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THE DEPENDENCE OF IONIC MOBILITY ON THE
VISCOSITY OF THE MEDIUM

BY

GUY YANDALL WILLIAMS

B. A. University of Oklahoma,
1906.

M. A. University of Oklahoma,
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M. S. University of Chicago,
1911.

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

1913

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YY665

May 29, 1913.

Dean David Kinley,
Graduate School.

Dear Sir:-

The Thesis of Mr. G. Y. Williams which was submitted in manuscript form will be published in the June number of the Journal of the American Chemical Society and arrangements have been completed for the printing of one hundred copies in thesis form, which will be deposited with the Librarian before July 1st, 1913.

Very sincerely,

W. A. Noyes



1913
1568

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THE GRADUATE SCHOOL

May 12, 1913.

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

GUY YANDALL WILLIAMS

ENTITLED THE DEPENDENCE OF IONIC MOBILITY ON THE VISCOSITY OF THE MEDIUM.

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Doctor of Philosophy

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May, 15, 1913.

I take it that the first copy is on the regulation thesis paper. It seems to me that there is not sufficient margin left for neat binding.

On page 1 would it not be better to replace the word "thesis" by the word "paper".

Chas. T. Knipp—

This thesis manuscript, which is in condition for the press and the publication of which has been provided for, is presented in this form in accordance with Rule 12 of the "Instructions for the Preparation of Masters' and Doctors' Theses".

Before the dependence of ionic mobility upon the viscosity of the medium can be determined within say a tenth of one per cent, two problems have to be solved. The first problem consists in devising a viscosimeter that will obey Poiseuille's Viscosity law within this degree of accuracy, for otherwise a more or less arbitrary empirical correction for the deviations of the viscosimeter from this law must be applied. Part I of this thesis is a description of a quartz viscosimeter, of the Ostwald type, that has been found to obey Poiseuille's law within 0.03 per cent.

The second problem involves the selection of a stable, inert non-electrolyte by means of which the viscosity of the medium can be varied within quite wide limits. Since the conductances of salts are to be measured in this medium it follows that the substance used must be prepared in a very high state of purity, for otherwise a very appreciable error may be introduced in making the so-called "water correction". Part II of this thesis is a description of a substance, raffinose, that has been found to fulfill the above requirements.

PART I.

A PRECISION VISCOSIMETER FOR THE MEASUREMENT OF RELATIVE VISCOSITY, AND THE RELATIVE VISCOSITIES OF WATER AT 0°, 18°, 25° and 50°.

Contents.

1. Introduction. 2. Design and Construction of the Viscosimeter. 3. The Measurement of Time. 4. Temperature Control. 5. Experimental Procedure and Reproducibility of Results. 6. Poiseuille's Law and Methods of Standardizing a Viscosimeter. 7. Standardization by Varying the Pressure. 8. Standardization by Varying the Viscosity. 9. The Relative Viscosities of Water at 0°, 18°, 25° and 50°. 10. Summary.

1. Under the titles of the two parts, this thesis will be published as two separate papers in the J. Am. Ch. Soc., 35, (June 1913).

1. INTRODUCTION.

This paper and the one following it deal with the results of some preliminary investigations which were undertaken in preparation for what is planned to be a fairly comprehensive study of the relation between ion-conductances and the viscosity of the medium in aqueous solutions. The present paper describes the results of an attempt to improve the Ostwald type of viscosimeter so as to increase both the accuracy and convenience of relative viscosity measurements.

Probably the largest and most common source of error which affects the existing data concerning the relative viscosity of liquids is due to the neglect on the part of observers to standardize their instruments and to determine and apply, if necessary, a correction for the deviation of the viscosimeter from the law of Poiseuille. Since the publication nine years ago of Gruneisen's ²⁾ thorough inves-

2) Gruneisen, Wiss. Abhandl. phys. tech. Reichsanstalt. 4, 159, 241 (1904).

gation of the relation between the dimensions of a viscosimeter and the magnitude of its deviation from Poiseuille's law it would seem that all recent measurements of relative viscosity ought to be free from this source of error. It is, however, not uncommon even at the present time to see published what purport to be accurate viscosity determinations made with a viscosimeter whose behavior towards Poiseuille's law had apparently never been investigated. Even the revised (1910) edition of Ostwald-Luther's Physico-Chemische Messungen contains no reference to this important factor or to Gruneisen's discussion of the theory of the Ostwald viscosimeter.

Gruneisen should that by properly designing the viscosimeter the deviation from Poiseuille's law could be reduced to a minimum and that in any case if the instrument were properly standardized the effect of even a comparatively large deviation from this law could be largely eliminated by applying a suitable correction. The principles upon which a viscosimeter of the Ostwald type should be constructed and a method ³⁾ by which the measurements can be corrected for any deviations from

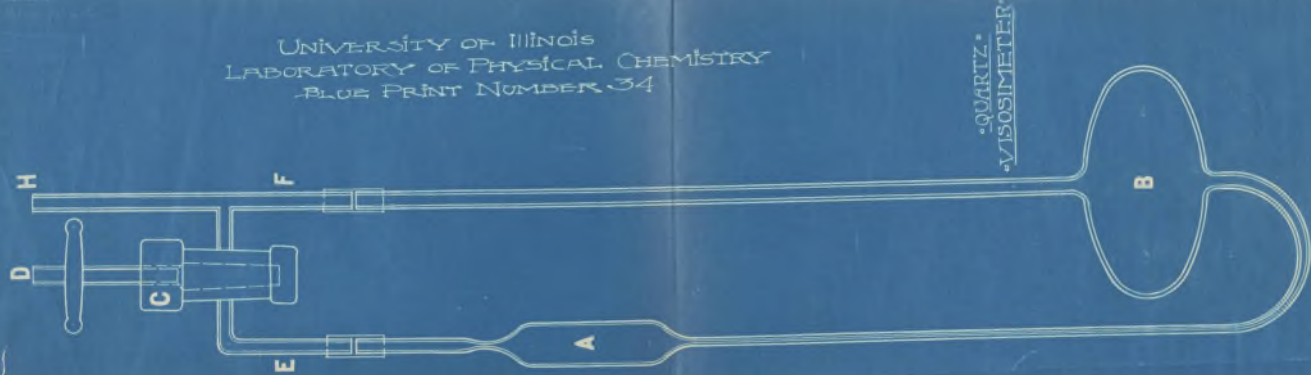
3) Cf. Washburn and MacInnes, This Jour. 33, 1692 (1911).

Poiseuille's law are fully described by Gruneisen and all of the relative-viscosity data which he obtained were corrected in this manner.

