SOME APPLICATIONS OF THE CONDUCTIMETRIC METHOD WITH PRELIMINARY WORK FOR A STUDY OF THE MAGNETIC SUSCEPTIBILITY OF ADSORBED GASES.

A Thesis submitted to the University of London for
the degree of Master of Science

by

JOAN PEAKE PHILPOT.

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The magnetic work described in the first section of this thesis was carried out in the Physical Chemical Laboratory of Bedford College under the direction of Professor J.F. Spencer. The author wishes to thank Professor Spencer for his interest in the work and also Dr. V.C.G. Trew for her assistance with the experimental part of the work.

The electrolytic work described in the second section of the thesis was carried out in the Physical Chemical Laboratory of Battersea Polytechnic under the direction of Dr. C.W. Davies. The author is extremely grateful to Dr. Davies for his unfailing help and interest and also to Dr. E.C. Rhodes for his assistance with the earlier part of the work.

Thanks are due to Mr. R. Faraday Innes and other members of the British Leather Research Association for the provision of tan extracts, to Dr. J.F.J. Dippy of Cardiff Technical College for providing pure specimens of a number of organic acids and to Dr. J. Kenyon for purifying a specimen of lactic acid.

J. P. Philpot

SOME APPLICATIONS OF THE CONDUCTIMETRIC METHOD WITH PRELIMINARY WORK FOR A STUDY OF THE MAGNETIC SUSCEPTIBILITY OF ADSORBED GASES.

by

Joan Peake Philpot.

Abstract of Thesis.

Section I of the thesis deals with the determination of the magnetic balance constant and with the preparation and preliminary measurements of a platinum adsorption medium preparatory to a study of the magnetic properties of adsorbed gases.

Section II deals with conductimetric measurements. A description of the apparatus and technique used is given. The method was used, in conjunction with analyses carried out at the British Leather Research Association, for the investigation of a number of natural tan extracts to which it was believed that foreign substances had been added. The mobility of the pyridinium ion was also determined, and an attempt made to determine the mobility of the ammonium ion. Finally a rapid method for determining the mobilities of acid anions was studied. It was found unsuitable for difficultly soluble acids, but for easily soluble acids good results were obtainable. The method was used to determine the mobility of the lactate ion.

CONTENTS.

SECTION I.

Some Preliminary Work in an Investigation of the Magnetic Properties of Adsorbed Gases.

Abbreviations used in Section I of Thesis.

I	Intensity of magnetisation or magnetic moment per unit volume.
H	Magnetic field or force on unit charge.
B	Induction. $B = H + 4\pi I$. (Magnetisation and field parallel).
K	Susceptibility I/H.
μ	Permeability $= B/H$. $\mu = 1 + 4\pi K$.
V	Volume.
F	Force.
d	Density.
X	Susceptibility per unit mass $= K/d$.
A	Area.
α	Balance constant.
M	Magnetic moment.

SECTION I.

Some Preliminary Work in an Investigation of the Magnetic Properties of Adsorbed Gases.

Introduction.

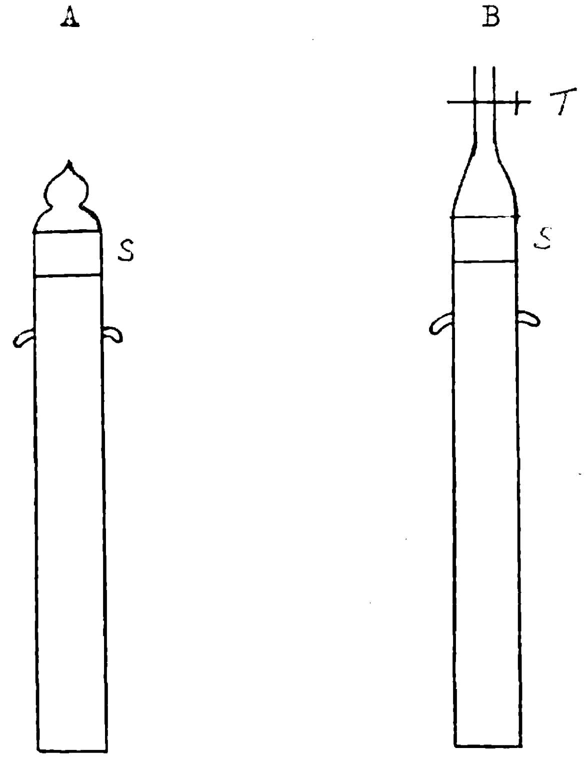
It was suggested that measurements of the magnetic moment and susceptibility of gases such as hydrogen adsorbed on materials such as platinum, palladium, silica gel, would afford information as to the mechanism of adsorption. Work was commenced with this object in view.

Measurement of Magnetic Susceptibility.

The balance used was of the Gouy type. The balance itself was similar to an ordinary chemical balance capable of weighing by oscillations to 0.00001 gm. Hanging from the left-hand arm of the balance was a hook on which was suspended a thread carrying a stirrup. A susceptibility tube, as in figure I, was hung on this stirrup so that the bottom of the tube hung between the pole-pieces of a powerful electro-magnet. It was carefully arranged so that the bottom of the tube was as near as possible to the centre of the pole-pieces so as to be in a uniform field. A mark was scratched on the susceptibility tube about 7 cm. above the base. This was high enough above the pole-pieces to be in zero field when the magnet was switched on. The tube was always filled to this mark. The pole-pieces were surrounded by a wooden box to prevent interference with the

FIGURE I (SECTION I)

Susceptibility Tubes.

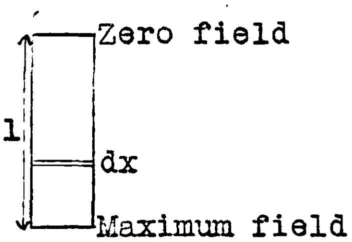


S Ground glass stopper.

T Tap.

readings by currents of air. The temperature between the pole-pieces was kept constant within about 5° C. by cooling the magnet with an electric fan after one or at most two readings.

A measurement was made by weighing the tube first with the magnet off and then with it on. The difference gave the force exerted by the magnet on the tube. The formula used in calculating the results is obtained as follows.



Force in direction x on small magnet (formed by taking a cross section of length dx through the susceptibility tube)

$$= M.dH/dx \quad = \quad KHV.dH/dx \qquad (\text{Since } M = IV = KHV)$$

$$\therefore \quad \text{Force} = \tfrac{1}{2}KV.dH^2/dx$$

$$\therefore \quad \text{Force on whole} = \tfrac{1}{2}KA\int_0^{l} \frac{dH^2}{dx}\,dx$$

$$= \tfrac{1}{2}KA\int_{H_0}^{0} dH^2 \qquad H_0 = \text{field where } x = 0$$

$$= -\tfrac{1}{2}KAH_0^{\,2}$$

$$K = \frac{\mu - 1}{4\pi} \qquad \therefore \; F = \frac{(\mu - 1)AH_0^{\,2}}{8\pi}$$

$$\mu = 1 + 4\pi K.$$

Let $n_1 = 1 + 4\pi(Xd)$ subs.

Let $n_2 = 1 + 4\pi(Xd)$ air.

Then $$F = \frac{(n_1 - n_2)AH_o^2}{8\pi}$$

$$= \frac{(Xd)\text{ subs.} - (Xd)\text{ air}}{2} AH_o^2 .$$

(Xd) air $= 0.03 \times 10^{-6}$

$$\therefore \frac{2F}{AH_o^2} = Xd - 0.03 \times 10^{-6}$$

$$X = \frac{2F}{dAH^2} + \frac{0.03 \times 10^{-6}}{d}$$

$$= \frac{2Fl}{dVH^2} + \frac{0.03 \times 10^{-6}}{d}$$

$$\frac{2.10^6\, Fl}{H^2} = \alpha = \text{balance const.}$$

$$\therefore \quad 10^6 X = \frac{\alpha F}{dV} + \frac{0.03}{d}$$

$$\alpha = \left[10^6 X - \frac{0.03}{d}\right] \frac{dV}{F} .$$

Determination of Balance Constant.

First the pull exerted by the magnet on the empty tube was measured. The balance constant was then obtained by filling the tube with a liquid of known susceptibility and measuring the pull as described above. The volume of the tube to the mark was determined by filling with water at a known temperature and weighing.

Various organic liquids were dried and redistilled and used for the determination of the nalance constant. The constant was determined first using a tube of type A (figure I). Finally tubes of type B were used.

All susceptibilities and densities quoted are taken from the International Critical Tables.

N.B. a negative pull is taken as one which decreases the weight of the tube. i.e. diamagnetic substances.

Tube A.

Pull on empty tube – 4.32 mg. (mean of 9 values).

Volume of tube to mark 2.8260 c.c. (mean of 2).

Length of tube to mark 7.32 cm. approx.

Nitrobenzene.

X -0.499×10^{-6}. d 1.2032.

Pull on tube and liquid – 7.17 mg. (mean of 5).

Pull on liquid – 2.85 mg.

Balance constant 0.6247.

Benzene.

X -0.712×10^{-6}. d 0.8788.

Pull on tube and liquid – 7.28 mg. (mean of 6).

Pull on liquid – 2.96 mg.

Balance constant 0.6264.

Toluene.

X -0.729 x 10^{-6}. d 0.8658.

Pull on tube and liquid - 7.31 mg. (mean of 4).

Pull on liquid - 2.99 mg.

Balance constant 0.6248.

Tube B.

Pull on empty tube - 3.53 mg. (mean of 14).

Volume of tube to mark - 3.515 c.c. (mean of 4).

Length of tube to mark 7.32 cm. approx.

Benzene.

Pull on tube and liquid - 7.21 mg. (mean of 5).

Pull on liquid - 3.68 mg.

Balance constant 0.6263.

Mean cohstant for a tube of length 7.32 cm. is 0.6255.

Tube C.

This tube was of similar design to tube B. It was annealed for five hours at approximately 500°C. and the pull exerted by the magnet on it was measured.

Pull on empty tube - 2.99 mg. (mean of 7).

Preparation of the Adsorption Medium.

Platinum was chosen for the first measurements. Attempts were made to coat the metal on to glass which could then be slipped into the susceptibility tube. Hard glass tubing of about 0.5 cm. diameter was sealed off in the blowpipe and the end flattened.

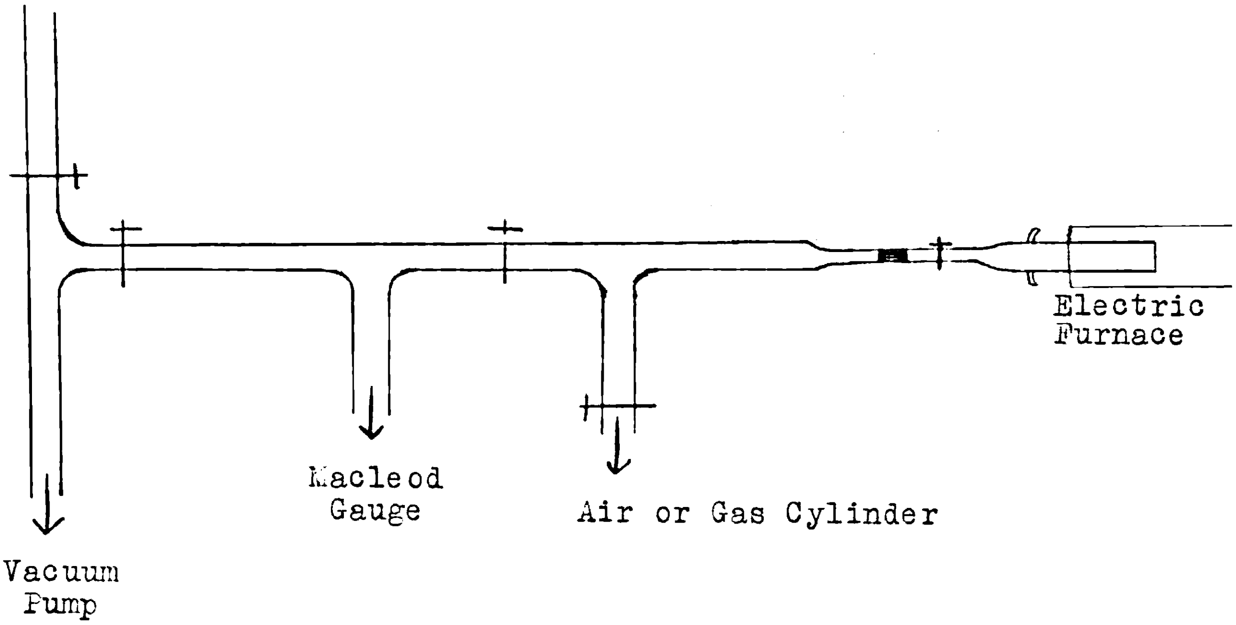
Platinum was warmed with aqua regia till dissolved; the resulting solution was evaporated to dryness in presence of hydrochloric acid. The chloroplatinic acid thus obtained was dissolved in oil of bergamot and the solution coated on to the sealed off glass tubing. It was brushed as evenly as possible over the flat end and to a height of about 7.5 cm. up the tube. The whole thing was then heated carefully in a Bunsen flame until a deposit of platinum was left on the glass. The top end of the glass tubing was then sealed off about one centimetre above the end of the platinum. Attempts to seal it earlier met with no success as the heat of the Bunsen softened the glass, expanded the air within and blew a bulb in the tubing.

After several attempts it was decided that it was impossible to coat the platinum evenly. As an uneven coating would render the results valueless from a theoretical point of view, the method was abandoned. A uniform platinum tube, thickness 0.01 cm., length 7.4 cm., diameter 0.7 cm. was prepared by Johnson and Matt~~by~~hey and later a similar palladium tube was obtained.

Apparatus for Annealing, Evacuation and Adsorption.

Apparatus as shown in figure II was set up; all the joints were made by sealing the glass tubing. Provision was made for attaching the susceptibility tube by means of pressure tubing which was wired on. Special rubber grease was used on

FIGURE II (SECTION I)



the tap of the susceptibility tube. The temperature of the electric furnace was measured with a thermo-couple and adjusted by means of the rheostat. The pump used was a Megavac pump capable of producing a vacuum of 0.001 mm. or less.

Constants for Platinum Tube.

The length and diameter of the tube were measured by means of calipers; a number of measurements were made and the mean taken.

Length	7.33 cm.
Diameter	0.70 cm.
Weight	3.15135 gm.

A mark was made at one end of the platinum tube so that it could always be inserted in the susceptibility tube the same way. The pull exerted by the magnet on it was measured.

Pull on tube B and platinum tube 6.21 mg. (mean of 7).

Pull on platinum tube = 6.21 + 3.53 = 9.74 mg.

" " " " inverted 13.32 mg.

Density of platinum 21.45

From these data X for platinum was calculated; using the first value given for the pull.

Hence X = 1.9354 compared with X = 1.10 given in the Critical Tables.

The platinum tube was then heated in a Bunsen burner and cooled.

Pull 5.73 mg. (mean of 3).

Tube inverted, pull 6.09 (mean of 2)

As before X = 1.152.

It was then discovered that the tap of the susceptibility tube was too close to the furnace during annealing operations and that the heat ruined the tap grease. A tube with a longer neck was obtained (tube C). The platinum tube was placed in this tube and annealed for five hours at about 500°C.

Pull 5.87 mg. (mean of 7).

Tube inverted, pull 6.27 mg. (mean of 6).

The difference between the measured value of X for platinum and that recorded in the literature may be due to a difference in the physical form of the specimens of platinum measured.

