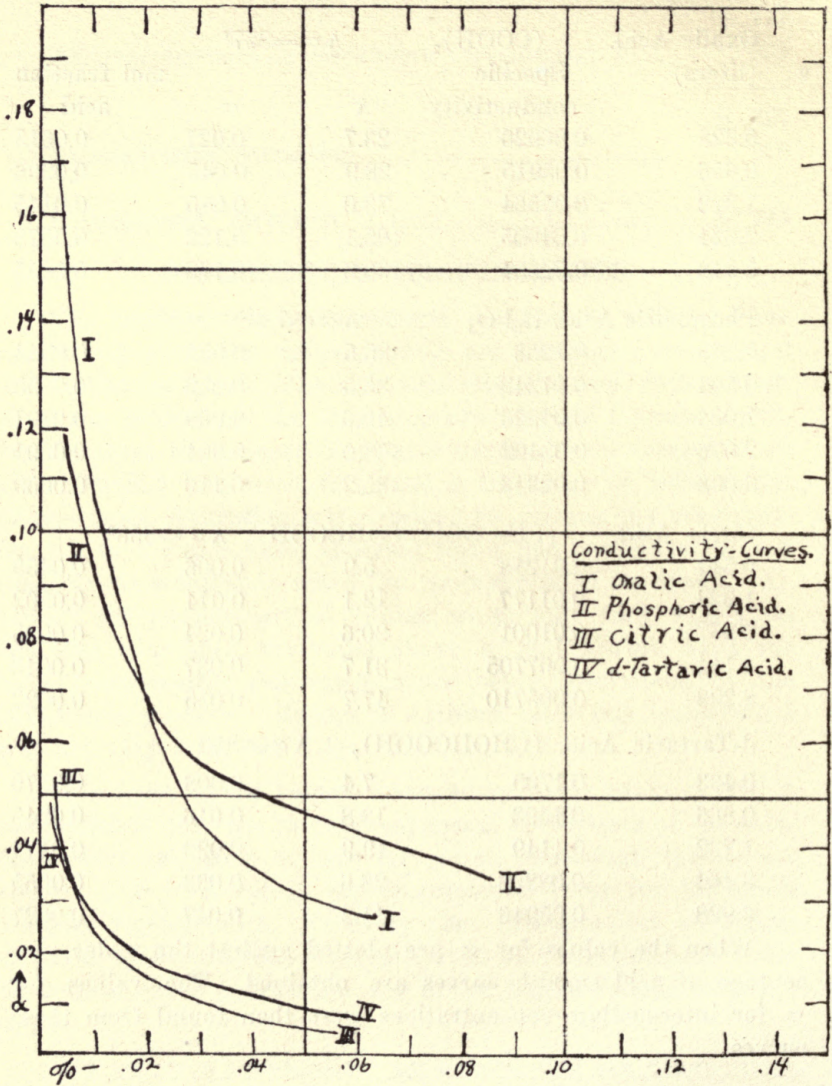
When the values for  $\alpha$  are plotted against the molar percentage of acid smooth curves are obtained. The values for  $\alpha$  for intermediate concentrations were then found from these curves.

<sup>1</sup>J. Johnston, Jour. Am. Chem. Soc. **31**, 1010, (1909).

<sup>2</sup>Noyes, loc. cit. p. 262.

<sup>3</sup>J. Johnston loc. cit.







## BOILING-POINT RESULTS

The following acids have been used in this investigation;

Acid	Ionization constant at 25°	
Boric	$1.7 \times 10^{-9}$	1
Succinnic	0.000068	2
Citric	0.00082	3
d-Tartaric	0.00097	4
Phosphoric	$0.0070 + 0.0013(1 - \alpha)$	5
	$\alpha$	
Oxalic	0.010	6

It is evident that we have here a continuous series from a typical weak acid to a typical strong acid. The ionization constants at 25° are given merely for comparison. In this work the ionization was determined only for solutions of the high concentrations investigated and no measurements were made on solutions dilute enough to give an ionization constant.<sup>7</sup>

In the following tables  $\alpha$  represents the degree of ionization,  $y$  the calculated mol fraction of solute, and  $\Delta T$  the boiling-point elevation. Ionization in the cases of boric and succinic acids has not been considered as it is sufficiently small to be neglected. In the diagram the curves are shown between concentrations of 2 and 6% molar. All of the curves, however, continue with perfect regularity to the origin. The theoretical boiling-point of pure water was obtained by extrapolation from the curves as it cannot be measured directly.<sup>8</sup> The same value for the boiling-point of water was obtained from each curve.

<sup>1</sup>Walker and Cormack, Jour. Chem. Soc. 77, 5, (1900).

<sup>2</sup>Rivett and Sidgwick, Ibid, 97, 1677, (1910).

<sup>3</sup>Walden, Zeit. Phys. Chem. 10, 563, (1892).