Of the more recent investigations of the relative viscosities of aqueous solutions, the measurements carried out by Appleby ⁴⁾ and by Merton ⁵⁾ in the Laboratory

4) Appleby, Jour. Chem. Soc., 97, 2000 (1910)
5) Merton, Ibid, 97, 2454 (1910)

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•QUARTZ•
•VISOSIMETER•

of Physical Chemistry of Oxford University may be cited as good examples of careful viscosity determinations carried out with due regard to all of the factors emphasized by Grüneisen. The results obtained by these two observers also show that there are practically only two remaining sources of uncertainty and inconvenience which require further study before an accuracy of 0.01 per cent is attainable in the determination of relative viscosity. The two improvements which are required are (1) the elimination of the inconvenience and uncertainty which arises from the variation in the water-constant of the instrument, requiring as it does the frequent redeterminations of this quantity; and (2) an improved method for standardizing the viscosimeter and for detecting and measuring any deviation from Poiseuille's law.

The first of these difficulties is only too familiar to every one who has had occasion to use the Ostwald viscosimeter⁶⁾. The chief causes of the variation are

6) The following experience described by Boussfield, (Phil. Trans. A, 306, 108 (1906)), although perhaps rather an extreme case, will nevertheless be appreciated by many who have had similar experiences in using the Ostwald viscosimeter: "No amount of washing will bring the apparatus to a steady condition. In dealing with very dilute solutions the variations of the water constant are often of the same order of magnitude as the variations due to variation of concentration of the solution. Hence the only safe method of operation is to interpose between the observations of salt solutions observations of water, which, of course, involves a thorough rinsing of the apparatus, which may in itself introduce some change in its condition. When a series of observations of solutions with interposed observations of water shows no material change in the water constant, it is assumed that the conditions were the same throughout, and that the observations are therefore accordant. But this assumption is not always true. A very large number of observations on dilute NaCl solutions were made, many of which had to be rejected in whole or in part, on account of variations in the water constant."

(1) the presence of small solid particles which lodge in the capillary; (2) a continuous change in the size of the capillary owing to the solvent action of the water and of the solutions employed in cleaning the viscosimeter; (3) temperature hysteresis similar to that which occurs with a thermometer; and (4) contamination of the water by dissolved glass. The first of these causes can be practically

eliminated by using a capillary of such a diameter that the very small particles of dust which cannot be entirely excluded without extreme care will be too small to lodge in the capillary. The second and fourth causes can be reduced by using a resistant glass and avoiding hot water or hot cleaning solutions. To eliminate the third cause the viscosimeter, if constructed of glass, must be kept continuously at the temperature at which it is to be used. These precautions would prove troublesome for work at temperatures very far from room temperature and would require a separate viscosimeter for each temperature in case it was desired to study a liquid over a considerable temperature range.

The desirability of improving the method of standardization is indicated by Appleby in the following remark ⁷⁽⁶⁾ upon the standardization of his own viscosimeter:

 7
 2.) Appleby, l. c., p. 2009

"The experimental error in standardizing is unfortunately greater than that of the viscosity determinations. It is thus not quite certain that the tube obeys Poiseuille's law with the necessary accuracy".

2. DESIGN AND CONSTRUCTION OF THE VISCOSIMETER.

Dimensions.--Where a viscosimeter is to be used over a considerable temperature range the variations, mentioned above, in the water constant due to temperature hysteresis and to the solvent action of the water occur very frequently and we have found them a source of considerable annoyance and uncertainty. In the endeavor to eliminate these difficulties a viscosimeter of the Ostwald type, made of fused quartz, was constructed, having the relative dimensions shown in figure 1. (scale $1/3'' = 1''$). These dimensions were computed, according to the relations discovered by Grtheisen, so that the deviation from Poiseuille's law should be a minimum. The diameter of the capillary was fixed at about 0.05 mm. which is large enough to eliminate any danger of error due to small dust particles. The actual

diameter of the capillary of the viscosimeter received from the makers was found to be 0.0490 mm. The length of the capillary was 195 mm. and the volume of the

8.) The Silica Syndicate Lt. 82 Hatton Garden, London, England. This firm is prepared to furnish viscosimeters constructed in accordance with these specifications, at a very reasonable price.

small bulb, A, between the upper and lower marks, was 9.01 cc. The large elliptical lower bulb B was 45 mm. high and 80 mm. wide. The perpendicular distance between the centers of the two bulbs, which was also the mean head of the liquid during its flow through the capillary, was 300 mm. This distance aided by the shape and the size of the lower bulb is great enough to eliminate any appreciable effect arising from variations in the volume of liquid introduced into the viscosimeter if a pipette is employed for this operation. At the upper and lower ends of the capillary the change in diameter was made as gradual as possible so as to prevent eddy currents and the constriction at the upper end of the small bulb, A, was made symmetrical with the one at its lower end so as to eliminate any unequal surface tension effect which might otherwise exert an appreciable influence upon the time of flow for liquids with surface tensions very different from that of water. The total length of the viscosimeter exclusive of the three-way stop-cock, S, attached to the top, was 365 mm.

9.) The figure of the viscosimeter given in Ostwald:Lather's Handbuch, although not so labeled, is perhaps intended to illustrate the way in which a viscosimeter should not be constructed.

Filling the Viscosimeter.-The viscosimeter was always filled by means of a 65 cc. pipette. In order to determine the variation in the time of flow which would be caused by a given variation in the volume of liquid in the viscosimeter the following experiment was made. The viscosimeter was filled as usual with 65cc. of water and the time of flow determined and found to be 1161.35 sec. The amount

of water was then increased by 2 cc. and the time of flow redetermined and found to be 1163.24. That is, an error of a whole cubic centimeter in filling the viscosimeter would not change the head of liquid by more than 0.04 per cent. Since the ordinary error in filling by means of a pipette will not exceed 0.05 cc., it is evident that the error (0.002 o/o) from this source is quite inappreciable. Furthermore the temperature of the liquid when it is introduced into the viscosimeter does not need to be controlled. The viscosimeter may be filled at "room temperature" in practically all cases where the relative viscosity of an aqueous solution is being determined, even though the determination itself be carried out at a much higher or lower temperature. In case the relative viscosity of a given liquid at one temperature is being determined in terms of its own viscosity at another temperature, however, a small correction for the change in head should be made if the viscosimeter is filled at room temperature. Thus if the relative viscosity of water at 100 were being determined in terms of the viscosity at 35 and the viscosimeter were filled at 35, the decrease in head at 100, due to the expansion of the water, will be 0.105 per cent for our viscosimeter and the observed time of flow at 100 should, therefore, be increased by this amount. Similarly the correction for 50 would be +0.023 per cent and that for 0, -0.007 per cent. For all except the most exact measurements these corrections are evidently negligible.