Some preliminary experiments were carried out on the susceptibility of the platinum tube in a vacuum but trouble was experienced owing to leakage through the ground glass stopper of the susceptibility tube. It was finally decided to have the top of the susceptibility tube sealed on with the platinum tube inside.

SECTION II

Some Applications of the Conductimetric Method.

Abbreviations used in Section II of Thesis.

K	Specific conductivity.
Λ	Equivalent conductivity.
Λ_0	" " at infinite dilution.
c	Concentration in gram-equivalents per 1000 c.c.

SECTION II

Introduction.

An extensive survey of the literature on conductimetric titrations has been given in a thesis of E.C. Righellato[1]. He also describes applications of the method in the investigation of leather extracts and in the determination of the mobilities of the cations of weak bases.

In the present work a further application of conductimetric titrations to the investigation of leather tan extracts is described. The method has been used to obtain the mobility of the pyridinium ion and also the mobilities of a number of acid anions.

Part I.

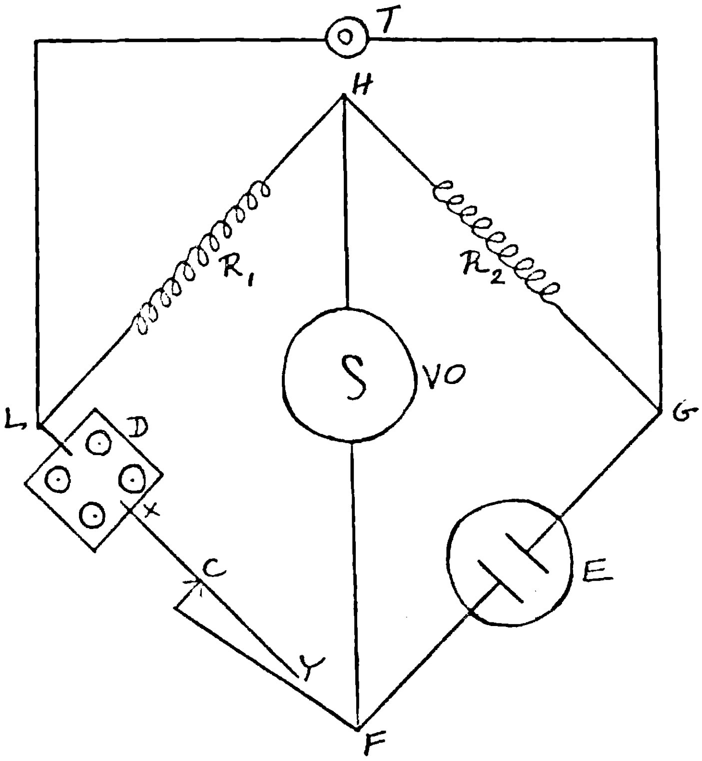
General Experimental.

The primary requirement of the work was for apparatus for determining the conductivity changes of a solution during the process of titration.

The Bridge.

The first type of bridge used was as shown in figure 1. The resistance R_1 and R_2 were nominally each equal to 100 ohms. They were "tapped off" from a non-inductively wound decade resistance box. D was a decade resistance box by Messrs. Leeds and Northrup and was of the low inductance type. XY was a uniform Pt-Cu bridge wire[1]. A single telephone earpiece served to detect the null-point and as source of current a valve oscillator of the Woolcock and Murray-Rust[2] type was used. This was screened by enclosing it in an iron box and it was placed remote from the bridge. The "supply leads" were of metal shielded copper wire and were arranged to run at right angles to the direction of the bridge wire. Both the oscillator screen and the casing of the "supply leads" were earthed. A double-pole double-throw switch permitted the oscillator leads to be reversed in direction of application to the bridge and also served as an on-off switch. Heavy gauge Cu wire was used for connections.

FIGURE I.



XY 100 cm. uniform bridge wire of Pt-Cu.

C Sliding contact.

D Decade resistance box.

E Conductivity cell.

VO Valve oscillator.

T Single telephone earpiece.

R_1, R_2 Equal resistances of approximately 100 ohms.

Calibration of Resistance Box.

The resistance box used was calibrated by comparison of each individual resistance with the corresponding resistance of a low inductance decade box recently calibrated at the National Physical Laboratory. The usual Wheatstone bridge circuit was used for the purpose; the details of the actual apparatus used are described in a thesis of W.H. Banks[3]. The results of this calibration are given in Table I.

TABLE I.

Calibration of Low Inductance Decade Resistance Box by Messrs. Leeds and Northrup.

Resistance in ohms.

Nominal Resistance	True Resistance	Nominal Resistance	True Resistance
1000	1000.1	100	100.07
2000	2000.8	200	199.96
3000	3000.1	300	299.96
4000	4000.0	400	399.95
5000	5000.0	500	500.01
6000	6000.6	600	599.98
7000	7003.7	700	699.99
8000	8000.7	800	799.92
9000	9000.7	900	899.88

The other two decades were calibrated in the same way and in only one instance was the agreement poorer than that shown above. The poorest agreement was shown in the case of the unit where the true resistance was found to be 1.032 ohms. This, however, was always used in conjunction with other coils making up a total resistance of 70 ohms or more. The error due to the unit coil, therefore, amounted to less than 1 in 2000.

The resistances R_1 and R_2 were measured in the same way and found to be 99.63 and 99.85 ohms respectively

$$\text{i.e.} \quad \frac{R_2}{R_1} = 1.002 \, .$$

The total resistance of the metre bridge wire was 15.954 ohms.

Calculation of Conductivity from Bridge Readings.

The results were calculated as follows:- at the null point, i.e. with minimum sound in the telephone

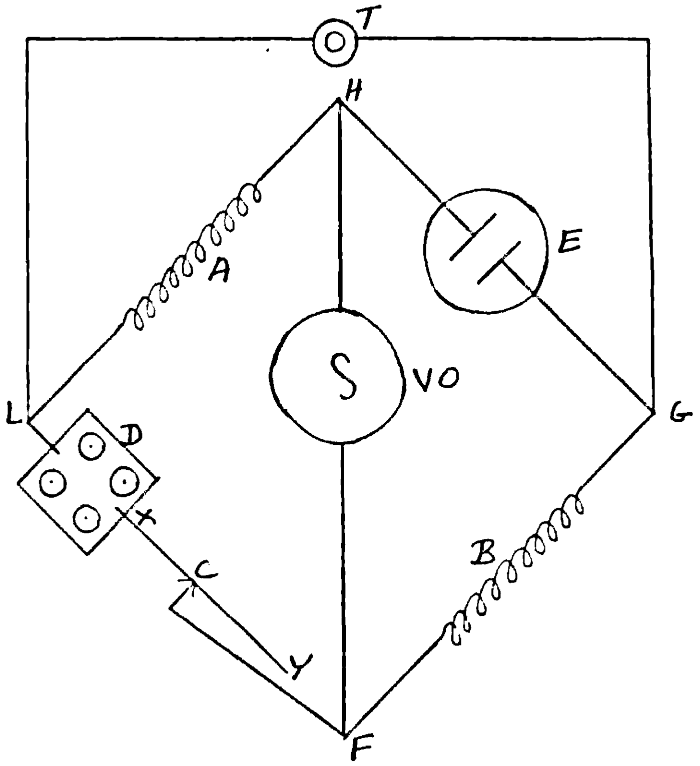
$$\frac{R_2}{R_1} = \frac{\text{Resistance of electrolyte in cell}}{\text{Resistance in Box D + Resistance bridge wire XC}} \, .$$

Resistance of electrolyte in cell = 1.002 (Resistance in Box D + Resistance of bridge wire XC).

Specific conductivity of electrolyte in cell =

$$\frac{\text{Cell constant}}{1.002\,(\text{Resistance in Box D + Resistance of Bridge Wire XC})}$$

FIGURE II.



XY	100 cm. uniform bridge wire of Pt-Cu.
C	Sliding contact.
D	Decade resistance box.
E	Conductivity cell.
VO	Valve oscillator.
T	Single telephone earpiece.
A,B	Equal resistances of approximately 316 ohms.

of purified water. This made it possible to measure the conductivity of the water to be used in a titration, a precaution which previously had to be neglected.

On the first arrangement it was found that the null point was poorly defined for large resistances in the cell whilst with the second arrangement it was difficult to obtain an end-point for small resistances. The accuracy of the final result, however, differed little according to the method used. At first either the first or second arrangement was used according as the resistance to be measured was small or large. Eventually the second was used exclusively partly to avoid changing over from one to the other, but chiefly in order to obtain strictly comparable results.

Temperature Control.

The specific conductivity of a solution changes very rapidly with change of temperature. For this reason, a well-regulated thermostat was essential.

The thermostat used consisted of a glass tank of water, well stirred and fitted with a constant water level device to compensate for losses by evaporation. The temperature was controlled by a toluene regulator operating a carbon lamp through a relay: it was maintained at 25°C (±0.02°C) throughout the work. A Beckmann thermometer was standardised by means of a standard thermometer and kept immersed in the thermostat to act as a check on the temperature. The water of the thermostat was earthed. A metal shelf was fitted to the side of the tank to accommodate the conductivity cell. Leads from the cell were dipped into two mercury cups resting in the water of the thermostat; the connecting wires from the bridge also dipped into these. This device served to suppress heat interchange through the connecting wires between the electrodes of the cell and the atmosphere.

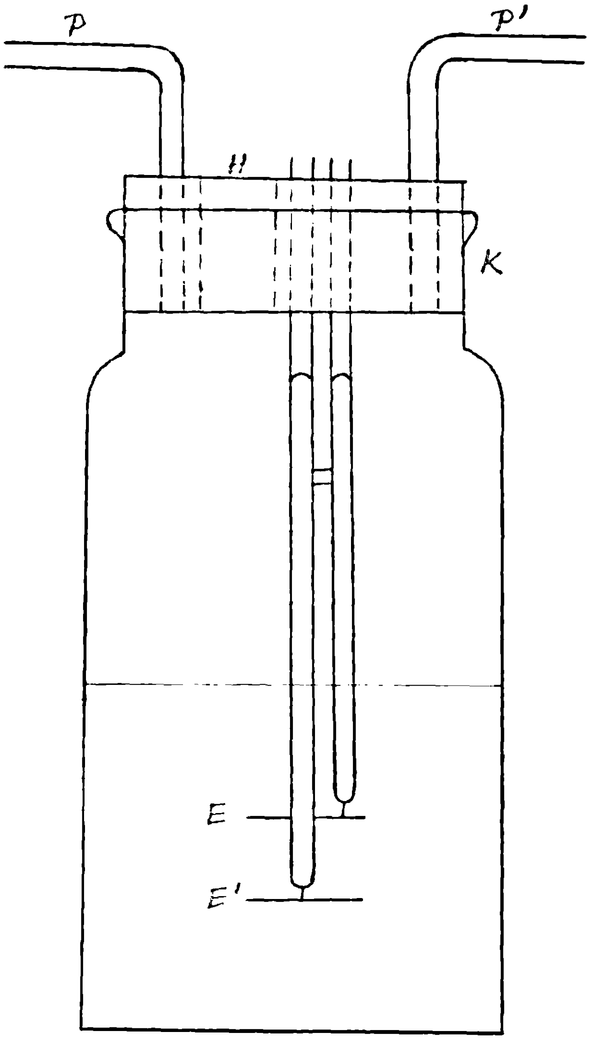
Before commencing a titration the cell was filled with the liquid to be titrated and left in the thermostat with occasional shaking until the temperature as shown by the conductivity remained constant. This usually took about half an hour. During a titration where only small additions were being made it was not usually found necessary to wait for the temperature to become constant as two succeeding readings agreed within the prescribed limits of error.

The Conductivity Cell.

The type of conductivity cell used is shown in figure III. A well-seasoned glass bottle of about 500 c.c. capacity was fitted with a waxed cork. Two glass tubes very firmly fixed in this cork were connected with a rigid support; into the lower ends of these tubes were sealed the platinum wires connected to the electrodes, E,E'. The tubes contained mercury into which were dipped amalgamated copper leads to make connection with the bridge circuit. The electrodes consisted of horizontal platinum discs of about 4 sq. cm. area; the tube

FIGURE III.

Conductivity Cell.



P,P' Inlet and outlet tubes for purified air.

E,E' Platinum electrodes.

K Waxed cork closing cell mouth.

H Entry through cork for burette tip.

carrying the lower disc passed through a hole in the upper one. The cork also carried two bent glass tubes, P,P', which served for the passage of pure air through the cell when necessary and which were closed at other times by means of rubber "policemen". A fifth hole, H, in the cork allowed for the introduction of the burette tip which was extended by means of a glass jet and piece of rubber tubing. This hole was closed with a small cork when not in use.

The electrodes were platinised originally and when necessary afterwards, i.e. when the null point became more indefinite than usual and the platinum black showed signs of flaking off, by the following process. The electrodes were immersed in a solution containing 1 gm. of chloroplatinic acid and 0.008 gm. lead acetate in 30 c.c. water; a current was passed between them just sufficient to bring about a gentle evolution of gas. The direction of the current was reversed every five minutes until a deep coating of platinum black was deposited. The electrodes were then washed thoroughly to remove adsorbed salts. The electrodes were always kept standing in water to prevent drying.

Determination of Cell Constant.

A knowledge of the cell constant is essential for the calculation of the specific conductivity of the solution in the cell. As this constant changes slightly from time to time it was necessary to measure it periodically throughout the work. According to Parker and Parker[5] the specific conductivity of a solution of potassium chloride containing 0.7463 gm. in 1000 gm. water (both apparent weights in air) is 0.00140789 at 25°C. A.R. potassium chloride was recrystallised twice from conductivity water (see below) and dried in the vacuum oven till the weight was constant. 0.7463 gm. was weighed in a small tube and slipped into a flask containing exactly 1000 gm. conductivity water. The cell was filled with about 200 c.c. of this solution and placed in the thermostat at 25°C. The resistance of this solution was measured after the temperature had become constant.

Cell constant = 0.00140789 x Measured resistance of solution

Specific conductivity of an electrolyte = Cell constant x Apparent conductivity.

Conductivity Water.

For the earlier part of the work "boiled out" water prepared free from air as described by Righellato[1] was considered good enough. As the earlier work was carried out with the first type of bridge arrangement it was not possible to measure the conductivity of each batch of water used. Later, however, the conductivity of a number of representative batches was measured after pipetting the water into the cell as in an experiment. The mean conductivity was found to be approximately 2 gemmhos. This value was negligible in dealing with material such as the tan extracts and was neglected. It became appreciable in connection with the determination of acid mobilities and it was during this work that this method of obtaining water was discarded.

For the later work conductivity water prepared in a still of the type described by Bourdillon[6] was used. The conductivity of this after pipetting into the cell varied from 0.8 to 1.0 gemmhos.

Calibration of Apparatus.

A calibrated set of brass weights was used for weighing. Graduated flasks were calibrated by weighing the water required to fill them to the mark and pipettes by weighing the water they delivered. The weights of water were converted to true cubic centimetres by reducing the weight to vacuum and temperature to 4°C.; the table given by Findlay[7] was used for this purpose. Burettes were calibrated by the Ostwald method using a pipette of 2 c.c. capacity. A calibration curve was plotted for each burette and all burette readings were corrected by this means.

The results of the calibration of the pipettes used are given in table II.

TABLE II

Temperature 17°C.