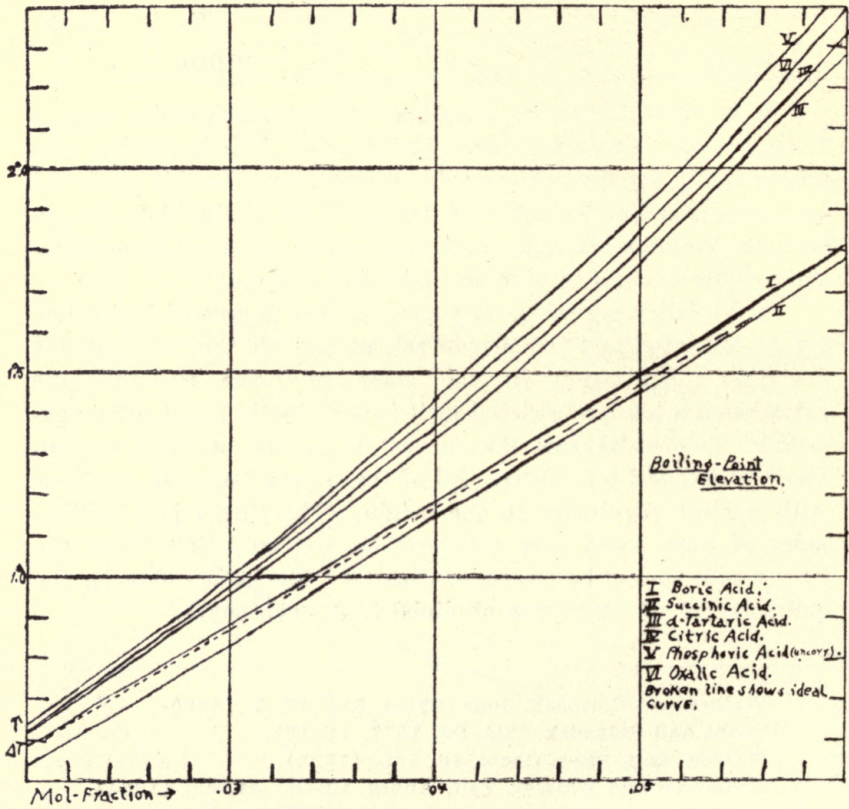
<sup>4</sup>Grossman and Kramer, Zeit. Anorg. Chem., 41, 43, (1904).

<sup>5</sup>Kendall, Jour. Chem. Soc., 101, 1294, (1912).

<sup>6</sup>Ostwald, Zeit. Phys. Chem. 3, 241, (1889).

<sup>7</sup>Kendall, Meddel, fran K. Vets. Akad. Nobel. Band 2, no. 38 (1915), for reasons why concentrated solutions do not give an ionization constant.

<sup>8</sup>No record has been found in the literature of anyone obtaining consistent results for the boiling-point of water by immersing the thermometer in the liquid. This fact is suggested in the calibration of a thermometer by calling 100°C the "steam point." For a full discussion on the boiling-point of water see Preston, Theory of Heat (1904) p. 360.





## I. Boric Acid

conc. wt. molar	$y$	$\Delta T$
0.5971	0.0106	0.291
0.9656	0.0171	0.492
1.1342	0.0200	0.578
1.6942	0.0295	0.878
2.2713	0.0392	1.155
2.2741	0.0393	1.164
2.8627	0.0490	1.476
3.5055	0.0593	1.786
4.1225	0.0691	2.114

The curve for boric acid follows the theoretical curve throughout the entire length investigated. No indication of hydration is apparent, as we would expect, since very weak acids are unable to form addition compounds with other weak acids—water in this case acting as an exceedingly weak acid.

## II. Succinic Acid.

conc. wt. molar	$y$	$\Delta T$
0.5634	0.0100	0.243
1.1276	0.0198	0.520
1.1322	0.0199	0.580
1.7186	0.0300	0.827
2.2973	0.0397	1.148
2.2987	0.0398	1.163
2.8755	0.0491	1.461
2.8798	0.0493	1.463
3.7226	0.0623	1.815
4.0369	0.0677	1.959

The curve for succinic acid is peculiar. At the lowest concentrations it falls below the theoretical. As the concentration is increased its slope gradually becomes steeper and the curve rises more rapidly until it crosses the theoretical curve at a concentration of about 6% weight molar. On investigating the facts known about this acid we find that the position of the curve is exactly as we would expect. Succinic acid, being associated in aqueous solutions,<sup>1</sup> would give a much lower concentration

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<sup>1</sup>Pedde and Turner, loc. cit.



than that calculated on the assumption of simple molecules. As the concentration is increased succinic acid would become more and more associated. At the same time the influence which is probably due to hydration would become more and more pronounced until it finally overbalances the association influence and the curve rises more rapidly. The temperature interval throughout the whole range is not great enough to have any appreciable effect on the association of the succinic acid molecules.