3. THE MEASUREMENT OF TIME.

In the initial experiments a stop-watch reading to 1/5 sec. was employed in measuring the time of flow of the liquid in the viscosimeter. The watch was always wound up tightly and then allowed to run for a definite period before being used and was always handled in a systematic manner. It was controlled by frequent comparisons with the seconds pendulum of a high grade Seth Thomas clock. It soon became evident, however, that the accuracy of the viscosity determinations were practically limited by the accuracy of the stop-watch which could not be relied

upon to measure a time interval to better than 0.2 seconds even under the most favorable conditions. The stop-watch was, therefore, replaced by a recording chronograph operated by a motor and automatically controlled by the standard clock. By means of this mechanism any time interval not exceeding one hour can be easily measured to 0.01 sec. A permanent record of each experiment was also obtained upon the tape ¹⁰⁾.

10) The chronograph is figured and described in the Cambridge Scientific Instrument Company's catalogue of Physical Instruments.

4. TEMPERATURE CONTROL.

The temperature coefficient of the viscosity of water is 2 per cent per degree and if an accuracy of a few hundredths of one per cent is desired in the measurement of the relative viscosity of aqueous solutions the measurements must be made in a bath whose temperature can be kept constant to within a few thousandths of one degree. The bath employed in this investigation was a cylindrical Dewar tube 50 cm. deep and 12 cm. inside diameter. It was silvered with the exception of two perpendicular strips 1 cm. wide and placed opposite to each other which served for making the observations. It was provided with an electrically driven stirrer, a heating coil, a standard thermometer and a Beckmann thermometer and a support for the viscosimeter. The support was of the excellent type devised by Appleby^{e/11)} for this purpose. It held the viscosimeter firmly and steadily in a

11) Appleby^e, l. c. p. 2007; description and figure.

perfectly perpendicular position and its construction insured the same position for the viscosimeter each time it was placed in the support.

For measurements at zero degrees the Dewar tube was filled with fine ice made from distilled water and the stirrer was kept in operation to insure a circulation of water through the mass. At 18, 25 and 50 the temperature of the

12) Contrary to the experience of Merton, (l.c. p. 2457) our results at zero degrees show that the temperature regulation was more exact than at higher temperatures. Plenty of ice and good circulation of the water will give a temperature constant to 0.001 in all parts of the bath.

bath was kept constant to two or three thousandths of a degree by means of the heating coil, using hand regulation.

The thermometers were completely immersed so as to avoid any stem exposure correction. The Beckmann thermometer was employed nearly as a thermoscope on account of the ease with which it could be read, the actual temperature of the bath being determined by means of standard thermometers graduated in $1/30^{\circ}$ and read with a cathetometer. Both thermometers were provided with electrical tappers which were kept in constant operation except at the moment when the reading was made. In each case the actual temperature of the bath was independently obtained from two standard thermometers which had been calibrated and standardized by the National Bureau of Standards. Immediately after the run both thermometers were removed from the bath and the zero depression determined in the usual manner. After applying the zero correction and the calibration corrections both thermometers gave the same result to 0.01.

5. EXPERIMENTAL PROCEDURE AND REPRODUCIBILITY OF RESULTS.

Experimental Procedure.—The viscosimeter is cleaned, washed, rinsed with the solution and allowed to drain. Sixty-five cubic centimeters of the solution are introduced, the three-way cock attached as shown in the figure and the viscosimeter placed in its support and immersed in the bath until the horizontal connecting tube through the stop-cock is covered. The stop-cock is then turned so as to connect the side tube, D, with the capillary arm of the viscosimeter and

suction applied until the small bulb is filled. The tube H is then closed and the stopcock turned so as to close the tube, D, and connect E with F. When the meniscus passes the upper mark of bulb, A, the observer taps a key, repeating the operation when the meniscus passes the lower mark. The times of these two observations are automatically recorded upon the tape of the chronograph beside the record made by the standard clock.

Constancy of Behavior.—As an example of the reproducibility of the results even at temperatures considerably removed from room temperature and also with liquids having long periods of flow the following data are given: At 0° the water constant obtained in three successive experiments was 1161.34, 1161.37 and 1161.34 sec. respectively. Mean, 1161.35; max. d. 0.03 sec. = 0.003 o/o; a. d., 0.001 per cent. At 50° the following values were similarly obtained: 360.08, 360.17 and 360.01. Mean 360.09, max. d. 0.08 sec. = 0.023 o/o; a. d., 0.017 o/o. With an aqueous solution of raffinose at 0° the following times of flow were obtained, 1224.44, 1224.53, 1224.42. Mean 1224.46; max. d. 0.07 sec. = 0.006 o/o; a. d. = 0.003 o/o. Another raffinose solution at 0° gave the values 1415.08, 1415.00, 1415.55, 1415.36. Mean, 1415.25; max. d. 0.25 sec. = 0.029 o/o; a. d., 0.014 o/o. These figures are typical of the general behavior of the viscosimeter as regards its reproducibility and constancy under a given set of conditions.

During the six months in which the viscosimeter has been in use its water constant has remained unchanged through many cleanings and washings, and large temperature variations. In one instance water was allowed to stand in the viscosimeter for a week and the time of flow redetermined and found to be unchanged, showing that the water is not appreciably contaminated by the viscosimeter. Experiment also demonstrated, as was to be expected, the absence of any appreciable temperature hysteresis.

The Variation in the "Reaction Time" of the Observer. When an observer records, by tapping a key, the time interval between two events which he observes visually the record thus obtained will differ from the actual time interval, if the time between the perception of the event and its registration by the tap of the finger is not a constant. This latter time interval, called by psychologists the "reaction time" of the observer, varies with the observer and the conditions of observation. In the present instance only the variation of the reaction time and not its absolute magnitude comes into play and in order to determine the magnitude of this variation under the conditions of our experiments the following experiment was made.

The quartz viscosimeter was replaced by a glass one containing mercury as the liquid. When the meniscus passed the upper mark it opened an electric circuit through a relay which set in operation the pendulum of a Bergström chronoscope. The tap of the key by the observer stopped the pointer of the chronoscope and the difference between these two intervals could be read to 0.001 second. The variation in this interval is equal to the variation in the reaction time of the observer. Twenty observations were made and the variations of the individual observations from the mean, expressed in thousandths of a second, were as follows:-

2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	Mean
+14	-5	-1	-1	+33	+38	-16	+14	-1	-7	+4	-34	-19	-31	+9	-41	+7	+4	+47	16

The average is 0.016 seconds, and this is, therefore, the probable error in a viscosity measurement which is due to the variability of the reaction time of the observer. The maximum deviation from the mean is 0.05 seconds and the maximum difference between any two observations occurs with numbers 17 and 20, and is 0.09 seconds. That is, if these two observations happened to be those taken at the beginning and at the end, respectively, of a given viscosity experiment the error in

this experiment would amount to 0.09 second. Variations of this magnitude will, however, evidently be of rare occurrence, and usually the error due to the variability of the observer will be quite insignificant. This is borne out by the results of the viscosity measurements, especially those recorded in table 2 which show remarkably close agreement between successive times of flow.