Nominal value of pipette.	Mean weight of water.	Corrected value.
2 c.c.	1.988 gm.	1.99 c.c.
5 c.c.	4.797 gm.	4.81 c.c.
10 c.c.	9.875 gm.	9.90 c.c.
25 c.c.	24.911 gm.	24.97 c.c.
50 c.c.	49.779 gm.	49.89 c.c.

Standard Solutions.

Standard alkali solutions of approximately tenth normal concentration were in use throughout the work. Their preparation is best described here.

All solutions were prepared using "boiled out" or, preferably, conductivity water. All the alkalies except pyridine were stored in a reservoir with attached burette and soda lime tube to prevent contamination with carbon dioxide. Sodium and potassium hydroxide solutions were stored in nickel vessels. The solutions were prepared as follows: the reservoir was swept out with purified air and almost filled with pure water (about two litres), purified air was passed through for about half an hour, the required quantity of alkali was introduced and well mixed with a current of purified air.

Sodium Hydroxide.

A.R. sodium hydroxide was used and the sticks well washed with pure water before dissolving. An approximately tenth normal solution of hydrochloric acid was prepared and standardised gravimetrically. Strength = 0.131 N. 25 c.c. of this solution was titrated with the sodium hydroxide solution using first phenolphthalein and then brom-phenol-blue as indicators. According to R.B. Warder[8] the phenolphthalein end-point occurs when all the hydroxide and half the carbonate are neutralised, whilst methyl orange gives the total alkali (brom-phenol-blue changes at the same pH as methyl orange).

Strength using phenolphthalein 0.125 N.
" " brom-phenol-blue 0.126 N.
∴ Strength of carbonate 0.002 N.
∴ Strength of hydroxide 0.124 N.
Total alkali strength 0.126 N.

Potassium Hydroxide.

Potassium hydroxide solution was prepared and standardised in the same way as sodium hydroxide.

Strength using phenolphthalein 0.0649 N.
" " brom-phenol-blue 0.0654 N.
Strength of carbonate 0.0010 N.
" " hydroxide 0.0644 N.
Total alkali strength 0.0664 N.

Barium Hydroxide.

About 20 gm. commercial barium hydroxide was dissolved in distilled water and shaken until the crystals disappeared leaving the barium carbonate as a powder. This was allowed to stand for two days to settle and then siphoned off into the container through which a current of pure air had been passed. The solution was standardised by titrating against potassium hydrogen tartrate using phenolphthalein as indicator.

Strength 0.03907 N.

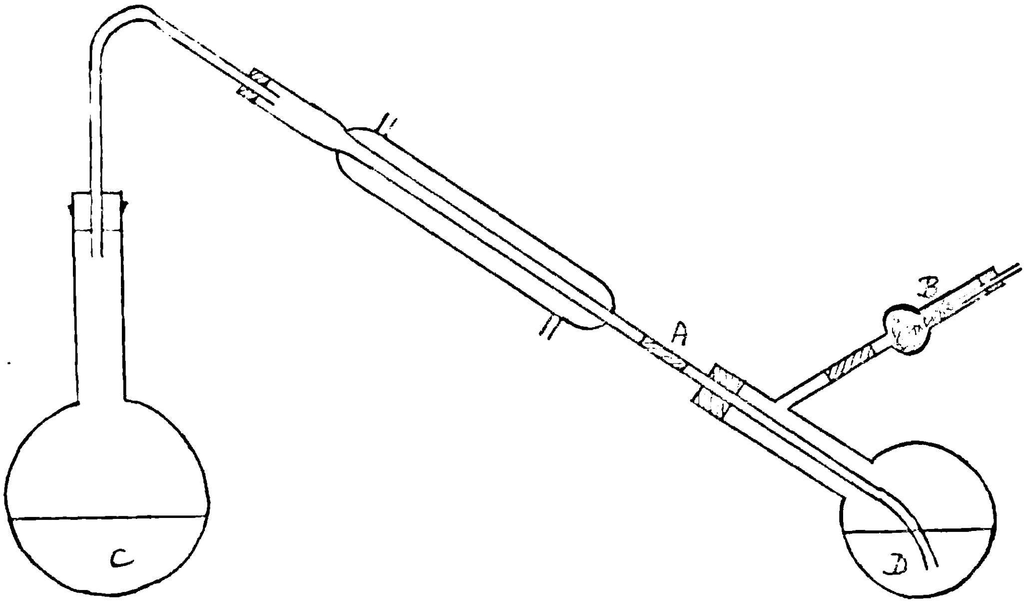
Ammonium Hydroxide.

Ammonia was distilled over potassium hydroxide as in figure IV. The receiving flask was marked roughly in 50 c.cs. When sufficient was thought to have distilled the apparatus was quickly disconnected at A and clipped. Pure air was blown in at B and some ammonia solution collected from the flask at A. This was titrated roughly with standard hydrochloric acid to determine how much was needed. The required amount of ammonia solution was blown into the reservoir of water by means of a current of pure air.

The ammonium hydroxide solution was standardised by titration against the standard hydrochloric acid solution using methyl orange as indicator. It was not possible to determine the amount of carbonate present, as phenolphthalein

FIGURE IV.

Distillation of Ammonia.



B	Soda lime tube.
C	0·880 ammonia and potassium hydroxide.
D	Boiled out water.

cannot be used for the titration of ammonia. It was assumed from the care taken in the preparation that the amount of carbonate present was negligible.

Strength of ammonium hydroxide solution = 0.2810 N.

Pyridine.

Pyridine was dried over potassium hydroxide and distilled, B.P. 114.5°C. 23 c.c. was introduced into the reservoir of pure water as described above, The solution obtained was standardised by a conductimetric titration (see below) with 0.131 N hydrochloric acid solution. The result of the titration is shown in table III and in figure V. 9.90 c.c. pyridine solution was taken and the end-point obtained was 9.63 c.c. acid.

$\therefore$ Strength of pyridine solution = 0.127 N.

FIGURE V

Standardisation of approx. 0·1 N
Pyridine Solution.

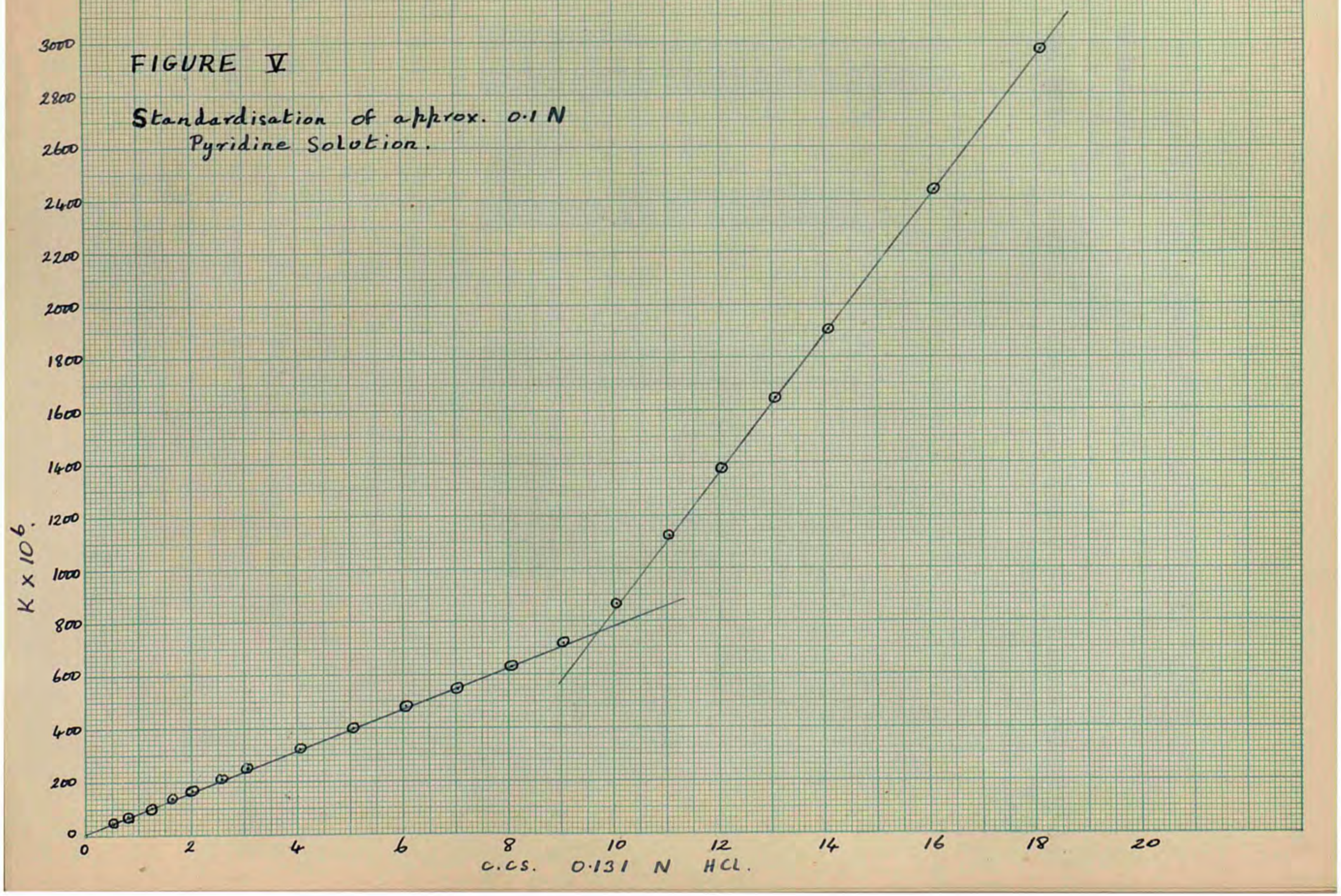


TABLE III

Standardisation of pyridine solution.

cc. HCl.	Resistance in box, in ohms.	Bridge reading in cms.	Total resistance	Conductivity x 10^6 corrected for dilution and cell constant.
0.00				0
0.50			1970	50.56
0.80			1336	74.66
1.20			951	105.1
1.60	730	12.0	731.92	136.1
2.00	593	13.0	595.08	168.7
2.50	483	8.0	484.28	207.8
3.00	408	9.5	409.52	246.3
4.00	312	10.5	313.68	323.0
5.00	253	13.5	255.16	399.2
6.00	213	12.5	215.00	476.1
7.00	184	12.5	186.00	553.0
8.00	162	9.5	163.52	632.2
9.00	143	7.5	144.20	719.9
10.00	118	6.5	120.08	868.8
11.00	92	9.5	93.52	1121
12.00	75	7.5	76.20	1382
13.00	63	8.0	64.28	1646
14.00	54	10.3	55.65	1910
16.00	42	12.0	43.92	2443
18.00	35	9.0	36.44	2973

Method used in carrying out a conductimetric titration.

The electrodes were first removed from the cell and drained but not dried; the cell was drained and dried as completely as possible with filter paper. A suitable quantity of the material to be titrated was introduced into the cell either by weight or by pipetting from a stock solution. The volume of solution was made up to 200 c.c. by pipetting in pure water. It was known that a volume of 200 c.c. in the cell used was sufficiently large for there to be no change of cell constant with further additions. The electrodes were replaced and the cell placed in the thermostat until the temperature of the solution was constant. The conductivity of the solution in the cell was measured. The extended tip of the burette containing the reagent to be added was completely filled with the solution in the burette and introduced into the cell until the tip was about half an inch from the surface of the liquid. It was then possible to add the reagent without loss by splashing. If a drop of liquid remained on the tip it was removed by raising the cell until the liquid in it touched the drop and removed it. Small additions of reagent were made, the cell was well shaken each time and the conductivity measured. Two readings were made after each addition, the cell being well shaken between the two; these usually agreed but if not further readings were taken until a constant value was obtained.

The specific conductivity was calculated in the manner described above, with the addition of a dilution correction, whereby each measured conductivity was multiplied by the ratio

$$\frac{\text{Total volume of solution in cell}}{\text{Initial volume of solution in cell}} .$$

This correction makes use of the fact that the specific conductivity of any electrolyte at constant temperature is roughly proportional to its concentration. It is only approximately correct since it ignores the slight mobility changes due to the diffusion of the ion atnosphere. In applying the same correction to mixtures containing weak electrolytes it ignores in addition the small changes in the degree of dissociation, but it is still a close approximation. For convenience of calculation tables were prepared showing (a) the resistance of a given length of bridge wire and (b) the logarithm of the dilution correction for a given volume of added reagent.

The results having been calculated a curve was plotted for each titration showing volumes of added reagent against the corresponding specific conductivities.

Accuracy of the Method.

Using either of the bridge arrangements described above the conductivity of a solution could be measured with an accuracy of 0.1%. In all cases the results were obtained from curves drawn on a much larger scale than those reproduced here. It has not been considered necessary to show the tabulated results of every conductimetric titration; representative curves are shown.

Summary.

A description of the apparatus and technique used in conductimetric titrations has been given.

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2. Woolcock & Murray-Rust. Phil. Mag. 5, 1130. (1928).

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4. H.J.S. Sand, in a review of "The Conductivity of Solutions" by C.W. Davies, Chapman & Hall, 1933 in Trans. Fad. Soc. 29, 8, p.878. (1933).

5. Parker & Parker. J. Amer. Chem. Soc. 46, 312 (1924).

6. Bourdillon, J.C.S. 103, 791 (1913).

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Mobility Values Used throughout Section II of Thesis.

In water at 25° C.

$H^{\cdot} = 349.72$		MacInnes, Shedlovsky and Longsworth. Chem. Reviews, August 1933.
$Na^{\cdot} = 50.10$		
$K^{\cdot} = 73.50$		
$C' = 76.32$		
$OH' = 196$	(approx. only)	
$NH_4^{\cdot} = 73.4$		Calculated from transport numbers of ammonium salts reported by MacInnes as being almost identical with those of the corresponding potassium salts.
$Ba^{\cdot\cdot} = 63.66$		Shedlovsky & Brown. J.A.C.S. (1934), <u>56</u>, 1066.
$HCO_3' = 45.0$		Kendall, J. Amer. Chem. Soc., 1916, <u>38</u>, 1480 and 2460.
$CO_3'' = 80$	approx.	Landolt-Bornstein, 5th Edn. P.1104 gives 70 as a very approximate value at 18°C; assuming a temperature coefficient of 0.02 per degree would make it 80 at 25°C.

Part II.

Examination of Tan Liquors.