### III. d-Tartaric Acid.

conc. wt. molar	$\alpha$	$y$	$\Delta T$
0.5628	0.023	0.0102	0.287
1.1256	0.016	0.0202	0.625
1.6856	0.013	0.0297	0.942
2.3027	0.010	0.0401	1.337
2.8598	0.008	0.0493	1.781
3.5027	0.006	0.0596	2.265

The curve for d-tartaric acid diverges widely from the theoretical, showing that the mol fraction of the acid must be much greater than that calculated from the weights of the components taken, or in other words, that part of the solvent has probably been removed by union with the acid.

### IV. Citric Acid.

conc. wt. molar	$\alpha$	$y$	$\Delta T$
0.8698	0.019	0.0157	0.486
1.0728	0.015	0.0192	0.598
1.2736	0.013	0.0227	0.702
1.6667	0.011	0.0294	0.950
1.8488	0.010	0.0325	1.080
2.0309	0.009	0.0356	1.192
2.5847	0.006	0.0448	1.552
3.5597	0.004	0.0605	2.346

The curve for citric acid is slightly more divergent than that for tartaric acid.<sup>1</sup> At 25° citric acid has a smaller ionization constant than tartaric acid, showing that at this temperature at least it is weaker acid. It might seem at first sight as though our theory had failed. An inspection of the conductivity curves,

<sup>1</sup>c. f. Juttner, *Zeit. Phys. Chem.* **38**, 112, (1901).



however, shows that in the more dilute solutions—those sufficiently dilute to give an ionization constant—at 100°, citric acid is more highly ionized, i. e. stronger, than tartaric acid and should therefore combine with water to a greater extent as the curves indicate.<sup>1</sup>

#### V. Phosphoric Acid.

conc. wt. molar	$\gamma$ (uncorr)	$\alpha$ (uncorr)	$\gamma$ (corr)	$\Delta T$
0.3807	0.0068	0.117	0.0075	0.216
0.7006	0.0124	0.096	0.0136	0.345
1.2226	0.0214	0.066	0.0229	0.686
1.5618	0.0275	0.061	0.0291	0.905
1.7340	0.0304	0.058	0.0319	1.019
1.7980	0.0313	0.057	0.0337	1.058
2.1344	0.0370	0.053	0.0388	1.354
2.2249	0.0385	0.051	0.0403	1.374
2.6222	0.0449	0.048	0.0470	1.663
2.9419	0.0510	0.046	0.0523	1.937
3.3646	0.0571	0.044	0.0591	2.369
3.9556	0.0664	0.041	0.0689	2.943

In the case of phosphoric acid it was thought best to show the uncorrected curve. The viscosity correction in this case is very large and the values for  $\alpha$  are at best only approximations. It is evident, however, that the corrected curve would lie somewhere between those for citric acid and oxalic acid.

#### VI. Oxalic Acid.

conc. wt. molar	$\alpha$	$\gamma$	$\Delta T$
0.5574	0.109	0.0110	0.347
0.5865	0.106	0.0115	0.364
1.0919	0.072	0.0206	0.659
1.1504	0.070	0.0217	0.730
1.4996	0.053	0.0276	0.934
1.5927	0.050	0.0292	0.982
2.0266	0.042	0.0368	1.265
2.6563	0.036	0.0471	1.704
3.0499	0.032	0.0535	2.026

<sup>1</sup>Between 0° and 35° the ionization of tartaric acid decreases slightly faster than the ionization of citric acid. (Jones and White, Am. Chem. Jour. 44, 159, (1910) ).

conc. wt. molar	$\alpha$	$\gamma$	$\Delta T$
3.3099	0.030	0.0578	2.244
3.3460	0.029	0.0584	2.310
3.6421	0.027	0.0631	2.491
3.9790	0.026	0.0647	2.513

The curve for oxalic acid shows the greatest divergency of the series. As oxalic acid is the strongest acid examined, its position is exactly that required by our theory of boiling-point elevation.

#### VII. Iodic Acid.

An attempt was made to use iodic acid. This resulted in a failure on account of the decomposition at the boiling-point of the solution. Even in very dilute solutions, iodine vapor could be plainly seen above the liquid. As there was no method of estimating the amount of decomposition at the time the temperature readings were taken, these results had to be discarded.

#### SUMMARY

The boiling-point curves for a series of acids have been examined, all measurements having been made under a constant pressure. In every case examined the elevation of the boiling-point was found to be proportional to the strength of the acid, the stronger the acid the greater the elevation of the boiling-point. This is taken as an indication that the hydration in solution increases regularly with the acidic strength, the abnormality of the boiling-point elevation being explained on the assumption that part of the solvent has combined with the solute, thus giving a higher concentration of solute than that calculated from the weights of the two components.



## VITA

Horatio Wales Jr., was born in Polo, Illinois on February 12th, 1894. He attended the public schools in that city and was graduated from the High School in 1911. In 1915, he received the degree of A. B., from Amherst College, and in 1917 was granted the M. A. degree at Columbia University. He was laboratory assistant in Chemistry at Columbia University from 1916 to 1918 while a student at the University.









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