(3) We wish to acknowledge our indebtedness to Professor Madison Bently^l of the department of psychology for his kindness in placing at our disposal the chronoscope and in personally assisting us in the study of the reaction times.

6. POISEUILLE'S LAW AND METHODS OF STANDARDIZING A VISCOSIMETER.

Poiseuille's law for a viscosimeter of the Ostwald type may be expressed as follows:

$$\frac{\eta}{pt} = k \quad (1)$$

where η is the viscosity (either relative or absolute) of the liquid, t is its time of flow under the mean pressure p , and k is a constant which depends only upon the dimensions of the instrument and the units in which η , p , and t , are expressed. In order to determine how closely a given viscosimeter obeys this law we may either measure the times of flow of a liquid of given viscosity under varying pressures or we may determine the times of flow of liquids of varying viscosities under the same or under different pressures. The first method has been the most common one and was employed by Grüneisen, by Appleby, and by Merton.

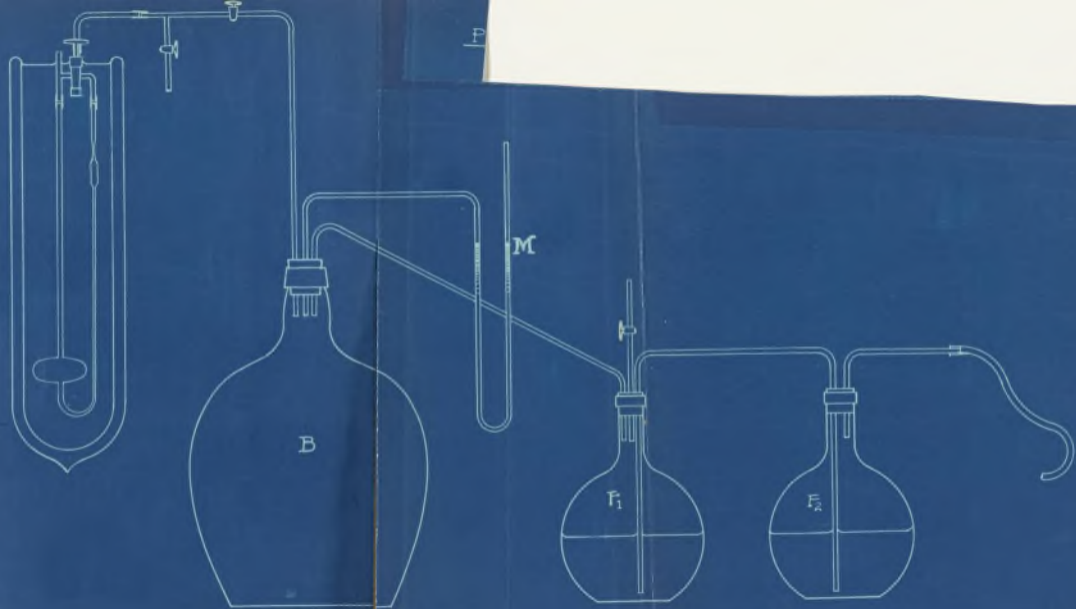
The second one has been used by Merton, by Washburn and MacInnes by Noyes and Lombard and by others. In applying the second method it has been customary to

 14 A. A. Noyes and R. H. Lombard, This Journal, 33, 1431, Note 4 (1911)

vary the viscosity by employing a solution whose viscosity has been previously determined by another observer who standardized his instrument by the first method. With a quartz viscosimeter, however, the second method can also be applied by using water alone and simply varying the temperature, for the dimensions of the instrument do not vary with temperature and hence no hysteresis is to be feared. Both methods were employed in the present investigation and are described below.

7. STANDARDIZATION BY VARYING THE PRESSURE.

The apparatus employed in this standardization was very similar to that used by Grüneisen and by Appleby and is shown diagrammatically in figure 2. B is a twenty liter carboy covered with felt and serves as a ballast. M is the manometer and F₁ and F₂ are two flasks containing water and so arranged that the observer



can vary the pressure in the carboy by forcing water from flask, F_2 into flask F_1 by lung pressure. In this way it is possible to keep the manometer reading constant throughout the period of flow.

The manometer employed in this standardization was a water manometer inclined at an angle of 45 degrees to the horizontal in order to give it greater sensitiveness. The sine of this angle ($\sin \theta$) was obtained by determining with a cathetometer the difference in level between two scale divisions of the meter stick to which the manometer tube was fastened. The two scale divisions employed for this purpose were 200 mm. apart and two measurements gave for $\sin \theta$ the values 0.7150 and 0.7148, respectively. The temperature of the manometer was also noted and thus its readings were easily converted into millimeters of water at 4° . The average pressure, p , under which the liquid is flowing in the viscosimeter is equal to the sum of the constant pressure shown by the manometer and the mean head of liquid in the viscosimeter. The value of the latter pressure will, for a viscosimeter constructed like the present one, be practically equal to the pressure at mean-time. In order to determine the pressure at mean-time the flow was stopped by turning the stopcock, C , as soon as half the period of flow had elapsed, and the difference in level of the liquid in the two bulbs determined with a cathetometer and found to be 200.13 mm. In two successive experiments made in this manner measurements made with the cathetometer showed that the meniscus in the upper bulb came to rest at the same level (to within 0.01 mm.) in both experiments.

Table I shows the results obtained in the standardization by this method. The times were measured by means of a stop watch and in each instance the value given in the table is the mean of two or three determinations at the corresponding pressure. It is evident from the results shown in this table that our viscosimeter obeys Poiseuille's law within the experimental error of the measurements, within the pressure limits 130 mm. and 300 mm. The maximum variation of the pt values from the mean is 0.04 per cent and the average only 0.03 per cent. By

employing one of the more accurate forms of

TABLE 1

Values of $p t$ at 35° under different pressures. $h =$ head at meantime = 300.13 mm.