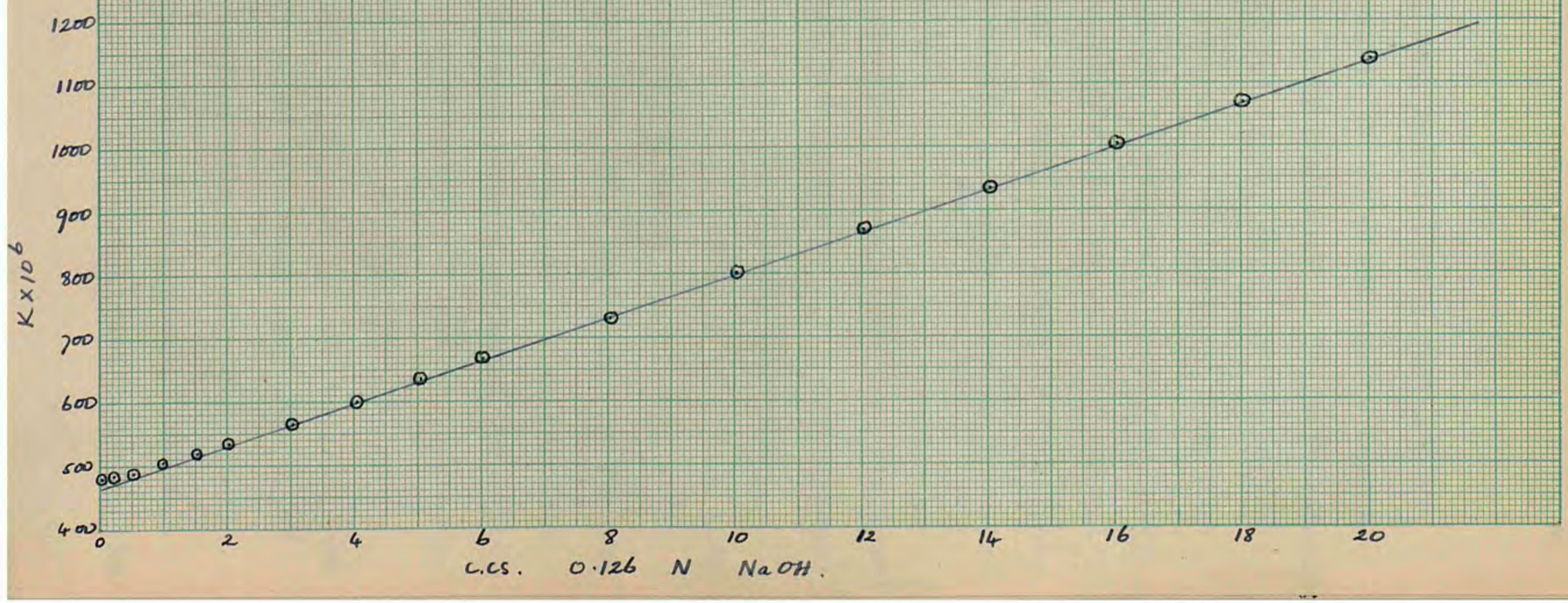
This work was undertaken at the suggestion of the British Leather Manufacturers' Research Association, for whom some applications of conductivity methods had previously been worked out in these laboratories[1]. The liquors supplied were reputed to be mimosa extracts that had been "doped", i.e. to which unknown substances had been added with a resultant lowering of the pH from 4.67 to values in the neighbourhood of pH 3. It was anticipated that conductimetric titrations with alkali would reveal the presence of added acids and would, by providing indications of their strength, facilitate their identification.

The Untreated Sample.

An untreated sample of mimosa extract (200 c.c. contained 25 c.c. tan liquor) was first titrated with 0.1 N sodium hydroxide. Neutralisation was not complete after the addition of 20 c.c. when the titration was discontinued. The curve (fig. VI) obtained was of the normal type for salt formation, and at first sight resembled the curve obtained in a similar titration of an extract of a leather that had been tanned with mimosa[2], i.e., after an initial kink the curve showed a linear relationship between specific conductivity and amount of sodium hydroxide added, corresponding to the

FIGURE VI

Titration of untreated sample of mimosa extract with sodium hydroxide.



progressive conversion of a weak acid into its sodium salt. Closer comparison showed however that whereas in the former work the straight line had a relative slope of 80 (corresponding to the sum of the mobilities sodium 50, anion 30), in the present case the slope was abnormally small, being only 53. Either the mobility of the anion is extremely small, or, more probably, sodium ions are being adsorbed or bound by the multivalent (colloidal?) anions of the tan, resulting in a conductivity decrease. This abnormality had to be borne in mind in considering the later results.

A sample of the untreated extract (200 c.c. contained 9.9 c.c. tan liquor) was next titrated with 0.1 N hydrochloric acid. The results, shown in fig. VII clearly show the reaction of the hydrochloric acid with the salt of a weak acid (buffer salt) in the extract, and, drawing the line a on the assumption that the mobility of the displaced anion is 30, the end point of the titration is 1.83 c.c., and the buffer salt content of the tan liquor is 0.024 gram-equivalents per litre. This acidified extract was now titrated with sodium hydroxide, in this titration the excess of hydrochloric acid is first neutralised, then the acid liberated from the buffer salt, and finally the tan. Fig. VIII shows this titration, the first points lie on a line with the theoretical slope ($\Lambda H - \Lambda Na$), and the final points have the same abnormally small slope already found in the titration of the untreated tan. For the

FIGURE VII

Titration of untreated sample of mimosa extract with hydrochloric acid.

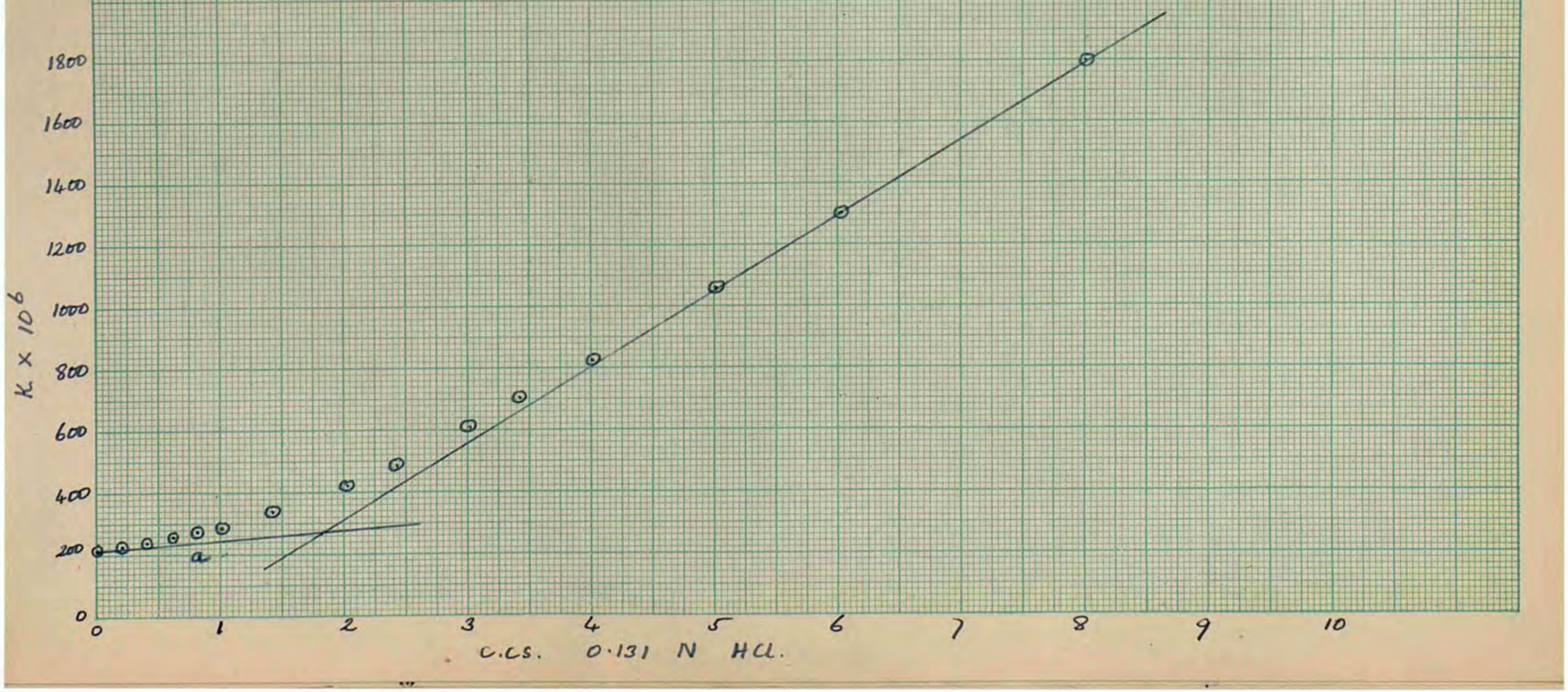
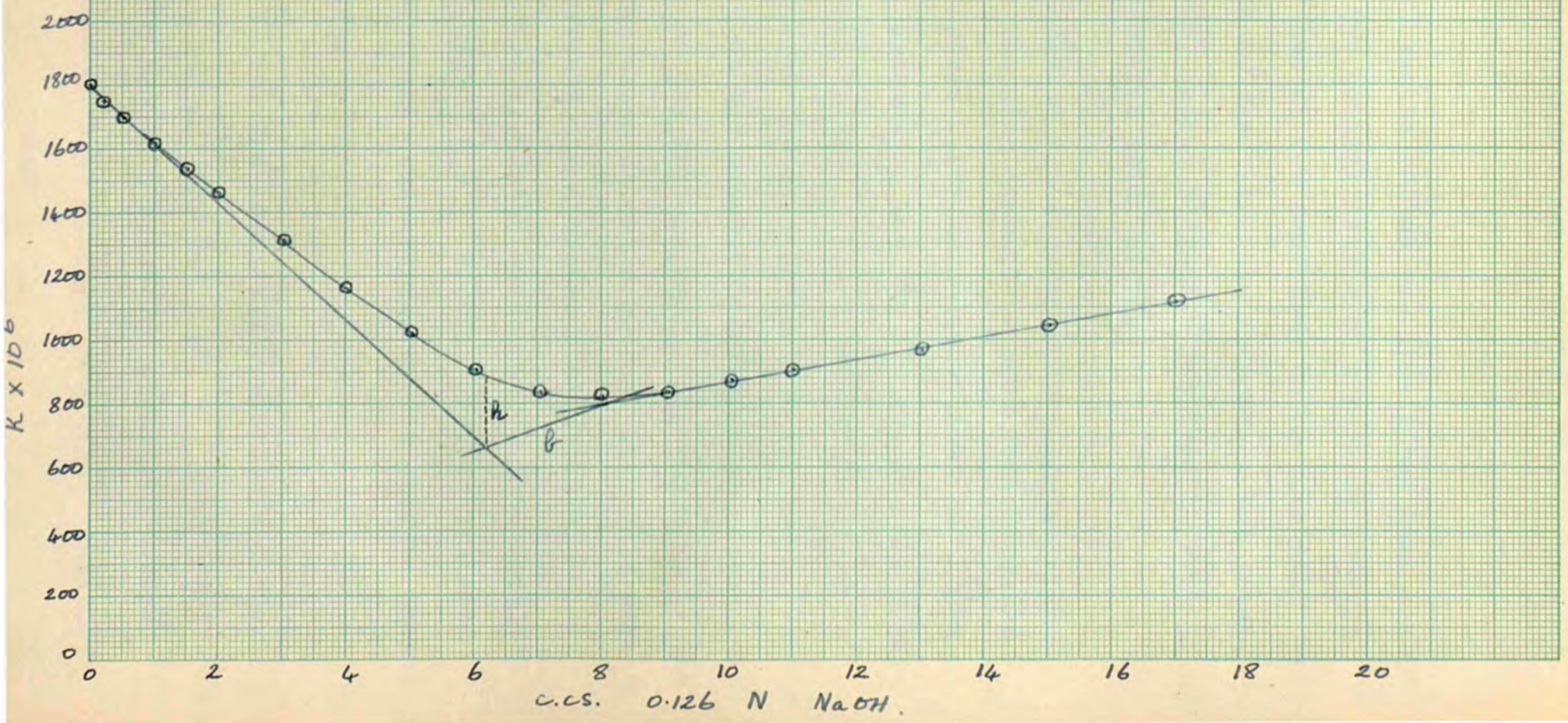


FIGURE VIII

Back titration of acidified untreated sample with sodium hydroxide.



intermediate part of the titration the line b has been drawn to correspond with the neutralisation of a carboxylic acid (anion mobility 30) and at the same time to be consistent with the ultimate section of the titration diagram. The intersection gives 6.2 c.c. sodium hydroxide required to neutralise the excess of hydrochloric acid, so that

$$8.00 - \frac{6.2 \times 0.126}{0.131} = 2.1 \text{ c.c. of hydrochloric acid}$$

have disappeared in the displacement of weak acid from the buffer salt; this gives 0.027 gram-equivalents per litre for the buffer salt content of the tan liquor, in fair agreement with the previous value. It now becomes possible to estimate the strength of the acid present in the tan as buffer salt. The height h on the graph (the divergence of the actual conductivity of the mixture NaCl + HX, where HX is the buffer acid, from the value it would have if this acid were undissociated) represents the specific conductivity ($K = 224 \times 10^{-6}$) of the liberated buffer acid, the concentration of which is $\frac{0.0255 \times 9.9}{200} = 0.00126$ gram-equivalents per litre. The equivalent conductivity of the acid is therefore

$$\frac{224 \times 10^{-3}}{1.26 \times 10^{-3}} = 178.$$

Taking $\Lambda_0 = 350 + 30$ for the acid, its approximate dissociation constant is $\frac{\Lambda^2 c}{\Lambda_0(\Lambda_0 - \Lambda)} = 5.2 \times 10^{-4}$. This application of Ostwald's dilution law to a solution containing sodium chloride gives a value that is slightly too high; but the detailed application of interionic force corrections is hardly justified by the accuracy of the figures, and the value may be taken as $K = 5.0 \times 10^{-4}$. This value is in fair agreement with the value $K = 4 \times 10^{-4}$ previously found[3] for the strength of the acid present as buffer salt in an extract of a leather tanned with sumach, and the acids may possibly be identical. It is remarkable, however, that in the previous work on leather extracts, mimosa tanned leathers were found to be free from buffer salts. It must therefore be concluded either that the buffer present in sumach is fixed by the hide whilst that in mimosa is not; or, and in view of the similarity in dissociation constant, and probably structure, this seems the more probable, that mimosa tan contains so much less buffer salt than sumach that the amount fixed by leather tanned with mimosa is negligibly small.

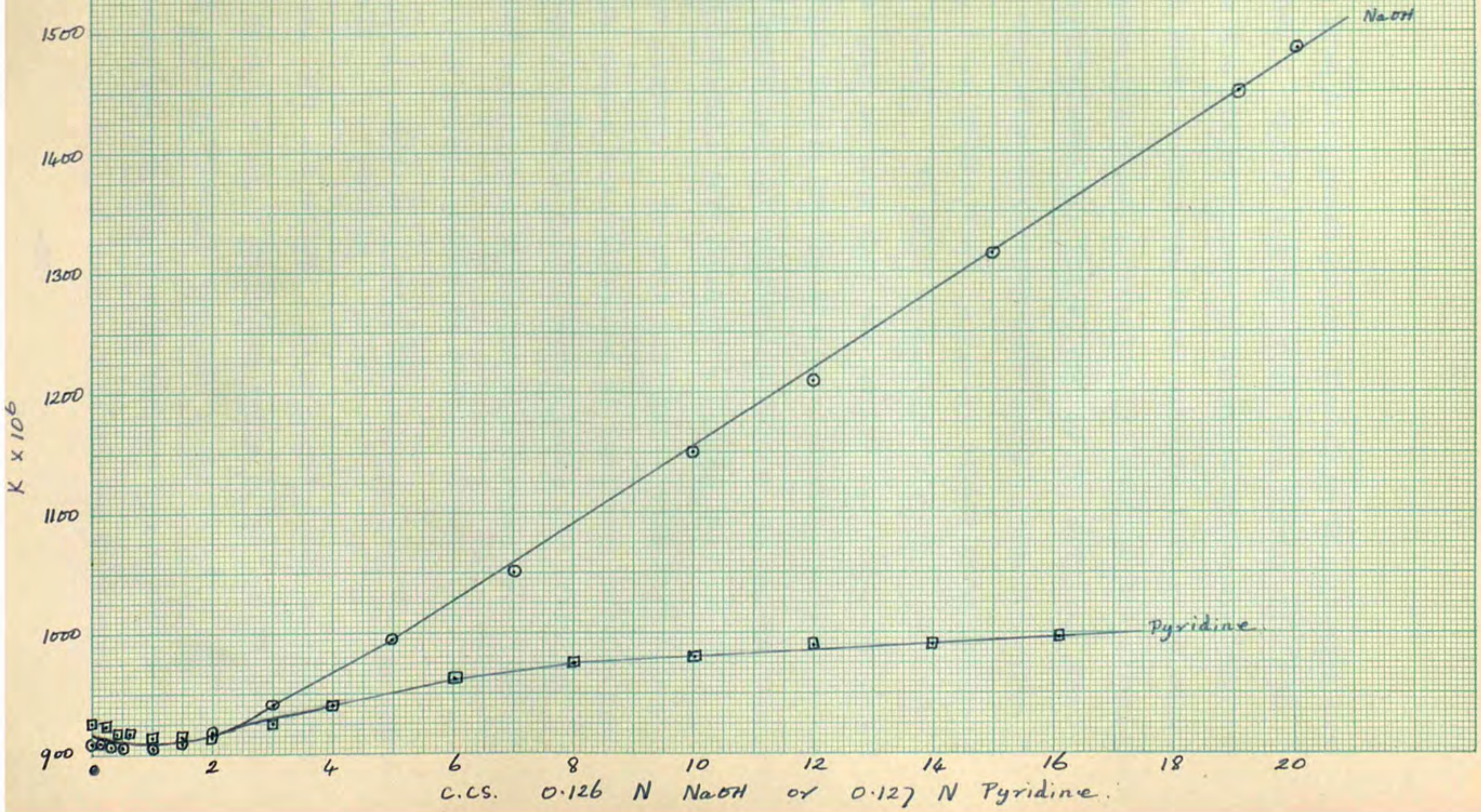
Finally, the initial conductivity of this untreated sample needs consideration. At the beginning of the titration this specific conductivity was 205×10^{-6}, and the solution, as has been mentioned, contained 0.00126 gram-equivalents per litre of buffer salt. Taking $50 + 30 = 80$ as the approximate Λ_o value of this salt, the contribution of buffer salt to the total conductivity was $80 \times 1.26 \times 10^{-6} = 100 \times 10^{-6}$ r.o., that is, half the total conductivity; as the behaviour of the tans themselves show them to be feeble electrolytes which would contribute little to the conductivity, the rest of the conductivity is probably due to small amounts of salts, present in approximately the same concentration as that of the buffer salt. This is in agreement with our earlier results on leather extracts in which the amount of salt found was comparable with that of buffer salt. Conductivity results therefore indicate that the total salt concentration of the solution examined was approximately 0.002 gram-equivalents per litre, corresponding to 0.004 gram-equivalents per 100 c.c. of the tan liquor sample. At our instance, the ash of all the samples was determined in the laboratories of the British Leather Research Association, and the figure supplied for the sample under discussion was 0.136 gm. per 100 c.c. liquor. Taking 40 as an average equivalent weight (CaO = 28, Na_2CO_3 = 53), the figure agrees reasonably well with our interpretation of the conductivity results.

Samples 1 and 2.

Specimens of these two samples (200 c.c. contained 25 c.c. tan liquor) were titrated with approximately 0.1 N solution of both pyridine and sodium hydroxide. The results were similar and the curves for sample 1 are shown in fig. IX. The presence of a reasonably strong (carboxylic) acid is clearly shown in the early part of the titration, but onwards from the point 2.25 c.c. at which the two curves diverge it is evident that only the feebly acidic tans are now present; the

FIGURE IX

Titration of sample I of mimosa extract with sodium hydroxide and with pyridine.



sodium line from this point on has the slope 53, as with the untreated sample, whilst the pyridine line hardly rises at all owing to the slight degree of interaction between the tan and the weak base. From the first end-point it is calculated that the concentration of carboxylic (?) acid in the solution is 0.00142 equivalents per litre, and as the original sample was diluted approximately eight-fold before this titration was carried out, this corresponds to 0.0114 equivalents per litre in sample 1 itself. It will be noticed that this concentration of free acid is less than the buffer salt content (0.027 equivalents per litre) of the untreated sample, so that a curve of the type described for sample 1 might be due to the addition of 0.0114 equivalents per litre of a <u>strong</u> acid to the untreated tan liquor. To test this hypothesis more closely the pH of the sample was calculated as follows: sample 1 on this basis would contain 0.0114 equivalents per litre of liberated acid together with 0.0156 equivalents per litre of the salt of this acid; hence we have

$$\frac{[H^{\cdot}][X']}{[HX]} = \frac{[H^{\cdot}]([H^{\cdot}] + 0.0156)}{(0.0114 - [H^{\cdot}])} = 5.0 \times 10^{-4} \text{ (see above)}$$

and this gives $[H^{\cdot}] = 0.00035$. This corresponds to pH = 3.46 which is in fair agreement with the value of pH = 3.32 determined by the British Leather Research Association. The calculations therefore provide strong support for the view that the acidity of the treated sample 1 is due to a partial displacement of the acid from the buffer salt present in the untreated sample, and no conclusions can be drawn as to the identity of the strong acid added. The above suggestions might have been directly tested by seeing whether a titration of sample 1 with hydrochloric acid showed a deficiency of buffer salt compared with the untreated sample, but unfortunately sufficient of the sample was not available to put this work in hand. One other point regarding sample 1 is worthy of note. Its conductivity is relatively very high compared with the untreated liquor, and the increase is far higher than can be attributed to the addition of strong acid. Salt, as well as strong acid, has therefore been added, and approximate calculations similar to those made on sample 7 indicate that about twice as much salt as acid have been added, agreeing with a finding of the British Leather Research Association that the ash of this sample is 0.334 gm. per 100 c.c., compared with 0.136 gm. per 100 c.c. for the untreated sample.

<u>Sample 2.</u>

The titration curves were similar to those of sample 1, but 2.6 c.c. of alkali were necessary to liberate the free acid, giving 0.00164 gram-equivalents per litre for its concentration in the solution titrated, or 0.0131 gm.-equivalents per litre in sample 2. Further, there is a greater drop in conductivity (compared with sample 1) during the neutralisation, and it can be calculated that the contribution of the free acid to the initial specific conductivity was 158 x 10^{-6} r.o. This would correspond to an apparent dissociation constant of 1.75 x 10^{-4}; but if we suppose, as before, that we are actually dealing with the original buffer salt from which some of the acid has been displaced by a strong acid, then in sample 2 the concentrations are free acid, 0.0131 equivalents per litre, buffer salt 0.0139 equivalents per litre. Hence

$$\frac{[H^{\cdot}][X']}{[HX]} = \frac{[H^{\cdot}]([H^{\cdot}] + 0.0139)}{(0.0131 - [H^{\cdot}])} = 5.0 \times 10^{-4} ,$$

and this gives $[H^{\cdot}] = 0.00044$. This corresponds to pH = 3.36 which is in poor agreement with the British Leather Research Association value 3.00, but nevertheless it gives

$$K = 0.0004 \times 381 \times 10^{-3} = 152 \times 10^{-6} \text{ r.o.}$$

for the conductivity of the acid, which agrees extremely well with the value deduced from the neutralisation curve. Finally, in sample 2, the conductivity due to neutral added salts is considerably less than in sample 1, and the B.L.R.A. also find a much smaller ash content (0.239 gm. per 100 c.c.) for this sample.

The B.L.R.A. suggest the presence of an acid salt, e.g. sodium bisulphate. They have also detected the presence of a little lactic acid (0.017 gm. per 100 c.c.).

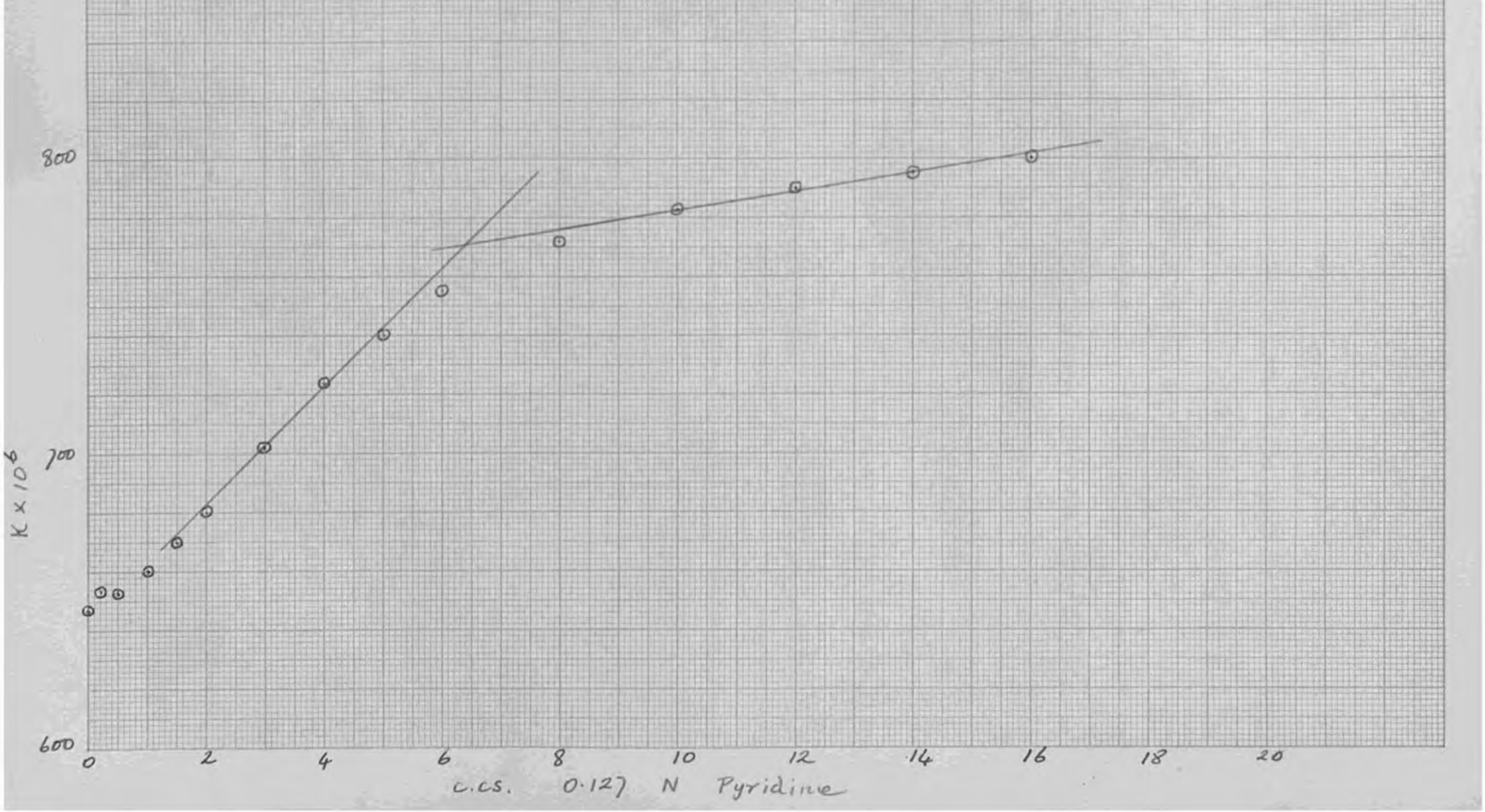
Samples 3, 4, 5, and 6.

These all resembled each other in type, and differed from samples 1 and 2 in that the free acid present was obviously much weaker. These four samples were only titrated with pyridine, and not with a strong base. In every case 25 c.c. tan liquor in 200 c.c. was titrated. The curve for sample 3 is shown in fig. X.

Sample 3 gave an end-point of approxmately 6.5 c.c. of 0.127 N pyridine corresponding to an acid concentration of 0.0083 equivalents per litre in the solution titrated, or 0.066 equivalents per litre in sample 3 itself. Sample 4 gave an end-point of 8.8 c.c., corresponding to acid concentrations of 0.0112 equivalents per litre in the solution titrated, or 0.090 equivalents per litre in the sample itself. As regards the strength of this acid, or acids, the fact that the curves show little hydrolysis proves that the added acid is much stronger than the tan acids, probably of dissociation constant not less than 10^{-6}. On the other hand the curves show that the free acid contributes very little to the conductivity of the sample. This curious anomaly suggests that the addition made to the tan in both these cases consisted of an acid with a dissociation constant of the order 10^{-5} in the presence of a large excess of one of its salts. Another unusual feature of these curves is the small slope of the neutralisation curve; the possibility suggests itself that the free acid is colloidal, like the tan, and the effect of the addition agent may have been to strengthen the acidity of the tan micelles by some chemical interaction.

FIGURE X

Titration of sample 3 of mimosa extract with pyridine.



Extracts 5 and 6 are closely similar to extract 3, except that the liberated acid exerts a higher conductivity, especially in 6; this suggests a smaller content of buffer salt, and this idea is strengthened by the fact that the initial conductivities of these samples are the lowest of all the treated samples. In agreement with this, the B.L.R.A. reported ash contents of 0.188 gm. per 100 c.c. for sample 5 and 0.156 for sample 6, values not greatly larger than that of the untreated sample.

The B.L.R.A. have subsequently obtained the following results.

<u>Sample 3.</u>

The presence of chestnut extract was detected. The yield of furfural obtained on distilling the solution with hydrochloric acid is greater than that which is obtained from mimosa and is of the same order as that obtained from chestnut extract; the extract also contains manganese, which is present in chestnut extract and not in mimosa extract. The acidity of chestnut extract is due chiefly to the presence of gallic acid.

Acetic acid was also found by a qualitative test on the distillate from the acidified solution. This may be derived from the chestnut extract since other workers have found acetic acid in chestnut extract; a test made in the present experiments did not show the presence of acetic acid in chestnut extract.

Sample 4.

Chestnut extract and formic acid were found but not acetic acid.

Sample 5.

0.038 gm. per 100 c.c. of lactic acid was found.

Sample 6.