Run No.	Effective Pressure mm. of Water, (in air) at 4° p	Time of Flow at 35° Sec- onds t	pt	Deviation from the Mean	Deviation from the Mean (Per cent.)
1	132.04	874.7	11550	+ 5	0.04
2	161.51	714.6	11543	- 3	.03
3	174.31	662.5	11548	+ 3	.03
4	199.31	579.4	11548	+ 3	.03
5	226.03	510.3	11546	+ 1	.01
6	244.48	472.0	11540	- 5	.04
7	272.97	423.0	11547	+ 3	.02
8	294.79	391.5	<u>11541</u>	- 4	.03
		Mean	11545	3.3	0.03 o/o

$$k = \frac{\eta_{35^{\circ}} h}{pt} = \frac{0.008926 \cdot 30013}{11545} = 154.73 \times 10^{-4}$$

differential micro monometers and using a sufficiently large ballast at constant temperature the degree of precision attainable in this method of standardization can evidently be increased if desired.

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In figure 3 the percentage deviations of the ρt -values from the mean are shown graphically, per cent deviation being plotted as ordinates and per cent increase in effective pressure as abscissae the lowest pressure being taken as 100. The radius of the circle drawn around the points is made equal to 0.05 per cent. For convenience in comparison the corresponding data obtained by Appleby^e and by Merton are also shown. In the standardization of his viscosimeter by the same method Appleby¹⁵ made 21 measurements of ρt between the pressure limits 104 mm. and 230 mm. and the average deviation from the mean was 0.12 per cent. Merton's¹⁵

15) Appleby^e, l. c., p. 2009, Merton, l. c., p.

standardization between 115 mm. and 365 mm. included 12 measurements of ρt and the average deviation from the mean was 0.2 o/o. No comparison with Grüneisen's standardization data can be made as none of the straight capillary viscosimeters employed by him obeyed Poiseuille's law.

The constant of our viscosimeter as defined by the equation (1) which may be written

$$k = \frac{\eta_{25}^{\circ} h}{\rho t} \tag{2}$$

is therefore, $154.73 \cdot 10^{-7} \pm 0.03$ o/o when η_{25}° is taken as 0.008926 c.g.s. units, h , the head at mean-time, is 200.13 mm. of water at 25, and ρt has the

16) Hosking's value, see table 3 below

mean value given in table 1.

8. STANDARDIZATION BY VARYING THE VISCOSITY.

By determining the times of flow of water at different temperatures the effect of a large variation in viscosity under a nearly constant effective pressure can be determined. In the present instance the times of flow of water were determined at 0° , 25° , and 50° and the following values obtained, 1161.35 sec., 579.28 sec., and 360.09 sec., respectively. The constant, $k = \frac{\eta_s h}{\rho t}$ may also be written $k = \frac{\eta}{d_a \cdot t}$, since the mean effective pressure during the operation of the viscosimeter under ordinary conditions is equal to $h \cdot d_a$ where h is the mean head of water in the viscosimeter and d_a is its density in air, both expressed in the same system of units. If we refer all densities to water ^{in air} at 4° the value of k computed from the expression, $k = \frac{\eta}{d_a \cdot t}$, should be the same as the value obtained above, from the data shown in table 1 and should be the same for all three temperatures.

In this way we obtain for the three temperatures, 0° , 25° , and 50° , the expressions,

$$k_0 = \eta_0 \cdot 862.33 \cdot 10^{-6}$$

$$k_{25^{\circ}} = \eta_{25^{\circ}} \cdot 1733.35 \cdot 10^{-6}$$

and

$$k_{50^{\circ}} = \eta_{50^{\circ}} \cdot 2803.02 \cdot 10^{-6}$$

In computing these equations the times of flow given above were first corrected for the small change in head at the different temperatures as explained in section 3. In order to compute the value of k from these equations it is necessary to know the absolute viscosity of water at the corresponding temperatures. If we employ Hosking's values for η at 0° , 25° and 50° (see Table 3 below) we obtain the following values for k , $154.60 \cdot 10^{-7}$, $154.72 \cdot 10^{-7}$ and $154.72 \cdot 10^{-7}$, respectively. Mean, 154.68; max. d. 0.05 o/o; a. d. 0.03 o/o. The agreement is better than could be expected in view of the fact that the values of η employed

TABLE 2

Relative Viscosity of Normal Potassium Chloride Solution at 18.00°.

$$\frac{\eta_s}{\eta_w} = \frac{D_s - \sigma}{D_w - \sigma} \frac{t_s}{t_w}, \text{ 37.2665 g of KCl in 521.910 g of Solution (Weights in air).}$$

	Water	Per cent Deviation from the Mean	Normal KCl Solution	Per cent Deviation from the Mean	η_s/η_w Washburn and Williams	η_s/η_w (Grüneisen)
VI	684.04	0.0015	643.66	0.0000		
Time of flow in seconds	684.05	.0000	643.66	0.0000		0.9815
	684.04	.0015	643.68	.0031		.9820
	684.06	.0015	643.65	.0016		.9822
Mean	684.05	0.0011	643.66	0.0016	0.98130	.9820
Av. Dev. per cent					0.003	0.02

cannot be relied upon to better than 0.1 per cent.

The Viscosity of a Normal Solution of Potassium Chloride at 18°. In order to compare the results given by our viscosimeter with those obtained by Grüneisen the relative viscosity of a normal solution of potassium chloride at 18° was determined. The salt employed was Kahlbaum's "Special K" recrystallized several times from conductivity water and fused in platinum. The solution was made up so as to have exactly the composition of that used by Grüneisen which was the same solution employed by Kohlrausch and Maltby⁽⁷⁾ in their conductance measurements.

 17) Kohlrausch and Maltby, Abhandl. phys. tech. Reichsanstalt, 3, 180, (1900)

The density of our solution was 1.04493. The value given by Grüneisen is 1.04493. Table 2 below shows the results of the viscosity measurements. Grüneisen determined the viscosity of the solution in three different viscosimeters and found the three values, 0.9815, 0.9820, and 0.9822. Our result 0.98130 agrees with Grüneisen's within the limit of error of his measurements, especially when his method of temperature control is considered. The data given in table 2 are a good illustration of the behavior of the quartz viscosimeter under the best conditions.

Conclusion.—The results presented in this section justify the conclusion that our viscosimeter obeys Poiseuille's law, certainly within 0.03 per cent., and probably within 0.01 per cent. provided the time of flow exceeds 300 seconds. We have not, thus far, investigated its behavior for higher velocities of flow as they will never be attained with aqueous solutions at temperatures below 50°.

o o o o

9. THE RELATIVE VISCOSITIES OF WATER AT 0 , 18 , 25 and 50 .

Our measurements at these four temperatures may be employed to compute the relative viscosities of water for these temperatures and as the results thus obtained are probably more accurate than any of the existing values for these quantities they are presented below in table 4 . For comparison the corresponding

values computed from the measurements of absolute viscosity made by Thorpe and Rodger, by Hosking¹⁸⁾, and by Bingham and White¹⁹⁾ are also given, together with

¹⁸⁾ Hosking, Proc. Roy. Soc. N. S. Wales, 43, 37 (1909).