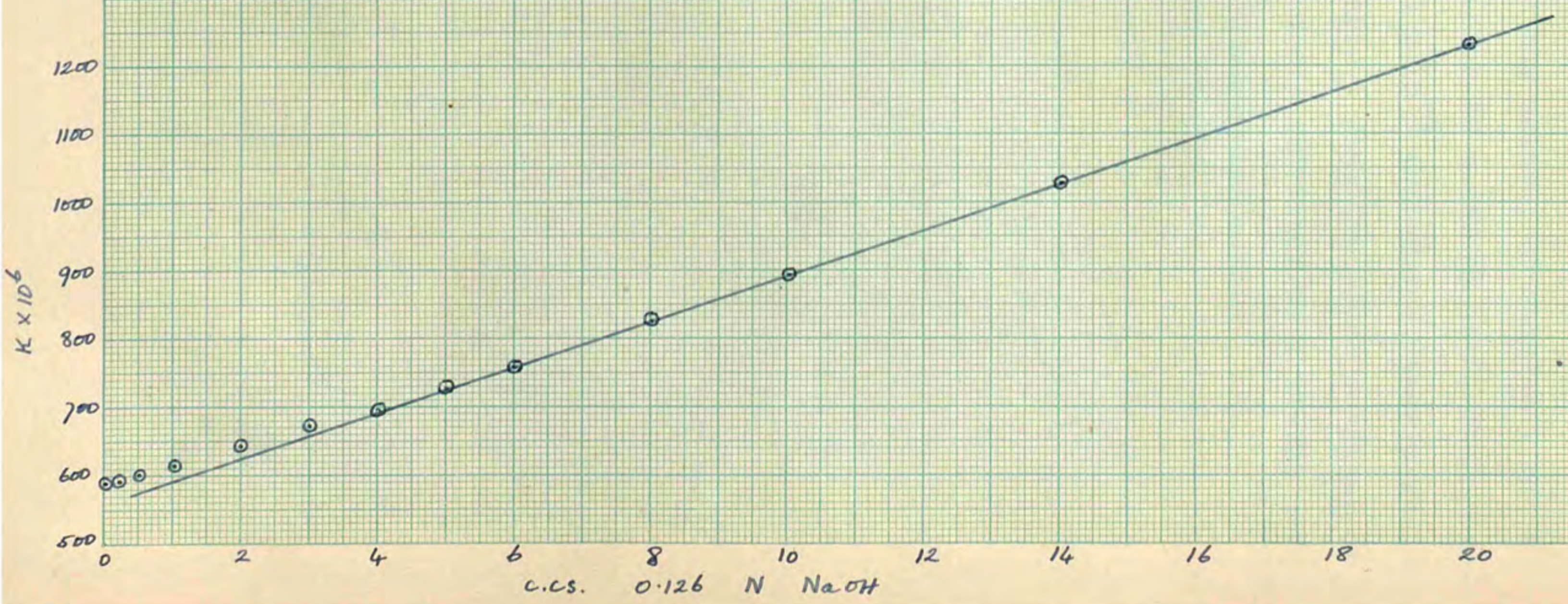
Tests for acetic, formic lactic acids and for chestnut extract gave negative results.

Addition of formic acid to untreated sample.

One other result deserves mention. In one of the measurements an attempt was made to simulate the shape of the curves for the treated samples by adding a small quantity of formic acid (20 c.c. 0.13 N acid per 100 c.c. sample) to the untreated sample. The solution obtained was titrated with sodium hydroxide; the curve (fig. XI) obtained was entirely unexpected. There was no trace of an acid of the strength of formic acid, the curve being parallel with that for the untreated sample, but higher throughout. The disappearance of the formic acid as such might have a chemical explanation, but perhaps it is more likely that the tan itself consists partly of salt and can exert a limited amount of buffer action, the hydrogen ions of the added acid being removed by metathesis or exchange adsorption. If this is true, the amounts of acid reported above as having been added to samples 1-6 would have to be increased by a further unknown quantity which has undergone reaction with the tan.

FIGURE XI

Titration of untreated sample of mimosa extract + formic acid with sodium hydroxide.



In conclusion, then, the acidity of samples 1 and 2 has been increased by the addition of a strong acid, which has displaced a weak acid of $K = 5 \times 10^{-4}$ that was already present in the tan in the form of a salt. With the other samples, on the other hand, considerably larger additions of a weaker acid (K probably equals $10^{-5} - 10^{-6}$) have been made.

Bibliography to Part II.

1. Righellato & Davies. Trans. Faraday Soc. 29, 437, (1933).

   Davies & Innes. J. Int. Soc. Leather Trades Chemists, Nov. 1932.

2. Righellato & Davies, loc. cit. Fig. 1, curve 4.

3. Righellato & Davies, loc. cit.

Part III

Determination of Mobilities.

Determination of the Mobility of the Pyridinium Ion.

Preparation of pyridine hydrochloride.

Pyridine was dried over potassium hydroxide and distilled. 50 c.c. was dissolved in 200 c.c. dry redistilled ether and dry hydrochloric acid passed in for about one hour. The precipitated hydrochloride was filtered, washed with ether and dried in vacuo over calcium chloride.

Chlorine found 30.68%, theoretical 30.70%.

A 0.0220 N solution of the hydrochloride was prepared. Owing to the deliquescent nature of the salt the weighing bottle and salt were dried in vacuo over calcium chloride before each weighing,both for the preparation of solution and for the analysis.

Hydrolysis and viscosity effects.

200 c.c. of a 0.00275 N solution was conductimetrically titrated with 0.126 N sodium hydroxide. The resulting curve is shown on figure XII. The high initial conductivity and curved neutralisation line are due to hydrolysis of the hydrochloride. The following experiment was carried out to determine the amount of pyridine it was necessary to add in order to suppress this hydrolysis. A fresh solution of the hydrochloride at the same concentration as before was prepared and

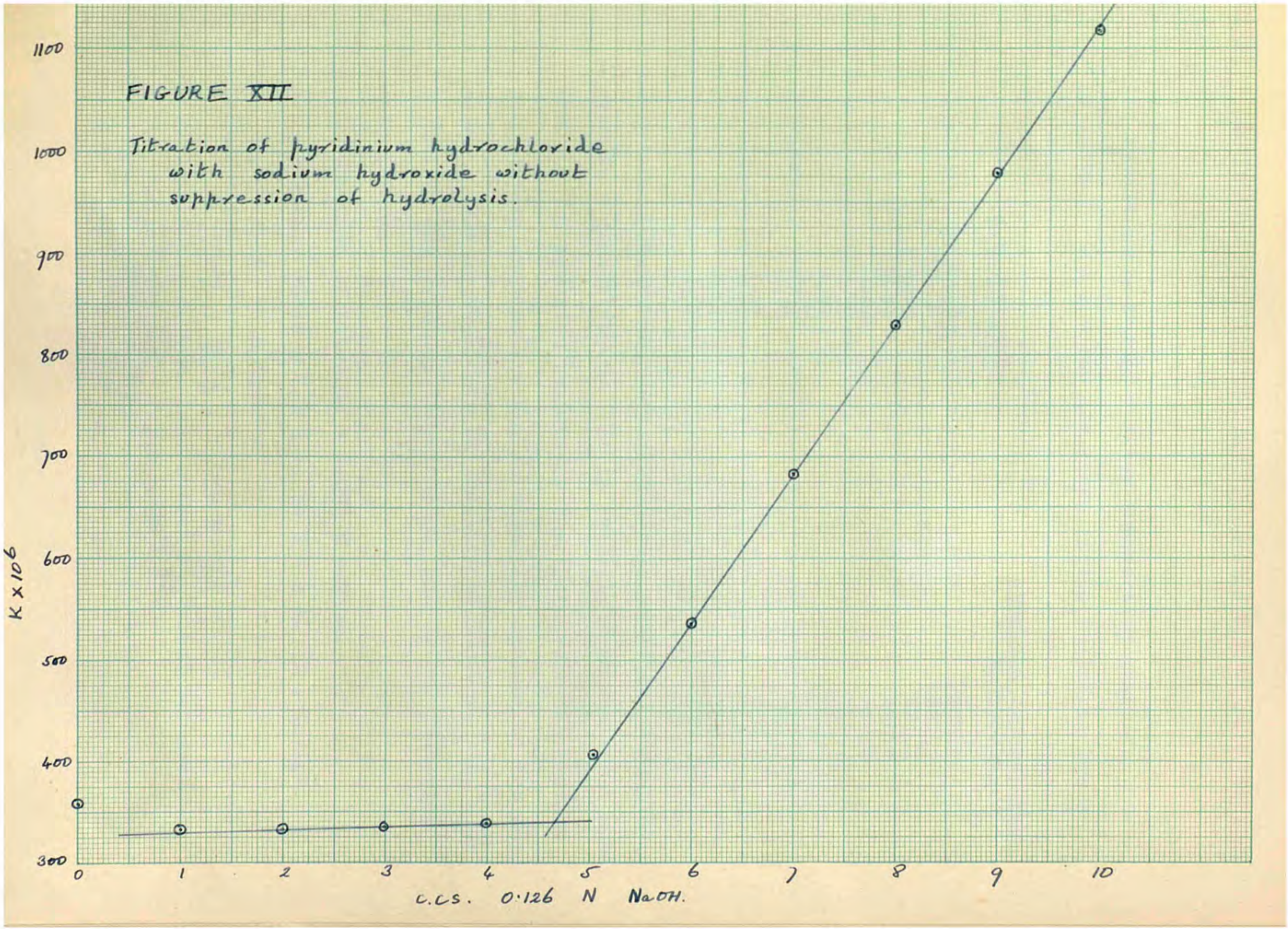


FIGURE XII

Titration of pyridinium hydrochloride with sodium hydroxide without suppression of hydrolysis.

its conductivity measured after consecutive additions of pyridine. The results are shown in the following table.

c.c. pyridine	specific conductivity in gemmhos.
0.00	356.1
0.10	321.7
0.20	321.3
0.30	320.7
0.40	320.3
0.60	319.4
0.70	318.6
0.80	317.6
0.90	316.4
1.00	316.6
2.00	313.9
4.00	308.4
8.00	297.5

The conductivity continually decreases and never reaches a steady value. It is probable that the first small addition of pyridine suppresses the hydrolysis and further conductivity changes are due to viscosity changes of the solution. This is confirmed by the work of Dunstan, etc.[1], on Viscosity and Chemical Constitution, and by the following calculation.

Strength of solution = 0.003 N approx.

Pyridine added = 0.1 c.c. to 200 c.c. of solution

$\therefore \quad [Py] = 0.00625\ N.$

$[PyH^{\cdot}] = [Cl'] = 0.003\ N$

$$\frac{[PyH^{\cdot}]\,[OH']}{[Py]} = 2.3 \times 10^{-9} \quad (2)$$

$$\therefore \quad [OH'] = \frac{0.00625}{0.003} \times 2.3 \times 10^{-9} \text{ approx.}$$

$$= 5 \times 10^{-9}$$

$$\therefore \quad [H'] = 2 \times 10^{-6}$$

$$\therefore \quad \text{Degree of hydrolysis} = \frac{2 \times 10^{-6}}{3 \times 10^{-3}} = 0.67 \times 10^{-3}$$

or 0.07%.

Increase in Δ for 1% hydrolysis = 0.01 (350 - 50, say)

= 3 r.o.

for 0.07% = 0.2 r.o.

True conductivity $= 321.7 \times 10^{-6} - 0.2 \times 0.000003 = 321.1 \times 10^{-6}$ r.o.

It was therefore considered sufficient to add 0.1 c.c. of pyridine as the error arising from hydrolysis is much smaller than the estimated final error. In the titration of a solution of twice the concentration of the above solution 0.2 c.c. of pyridine was added.

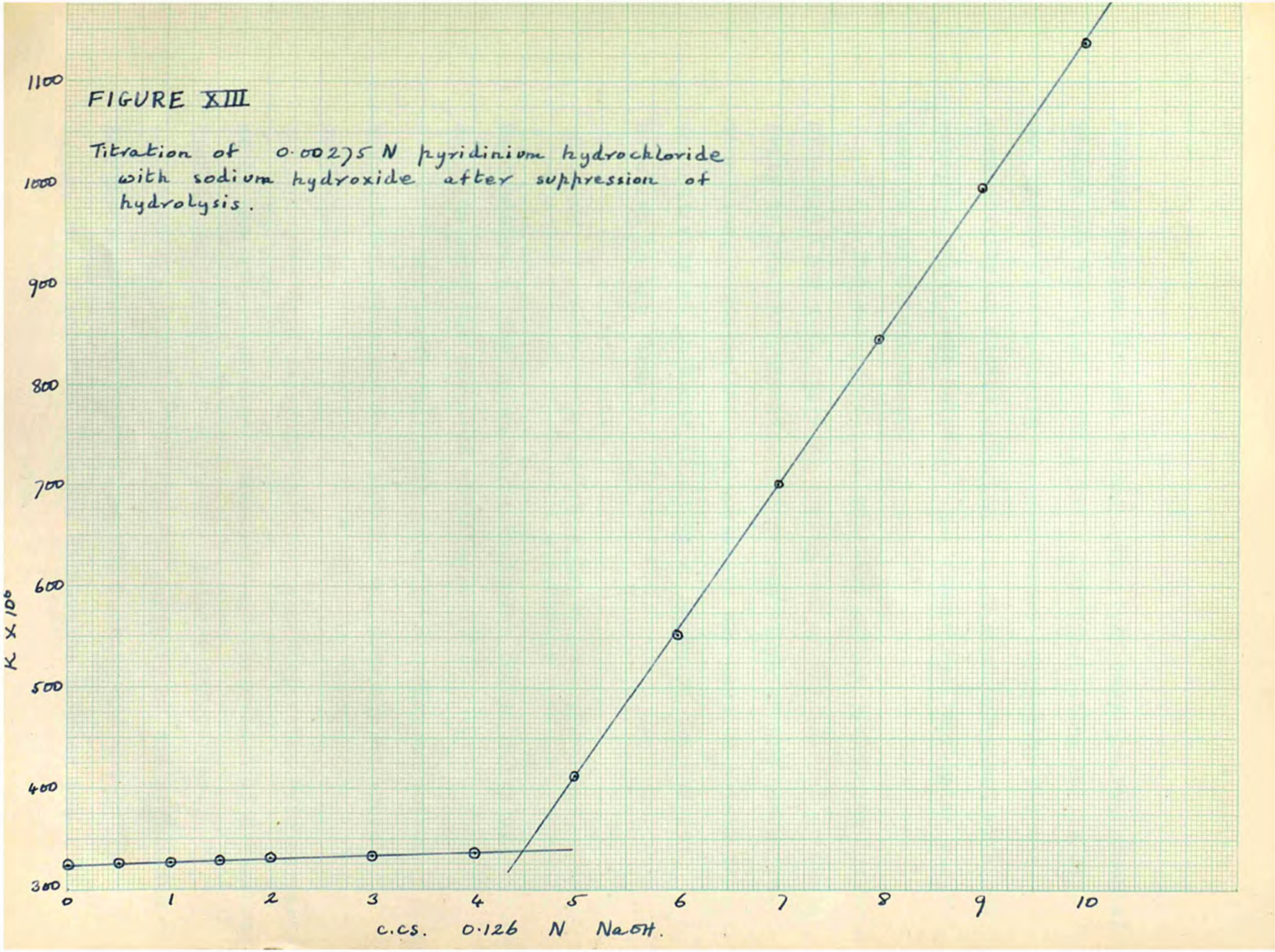
Determination of mobility.

Solutions of pyridine hydrochloride of concentrations 0.001625 N, 0.00275 N, and 0.00550 N were titrated with 0.1261 N caustic soda after addition of pyridine to suppress hydrolysis. A representative curve, that referring to the 0.00275 N solution is shown in fig. XIII.

Owing to some unknown factor the end-points obtained from the graphs differed from the theoretical end-points by

FIGURE XIII

Titration of 0·00275 N pyridinium hydrochloride with sodium hydroxide after suppression of hydrolysis.



amounts varying from 3% to 8%. In every case the experimental figure was too high. This is rather disquieting but is offset by the fact that the value obtained incidently for the conductivity of sodium chloride are in good agreement with the accepted value (see below). The theoretical end-point was used in the calculations.

Two values for the mobility of the pyridinium ion were obtained from each curve by making use of the initial conductivity of the hydrochloride and of the slope of the neutralistion line. The initial conductivity was used to obtain the conductivity at infinite dilution by means of the Onsager equation in the form:

$$\Lambda_0 = \frac{\Lambda + 59.78\sqrt{c}}{1 - 0.2271\sqrt{c}} \quad .$$

Subtraction of the known value 76.32 for the mobility of chlorine gave the required mobility.

The conductivity at infinite dilution of sodium chloride was obtained in a similar way from the end-point conductivity.

In each case the specific conductivities were corrected by the subtraction of a mean solvent correction of 2 gemmhos; "Boiled out" water was used for all these titrations.

The second value for the mobility of the pyridinium ion was obtained by subtracting the initial and end-point values for Λ_0 . This gave the difference between the mobilities of pyridinium and sodium; sodium was found to give the larger value as the titration line sloped upwards before the end-point, so the difference was subtracted from the accepted value 50.10 for sodium giving a second value for pyridinium. This method has the advantage of eliminating the solvent correction.

The results are shown below.

Normality of soln.	Corrected initial Λ	Initial Λ_0	Mobility of pyridinium.	End-point Λ	End-point Λ_0	Mobility from slope.
0.001625	118.7	122.3	46.0	124.4	128.0	44.4
0.00275	117.5	122.0	45.7	122.2	126.8	45.3
0.00275	117.0	121.5	45.2	121.3	125.9	45.7
0.00550	115.7	122.1	45.8	119.5	126.0	46.2

Mean value of mobility of pyridinium ion 45.5 ± 1.

Mean value of conductivity at infinite dilution of sodium chloride 126.7 cf. 126.4 taking the sum of the mobilities of $Na^{\bullet}$ and Cl'.

An interesting feature of this result is that the mobility of this positive ion is much greater than that of negative (carboxylate) ions of similar molecular weight. The same has been found by Righellato (Thesis, loc. cit.) for aliphatic compounds, and suggests an abnormally high retardation of carboxylate ions by solvation effects.

Mobility of the Ammonium Ion.

An attempt was made to determine the mobility of the ammonium ion by titration of a solution of ammonium chloride with standard potassium hydroxide solution. Potassium hydroxide was chosen because the mobilities of ammonium and potassium were known to be nearly equal. The curve obtained is of the form shown in fig. XIV. There is first a linear portion and then a curved portion due to hydrolysis around the end-point; the titration was never taken far enough to obtain the second linear portion after the end-point. The reaction over the first linear part of the curve is

$$NH_4^{\cdot} + Cl' + K^{\cdot} + OH' \qquad NH_4OH + K^{\cdot} + Cl'$$

Thus on addition of potassium hydroxide solution the change in equivalent conductivity is brought about only by the replacement of ammonium ion by potassium ion. This makes it possible to calculate the difference in mobilities of the two ions from the slope of the initial line as shown below.

The first necessity was to calculate the minimum strength of ammonium chloride solution at which the linear part of the curve would be sufficiently long for an accurate estimation of its slope. Suppression of the hydrolysis of a dilute solution with ammonium hydroxide was first examined theoretically.

Consider a titration of 5 c.c. 0.1 N ammonium chloride solution in 200 c.c. water, i.e. 0.0025 N ammonium chloride solution. Titrate with 0.1 N potassium hydroxide solution in presence of 0.1 N ammonium hydroxide solution to suppress hydrolysis.

Before commencing titration

$$[\mathrm{OH}'] = [\mathrm{NH_4^{\cdot}}] - 0.0025$$

$$[\mathrm{NH_4OH}] = 0.1 - [\mathrm{OH}'] = 0.1025 - [\mathrm{NH_4^{\cdot}}]$$

$$K_{\mathrm{NH_4OH}} = 1.8 \times 10^{-5} = \frac{[\mathrm{NH_4^{\cdot}}]\,[\mathrm{OH}']}{[\mathrm{NH_4OH}]}$$

$$= \frac{[\mathrm{NH_4^{\cdot}}]\left\{[\mathrm{NH_4^{\cdot}}] - 0.0025\right\}}{0.1025 - [\mathrm{NH_4^{\cdot}}]}$$

$$= \frac{\left\{[\mathrm{OH}'] + 0.0025\right\}[\mathrm{OH}']}{0.1 - [\mathrm{OH}']} .$$

Solving this equation and taking the positive root

$$[\mathrm{OH}'] = 0.00058.$$

Since $\Lambda_{\mathrm{NH_4OH}} \simeq 2 \times \Lambda_{\mathrm{NH_4Cl}}$ the contribution of the ammonium hydroxide to the total conductivity is approximately 30%.

At end-point

$$[\mathrm{NH_4OH}] = 0.1025 \qquad [\mathrm{NH_4^{\cdot}}] = [\mathrm{OH}']$$

$$\frac{[\mathrm{NH_4^{\cdot}}]\,[\mathrm{OH}']}{[\mathrm{NH_4OH}]} = \frac{[\mathrm{OH}']^2}{0.1025 - [\mathrm{OH}']} = 1.8 \times 10^{-5}$$

As before $[\mathrm{OH}'] = 0.00130.$

This method is therefore out of the question.

It then became necessary to consider the titration of a more concentrated ammonium chloride solution without the addition of ammonium hydroxide. Titrate a 0.02 N ammonium chloride solution with 0.1 N potassium hydroxide. At 1/10th replacement

$$[NH_4^{\cdot}] = [OH'] + 0.018$$

$$[NH_4OH] = 0.002 - [OH']$$

$$\frac{[NH_4^{\cdot}]\,[OH']}{[NH_4OH]} = \frac{\{[OH'] + 0.018\}\,[OH']}{0.002 - [OH']} = 1.8 \times 10^{-5}$$

$$[OH'] = 2 \times 10^{-6}.$$

It can be calculated as shown above that the conductivity of the ammonium hydroxide here is about 0.02% of the total conductivity.

Now consider the titration of a 0.01 N solution. At 1/5th replacement

$$[NH_4^{\cdot}] = [OH'] + 0.008$$

$$[NH_4OH] = 0.002 - [OH']$$

$$\frac{\{[OH'] + 0.008\}\,[OH']}{0.002 - [OH']} = 1.8 \times 10^{-5}$$

$$[OH'] \simeq 4.5 \times 10^{-6}.$$

Some idea of a suitable concentration of ammonium chloride having been obtained from these calculations, titrations were carried out at three different concentrations.

The curve obtained for the lowest concentration is shown in fig. XIV. Only two irregularities are to be expected. (1) Any carbon dioxide present in the solution will be converted to salt at the beginning of the titration; this should just displace the initial point of the titration from the straight line. (2) The largest potential source of error is the addition of non-reacting electrolyte impurity with the potassium hydroxide.

<u>Run 1.</u>

Concentration of ammonium chloride   0.00272 N

Total Volume   199.3 c.c.

From graph 1 c.c. 0.0645 N potassium hydroxide raises K by 1.60 gemmhos.

$$1000\,\Delta K = C\,\Delta\Lambda$$

$$1.60 \times 10^{-3} = \frac{1000}{199.3} \times 0.0000645 \times \Delta\Lambda$$

$$\Delta\Lambda = 4.95 \text{ units.}$$

The potassium hydroxide solution was 0.001 N with respect to carbonate. Δ K due to this would be given by

$$1000\,K = \frac{1000}{199.3} \times 1 \times 10^{-6} \times (74 + 80)$$

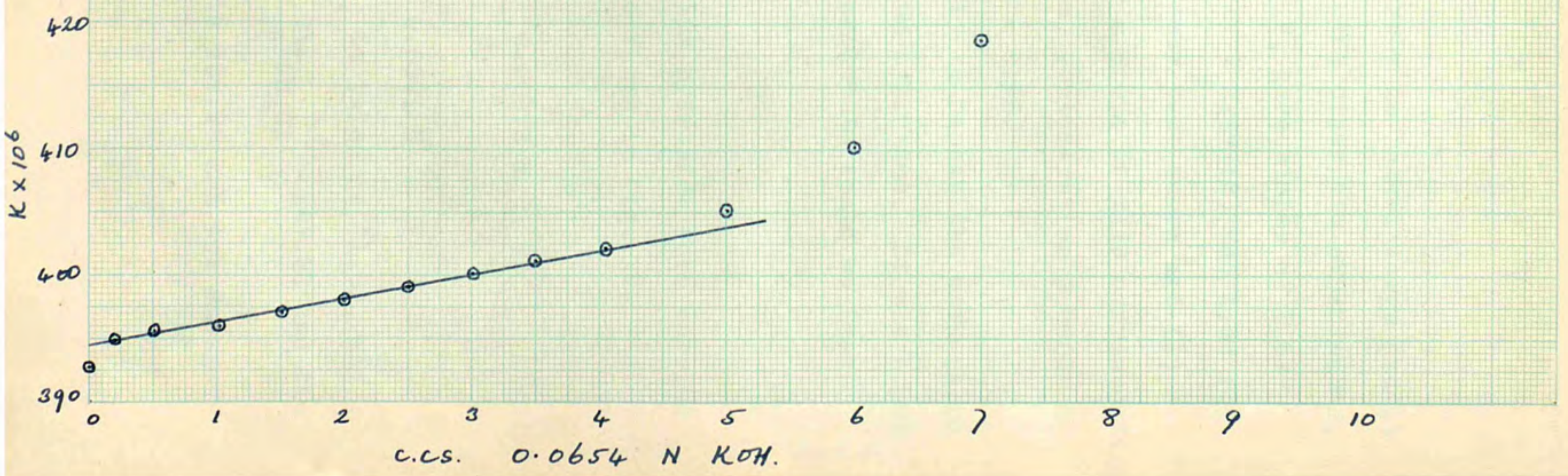
$$K = 0.77 \text{ gemmhos.}$$

$\therefore$ Corrected Δ K = 0.83

and corrected $\Delta\Lambda$ = 2.64 units (1).

FIGURE XIV

Titration of 0·00272 N ammonium chloride with potassium hydroxide.



The uncertainty in this error is rather large and it affects all three results equally. The other two experiments, concentrations 0.0141 N and 0.00560 N, gave slopes of 1.54 and 1.24 respectively which give $\Delta\Lambda$ = 2.47 (2) and 1.55 (3) units. Of these (2) comes from a very poor curve and (1) could equally well be drawn to give a slope of 1.40 corresponding to $\Delta\Lambda$ = 2.01. A fourth titration, concentration 0.00560 N gave a slope of 1.71 units and $\Delta\Lambda$ = 2.98.

It was considered necessary to repeat the work using barium hydroxide instead of potassium hydroxide. It was hoped that errors due to the presence of carbonate would be less important in this case.

Titrations with Barium Hydroxide.

Four titrations using barium hydroxide were carried out. One of the curves obtained is shown in fig. XV.

Run 1.

Concentration of ammonium chloride 0.00272 N

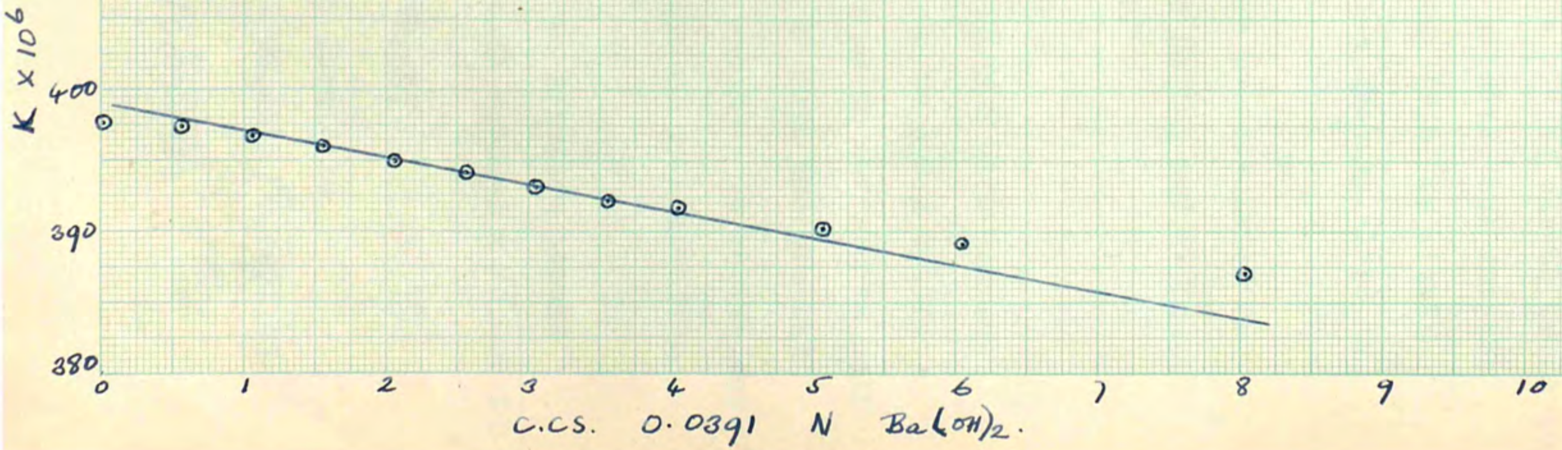
Volume of solution 199.3 c.c.

Concentration of barium hydroxide 0.0391 N

For purposes of correction $\Lambda_{o\,NH_4^{\cdot}}$ is taken as 71.50, and combining with $\Lambda_{o\,Cl'}$ = 76.32 gives $\Lambda_{o\,NH_4Cl}$ = 147.82 and the Onsager slope is 93.41. $\Lambda_{o\,BaCl_2}$ is 139.98 and the Onsager slope is 176.

FIGURE XV

Titration of 0.00272 N ammonium chloride with barium hydroxide.



The displacement line should really be curved owing to the progressive increase in inter-ionic effects, but for the first 4 c.c. addition this is not apparent (i.e. is within experimental error) and in this region the average slope is 2 gemmhos per c.c. added.

From these figures the mobility is calculated as follows using the principle suggested by Davies and Righellato[3]. After adding 4 c.c. the solution is

$$\frac{4}{1000} \times 0.0391 \times \frac{1000}{199.3} = 0.000785 \text{ N}$$

with respect to barium chloride and 0.001935 N with respect to ammonium chloride. Its ionic strength is $\frac{1}{2}(2 \times 001935 + 3 \times 0.000785) = 0.003113$, ionic strength being defined as half the sum of the equivalent concentration of each ion present multiplied by its valency. This ionic strength is equivalent to that of a pure barium chloride solution of concentration 0.002076 N.

The conductivity of the original solution should therefore be $0.00272 \times 10^{-3}(\Lambda_{o\,NH_4^{\cdot}} + 76.32 - 93.41 \times \sqrt{0.00272})$

$$= 0.00272 \times 10^{-3} (\Lambda_{o\,NH_4^{\cdot}} + 71.45)$$

and the conductivity after adding 4 c.c. should be

$$0.001935 \times 10^{-3} (\Lambda_{o\,NH_4^{\cdot}} + 76.32 - 93.41 \times \sqrt{0.003113})$$

$$+ 0.000785 \times 10^{-3} (139.98 - 176 \times \sqrt{0.002076})$$

i.e. $(\Lambda_{o\,\mathrm{NH_4^{\cdot}}} + 71.45) \times 0.00272 - (\Lambda_{o\,\mathrm{NH_4^{\cdot}}} - 71.11) \times 0.001935$

$$- 131.96 \times 0.000785 = 8.0 \times 10^{-3}$$

Hence $\Lambda_{o\,\mathrm{NH_4^{\cdot}}} = 69.8$

Run 2

Concentration of ammonium chloride 0.00560 N

Volume of solution 199.2 c.c.

For the first 6 c.c. added the displacement line was straight and ΔK was 15.2×10^{-6} for 6 c.c. After 6 c.c. addition solution is

$$\frac{6}{1000} \times 0.0391 \times \frac{1000}{199.2} = 0.001178 \text{ N with respect to}$$

barium chloride and 0.004422 N with respect to ammonium chloride. Its ionic strength is 0.006189 (which corresponds to a barium chloride solution of concentration 0.004126 N).