¹⁹⁾ Bingham and White, Z. physik. Chem. 80, 685 (1912).

the percentage deviation of their values from our own.

The absolute viscosities obtained by different observers are presented in Table 3. The values in this table are taken from Bingham and White's paper, with the exception of those of Hosking, all but one of which are taken from the table on page 38 of his paper. The value assigned to him for 18^o is interpolated by means of an empirical equation which he gives and which he finds represents his data very exactly. On the whole Hosking's values seem to be more uniformly consistent with one another than those of the other investigators and as is evident from table 4 the relative viscosities computed from them agree better, on the whole, with the values determined by us than do those of the other observers.

TABLE 3

Viscosity of Water by Different Observers.

Temp.	Poiseuille	Sprung	Slotte	Thorpe and Rodger	Hosking	Bingham and White
0°	0.01776	0.01778	0.01808	0.01778	0.017928	0.01797
18°	--	--	--	--	.01057	--
25°	.00897	0.00896	0.00896	.00891	.008926	.008948
50°	--	0.00553	0.00553	.005475	.00550	.00550

TABLE 4

Relative Viscosities of Water at 0.00°, 18.00°, 25.00° and 50.00°.

η_{18} / η_{25}	Washburn and Williams	Thorpe and Rodger	Dev. o/c	Hosking	Dev. o/c	Bingham and White	Dev. o/c
η_{18} / η_{25}	0.58978	--	--	0.5896	-0.03	--	--
η_{25} / η_{50}	.49741	.5020	+ .93	.4979	+ .10	.4979	+ .10
η_{50} / η_{18}	.30640	.3081	+ .55	.3067	+ .10	.3061	- .10
η_{50} / η_{25}	.61599	.6142	+ .35	.6162	+ .03	.6147	- .21
η_{18} / η_{50}	.5192	--	--	.5202	+ .12	--	--

1. An improved viscosimeter of the Ostwald type is described. The instrument is made of fused quartz and is shown to possess the following advantages:

(a) Its water-constant at a given temperature is not changed by cleaning with hot cleaning mixtures or by subjecting the viscosimeter to large temperature variations. It has remained perfectly constant within 0.03 second for the *Six* months during which the viscosimeter has been in use. (b) The water constant at 25° is 580 seconds and is repeatedly reproducible to about 0.03 seconds under a given set of conditions. This means that a precision of 0.01 per cent. or better is attainable in measurements of relative viscosity. (Cf. Table 2, p.) (c) For effective pressures within the limits 130 and 300 mm. of water the deviation of the viscosimeter from the requirements of Poiseuille's law is shown to be less than 0.03 per cent. (d) An error of a whole cubic centimeter in the amount of liquid introduced into the viscosimeter does not change the time of flow by as much as 0.05 per cent. (e) A single instrument can be used for a large temperature range since its dimensions do not alter with the temperature.

2. The following values for the relative viscosity of water at four different temperatures were obtained: $\eta_{18^\circ}/\eta_0 = 0.58978$, $\eta_{25^\circ}/\eta_0 = 0.49741$, $\eta_{50^\circ}/\eta_0 = 0.30640$ and $\eta_{50^\circ}/\eta_{25^\circ} = 0.61599$. They are probably accurate to 0.03 per cent.

3. The relative viscosity of a normal solution of potassium chloride at 18° is 0.98130.

Urbana, Ill.

PART II

THE VISCOSITIES AND CONDUCTIVITIES OF AQUEOUS SOLUTIONS OF RAFFINOSE.

INTRODUCTION.

In the second paper¹ in the series on "Concentrated Solutions" a method for

1) Washburn, This Jour. 33, 1461 (1911).

making the viscosity correction in computing degrees of ionization was proposed, based upon the relation, $\Lambda = kf^m$ where Λ is the equivalent conductance of an ion in a medium of fluidity, f , k is a constant and m is also a constant, not far from unity, which depends upon the nature of the ion. The evidence supporting this relation was largely confined to solutions in which the fluidity was varied by varying the temperature and in those cases the above relation is known to hold very exactly for all ions except hydrogen and hydroxyl. As pointed out in the paper referred to, it is very desirable to obtain further evidence regarding the applicability of this relation and especially to discover to what extent the value of the fluidity exponent, m , is influenced by the nature of the molecules which determine the fluidity of the medium through which the ion moves. Some experiments by Green in which the conductivity of LiCl was studied in aqueous solutions of cane sugar were also discussed and, as far as could be determined, his data

seemed to confirm the relation, $\Lambda = kf^m$ in the case of this salt.

In continuing the investigation of the relation between ion conductances and the viscosity of the medium, we have chosen raffinose as the first non-electrolyte to be employed for changing the viscosity. Owing to the high molecular weight of raffinose comparatively large changes in the viscosity can be produced without changing the activity of the water very much. This is important because it is essential in the first experiments that the degrees of hydration of the ions remain constant. Another advantage of raffinose over cane sugar is its stability in solution. Cane sugar slowly decomposes, especially in the conductivity cell under the catalytic influence of the platinum electrodes, and this decomposition results in an increased and uncertain conductivity and constitutes a considerable source of error. Raffinose, as shown below, is quite free from this objection. A further advantage in using raffinose lies in the fact that the results of the investigation can be easily correlated with the data concerning true transference numbers in solutions in which raffinose serves as the reference substance. The present paper is a preliminary one dealing with the preparation of pure raffinose and the conductivity and viscosity of its solutions.

2. PURIFICATION OF THE RAFFINOSE.

The data required in the proposed investigation are the Λ_0 values for a number of strong electrolytes in aqueous solutions of raffinose. In order to obtain the Λ_0 value with a reasonable degree of accuracy it is necessary that the solvent, itself, in this case the raffinose solution, have a very low specific conductance so that the conductance measurements of the salt solutions may be carried to high dilutions. A very high degree of purity, especially with regard to freedom from electrolytes, is therefore necessary on the part of the raffinose. This was secured by the following process of purification:

Kahlbaum's raffinose was employed as the "raw material". Its specific conductance in 0.1 molal solution at room temperature was 17.10^{-6} reciprocal ohms.

An excess of the crystals were treated with hot, dry, methyl alcohol (Kahlbaum's best grade, distilled from metallic calcium) and the clear solution decanted off from the residue. This solution was then cooled in a freezing mixture. The raffinose which precipitated out as a viscous mass was dissolved in conductivity water and the solution concentrated by evaporation in a platinum or quartz vessel.

The syrup thus obtained was then poured into a wide mouth quartz flask and while still hot was treated with pure ethyl alcohol in small portions until the precipitate which was formed just failed to dissolve on shaking. The flask was then set aside and the raffinose allowed to crystallize. The crystals were centrifuged in platinum and then recrystallized until the product had a specific conductance in 0.1 molal solution at 25° of less than $3 \cdot 10^{-6}$ reciprocal ohms. The final product was dried at $50^{\circ} - 60^{\circ}$ in an electric oven.

3. THE CONDUCTIVITY WATER.

The water was distilled from an alkaline permanganate solution. The distillate was collected hot, in 3-liter quartz flasks and had an average specific conductance at 25° of $0.6 \cdot 10^{-6}$ reciprocal ohms. The best water obtained in this way during the course of the work had a specific conductance at 25° of only $0.26 \cdot 10^{-6}$ reciprocal ohms. This water after standing over night in the quartz flask covered with tin foil had a specific conductance of $0.36 \cdot 10^{-6}$. At the end of 48 hours it had increased to $0.61 \cdot 10^{-6}$ and at the end of two weeks it was only $0.68 \cdot 10^{-6}$.

4. THE CONDUCTANCE CELL.

This was of the pipette type and is shown in figure 1. It was constructed of Jena Geräteglas and provided with two circular electrodes 2 cm. in diameter and 3 mm. apart. The inner face of each electrode ~~was~~ ^{had been} roughened by means of a sand blast. Two ground glass caps closed the cell after filling. The conductance measurements were made with the improved conductivity apparatus of Washburn and

2)
Bell .

2) Washburn and Bell, This Jour. 35, 177 (1913).

5. THE CONDUCTANCE MEASUREMENTS.

The raffinose crystals after drying for 3 hours at 50°-60° in a platinum dish, were transferred hot to a weighed quartz flask and allowed to cool in a desiccator. After weighing, the proper amount of conductivity water was weighed in by means of a quartz pipette. When solution was complete the conductance cell was filled through the detachable tube, T, shown in the figure, and after closing by means of the glass caps was placed in the constant temperature bath described in the preceding paper. The conductances were perfectly constant over a long period of time.

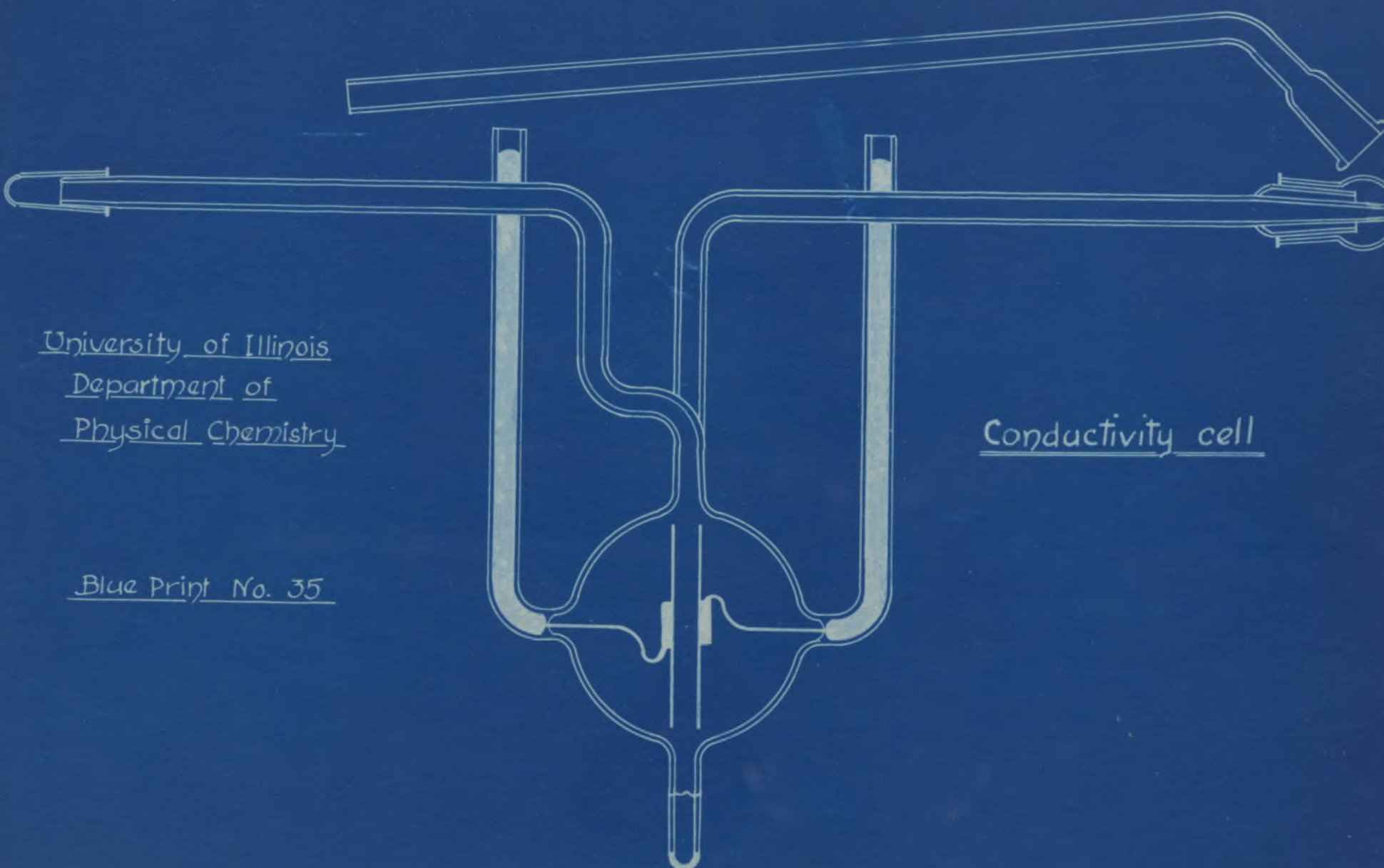
The conductance data are shown in table 1. The values given in column VI were obtained by subtracting from the corresponding values in column V, the specific conductance of the water divided by the viscosity of the solution. The very low values of the specific conductances of the raffinose indicate a high degree of purity. The sucrose employed by Green in the investigation referred to, had a specific conductance in 0.3 molal normal solution of $13.8 \cdot 10^{-6}$ reciprocal ohms at 25° .

Jour. Chem Soc, 93, 2056 (1908)
3) Green, ~~l. c. p. 2056~~, Cf. Washburn, Z. Ver. Deut. Zuckerind. 60, 381 (1910)

6. THE IONIZATION CONSTANT OF RAFFINOSE AS AN ACID.

The values of the equivalent conductance given in column VI of table 1 may be employed to calculate the order of magnitude of the ionization constant of raffinose as an acid. For this purpose they were first multiplied by the viscosity of the solution and then substituted in the equation,

$$\frac{\Lambda^2 C}{\Delta_0^2} = K,$$



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Conductivity cell

and the values of K given in column VII obtained. For Λ_0 the values 350 at 0° and 370 at 35° were employed. The values of K thus obtained, $0.5 \cdot 10^{-10}$ at 0° and $0.9 \cdot 10^{-10}$ at 35°, can of course be regarded as maximum values only.

7. THE VISCOSITY MEASUREMENTS.

The solutions prepared as described in the preceding section were filtered through hardened filters which had been previously washed and dried. The set of weights used in preparing the solutions and in the density measurements had been carefully standardized against a set certified to by the Bureau of Standards. All weights were reduced to vacuo. The viscosities were measured as described in the preceding paper. The results are tabulated below.

TABLE 1.

CONDUCTANCES OF AQUEOUS SOLUTIONS OF RAFFINOSE.

I	II	III	IV	V	VI	VII
Formula Weights of $C_{12}H_{22}O_{16} \cdot 5H_2O$ per Liter	Temperature	Specific Conductance of the Water $\times 10^6$	Specific Conductance of the Solu- tion $\times 10^6$	Corrected Specific Conductance of the Solu- tion $\times 10^6$	Equivalent Conductance of the Raf- finose $\Lambda \cdot 10^3$	Ionization Constant of Raffinose as an Acid $K \cdot 10^{-10}$
0.200	0.00 ⁰	0.15	0.600	0.49	3.5	0.4
.197	25.00 ⁰	0.35	1.34	1.00	5.0	.8
1.0349	0.00 ⁰	0.15	0.42	0.31	8.9	.5
.0346	25.00 ⁰	0.35	0.89	0.64	18.	.9

TABLE 2.
DENSITIES AND RELATIVE VISCOSITIES OF AQUEOUS SOLUTIONS OF RAFFINOSE.

Formula Weights Per Liter at t°	Temperature	Time of Flow	Mean Time of Flow	Density at t° /c	Relative Viscosity	Relative Visco- sity at Round Temperature
0.036083	0.00°	1234.44 .53 .42	1234.46	1.00796	1.06284	1.06284
.037973	24.94°	607.76 .77 .58?	607.76	1.00483	1.05604	1.05602
.037615	49.87°	375.01 .04	375.03	0.99556	1.04738	1.04723
.058632	0.00°	1263.30 .39 .37	1263.42	1.01318	1.10129	1.10129
.058466	24.94°	623.69 .66 .63	623.66	1.00897	1.08812	1.08809
.057925	49.87°	384.38 .44 .42 .41	384.41	0.99964	1.07737	1.07780
.102676	0.00°	1351.43 .76 .11	1351.43	1.02147	1.18881	1.18881
.102397	24.94°	659.87 .80 .83 .84	659.84	1.01179	1.16268	1.16262
.010240	49.86°	402.90 403.00 .00	402.97	1.00843	1.13200 * 1.1458	1.13100 * 1.1457 *
.131202	0.008	1415.08 .00 .55 .36	1415.25	1.02752	1.25233	1.25233
.120727	24.96°	687.39 .25 .10	687.25	1.02378	1.21719	1.21713
.129787	50.12°	417.59 .34 .56 .45	417.49	1.01407	1.19261	1.19272
.176625	0.00°	1524.40 .00 .25	1524.22	1.03645	1.36048	1.36048
.175818	25.00	734.50 .75 .74	734.66	1.03172	1.31230	1.31230
.174336	49.84°	443.06 .00 .13	443.06	1.02302	1.27083	1.27057

* Interpolated

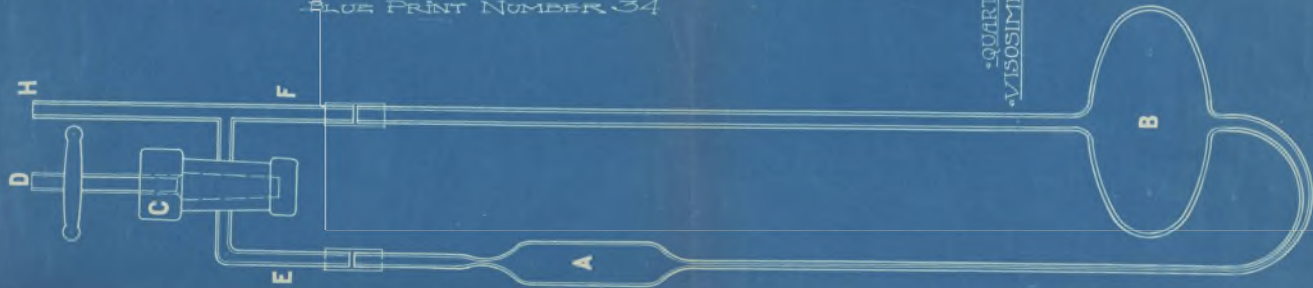
Biographical.

The writer received his early education in the schools of Amarillo, Texas, and Ball, Oklahoma. He graduated from the Ball High School in 1907, and entered the University of Oklahoma in the fall of that year. He has the degree of Bachelor of Arts, in Chemistry, 1909, and Master of Arts, in Chemistry, 1910. My thanks are due Professor E. W. Washburn, at whose suggestion this work was undertaken, for his valuable advice and sympathetic interest during the progress of the work. 1907, 1910, 1916, and 1917, and received the degree of Master of Science, in Chemistry, from that university, in the class of the fall semester quarter. During the years 1911-12 and 1912-13 the writer has held an leave of absence from Oklahoma and, for these two years, has held a Fellowship in Chemistry in the University of Illinois.

Biographical.

The writer received his early education in the schools of Amarillo, Texas, and Enid, Oklahoma. He graduated from the Enid High School in 1902, and entered the University of Oklahoma in the fall of that year. He has the degrees of Bachelor of Arts, in Chemistry, 1906; and Master of Arts, in chemistry, 1910, from Oklahoma. From 1906 to 1908 the writer was instructor in chemistry in the University of Oklahoma. Since 1908 he has been associate professor of chemistry in the same institution. He attended the University of Chicago during the summer quarters of 1907, 1909, 1910, and 1911, and received the degree of Master of Science, in chemistry, from that university, at the close of the 1911 summer quarter. During the years 1911-12 and 1912-13 the writer has been on leave of absence from Oklahoma and, for these two years, has held a fellowship in chemistry in the University of Illinois.

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