The conductivity of the original solution should be

$$5.60 \times 10^{-6} \, (\Lambda_{o\,\mathrm{NH_4^{\cdot}}} + 76.32 - 93.41 \times 0.0735)$$

$$= 5.60 \times 10^{-6} \, (\Lambda_{o\,\mathrm{NH_4^{\cdot}}} + 69.46).$$

After adding 6 c.c. conductivity should be

$$4.422 \times 10^{-6} \, (\Lambda_{o\,\mathrm{NH_4^{\cdot}}} + 76.32 - 93.41 \times 0.0765)$$
$$+ 1.178 \times 10^{-6} (139.98 - 176 \times 0.0595)$$

and proceeding as before

$$\Lambda_{o\,\mathrm{NH_4^{\cdot}}} = 71.8.$$

The remaining two runs were calculated similarly. The whole of the results obtained for the mobility of the ammonium ion are tabulated below.

Concentration of NH_4Cl.	Titrated with	Mobility	Deviation from mean.
0.00272	KOH	70.9	+ 0.2
0.0141	KOH	71.0	+ 0.3
0.00560	KOH	72.0	+ 1.3
0.00560	KOH	70.5	-0.2
0.00272	$Ba(OH)_2$	69.8	-0.9
0.00272	"	68.4	-2.3
0.00560	"	71.8	+ 1.1
0.00560	"	71.0	+ 0.3
	Mean	70.7	Average deviation 0.8

The uncertainty in the calculations was so much greater than had been expected and the results showed such poor agreement that they were abandoned completely.

Subsequently Shedlovsky has reported the mobility of ammonium to be 73.4.

A quick Method for the Determination of Mobilities of Acid Anions.

Introduction.

When a solution of a weak acid in water is conductimetrically titrated with a standard ammonium hydroxide solution a curve is obtained of the type shown in figure XVI. The mobility of the acid anion can be calculated from the curve in the following manner. The final straight line obtained by the addition of ammonium hydroxide to the ammonium salt of the acid is produced backward to the end-point. This end-point is calculated from the known concentration of the acid; the conductimetric titration itself forms a useful check where the acid is not too weak. The end-point specific conductivity thus obtained is that of the ammonium salt of the acid at a concentration equal to the initial concentration of the acid, as all conductivity values are corrected for dilution before plotting.

The equivalent conductivity obtained from this specific conductivity by means of the formula $\Lambda = K.1000/C$ is extrapolated to infinite dilution by means of the Onsager equation $\Lambda_0 = \Lambda + \alpha\Lambda_0\sqrt{c} + \beta\sqrt{c}$ used in the form $\Lambda_0 = \dfrac{\Lambda + \beta\sqrt{c}}{1 - \alpha\sqrt{c}}$ where $\alpha = 0.2271$, $\beta = 59.78$.

For concentrations of 0.004 N and over the modified equation $\Lambda_0 = \dfrac{\Lambda + \beta\sqrt{c}}{1 - \alpha\sqrt{c}} - Bc$ is used. This has been shown by Shedlovsky[4] to hold for uni-univalent salts where B is a constant which is approximately equal to the Onsager slope or $\alpha\Lambda_0 + \beta$. The correction is a small one and it was therefore sufficiently accurate for our purpose to take B as being equal to the Onsager slope. The modified equation was used in the form

$$\Lambda_0 = \frac{\Lambda + 59.78\sqrt{c}(1 + 0.2271\ c - \sqrt{c})}{(1 + 0.2271\ c)(1 - 0.2271\sqrt{c})} \ .$$

Subtraction of the mobility of ammonium = 73.4 from the equivalent conductivity at infinite dilution of the salt gives a value for the mobility of the acid anion.

It was hoped that it would be possible to obtain these values with an accuracy of one in a thousand but owing to difficulty in reproducing results to this degree of accuracy it was found impossible to get results of a greater accuracy than ± 0.3. This would usually be sufficiently accurate where the value was required for the calculation of the degree of dissociation of the acid. The advantage of the method lies in the fact that a titration can be completed in $1\frac{1}{2}$ hours; also there is no necessity to prepare a pure specimen of the salt, the pure acid being more easily obtainable.

"Boiled out" water was used for the earlier work. A mean solvent correction of 2 gemmhos was subtracted. The uncertainty attached to this solvent correction was inconsistent with accurate results. For the later work conductivity water was used; the conductivity of this after pipetting into the cell varied from 0.8 to 1.0 gemmhos. The conductivity of "equilibrium" water at 25°C is 0.8 gemmhos[5]. It was therefore concluded that the water used consisted of a saturated solution of carbonic acid, with no other impurity present in appreciable quantity. The concentration of carbonic acid in such a solution is 1.40×10^{-5} moles per litre[5]. The end-point specific conductivity due to this concentration of ammonium bicarbonate is approximately 2 gemmhos ($1000 K = C\Lambda$). This was subtracted from the end-point specific conductivities.

The method was first tried on a number of acids whose mobilities were accurately known.

Difficultly soluble acids.

The first acids to be attempted were benzoic, ortho- and meta-chlorbenzoic acids. Although, with the exception of meta-chlorbenzoic acid at 0.005 N, the acids were soluble in water at the concentrations used they could not be dissolved in cold water. It was thought at first that this did not matter as they would be soluble in ammonium hydroxide just past the end-point and would give the correct straight line. This would have made it possible to apply the method to insoluble acids. It was found, however, that even after the end-point some of the acid remained undissolved.

Various devices were employed to overcome this difficulty. The acid was left in the cell overnight to dissolve, this was not successful as in most cases a small amount of acid still remained undissolved. Then the acid and water were warmed in the cell by immersion in warm water; this was fairly successful but slow and inconvenient. Finally the acid was dissolved by boiling with water in a beaker, transferred to the cell, made up to approximately 200 c.c. and weighed to obtain the weight of solution; it was sufficiently accurate to take the density of the solution as equal to that of the pure solvent. The boiling of the acid in a beaker was open to objection but was unavoidable. Meta-chlorbenzoic acid at 0.005 N was tried in this way in the hope that it would crystallize in a more easily soluble form; this was not realized and this acid was abandoned.

Benzoic acid.

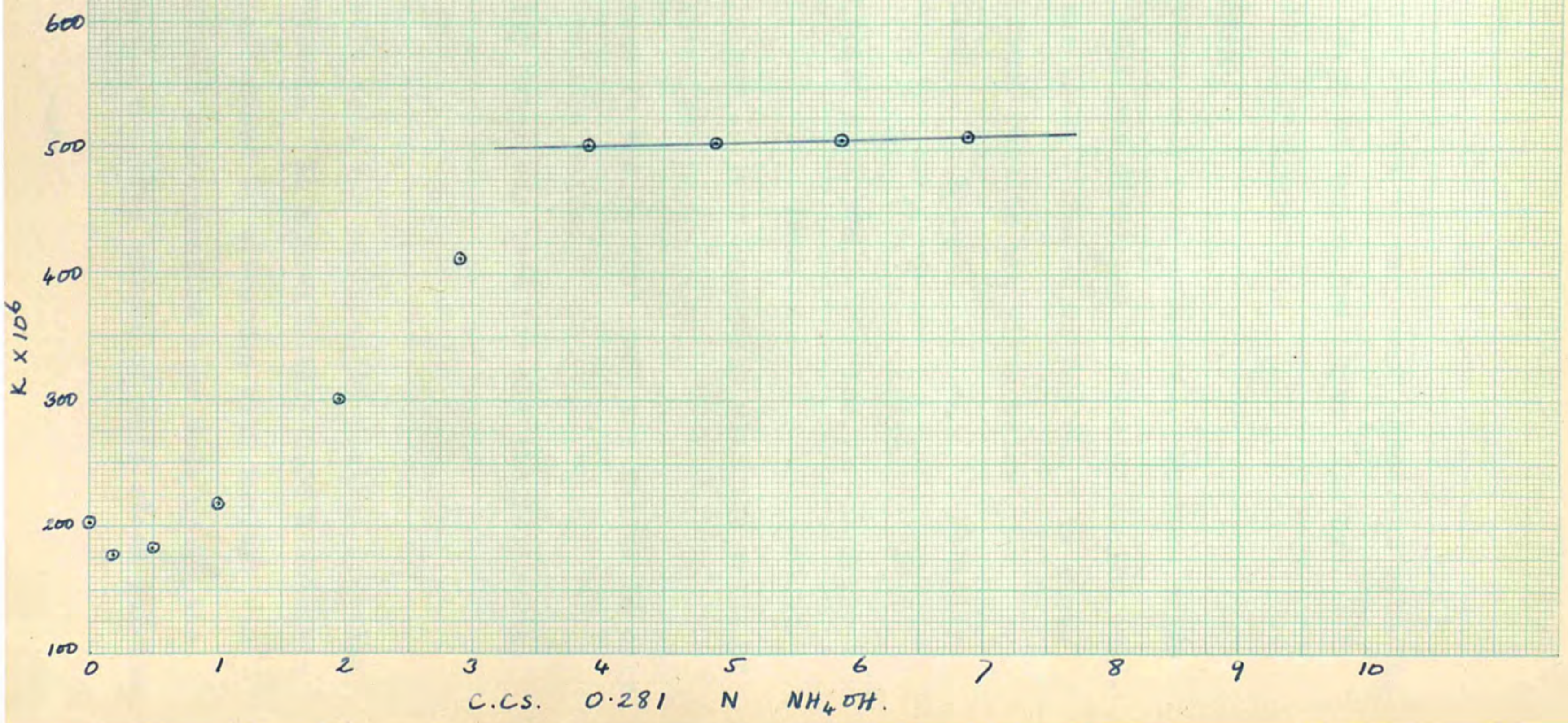
Four titrations using "boiled out" water were carried out. In runs 1 and 2 the acid was dissolved by standing overnight and by shaking respectively; in runs 3 and 4 the acid was dissolved by boiling. In all cases the acid was weighed in order to obtain its concentration. The curve for run 1 is shown in fig. XVI.

The calculated results are given in the following table:

Run	Conc.	End-pt. $K \times 10^6$	Λ_0	Mobility
1	0.005 N	497.7	105.1	31.7
2	0.0025 N	253.0	105.4	32.0
3	0.005 N	499.0	105.3	31.9
4	0.00250 N	252.5	105.2	31.8
			Mean	31.85

FIGURE XVI

Titration of 0·005 N benzoic acid with ammonia.



These values are not in very good agreement with the values of 32.24 and 32.38 by Saxton and Mayer[6] and by Brockman and Kilpatrick[7] respectively.

Ortho-chlorbenzoic acid.

Two titrations only were attempted. In both cases a weighed amount of acid was dissolved by warming in the cell. "Boiled out" water was used. The curve for run 1 is shown in fig. XVII. The final results are given below

Run	Conc	End-pt. $K \times 10^6$	Λ_0	Mobility
1	0.005 N	486.5	102.8	29.4
2	0.00175 N	175.5	103.7	30.3
		Mean		29.85

These again are in poor agreement with the value of 30.24 obtained by Saxton and Meyer[8].

At this stage it was decided that the method is only suitable for easily soluble acids.

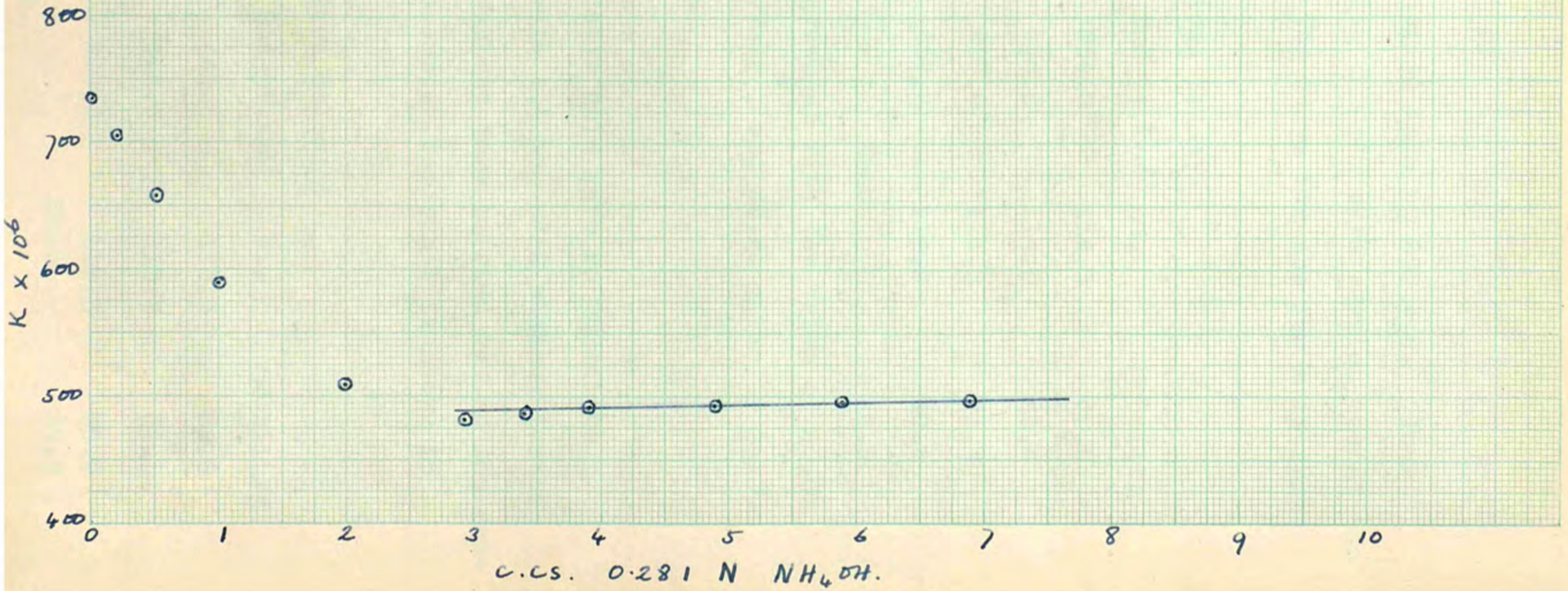
Conductivity water was used for all the following work.

Acetic acid.

Analar acetic acid was purified by partial freezing and separation of crystals. An approximately 0.05 N solution was prepared and standardised by titration with baryta. Solutions of the required concentration were made up in the cell by pipetting in the required amount of this stock solution

FIGURE XVII

Titration of 0·005 N ortho-chlorbenzoic acid with ammonia.



together with sufficient water to make up 200 c.c. Four conductimetric titrations with ammonia were carried out at two different concentrations. The curve for the run 1 is shown in fig. XVIII.

The results are given below:

Run	Conc	End-pt. $K \times 10^6$	Λ_0	Mobility
1	0.002417 N	266.0	114.3	40.9
2	0.006084 N	656.0	114.0	40.6
3	0.002417 N	267.0	114.8	41.4
4	0.006084 N	657.0	114.2	40.8
			Mean	40.9

This is in good agreement with the value of 40.87 given by MacInnes and Shedlovsky[9], and 40.81 given by Saxton and Langer[10].

<u>Monochloracetic acid.</u>

Analar Monochloracetic acid gave no immediate precipitate with silver nitrate and was used without further purification. The determinations were carried out in the same way as for acetic acid. The curve for run 1 is shown in fig. XIX.

The results are given below:

Run	Conc	End-pt. $K \times 10^6$	Λ_0	Mobility
1	0.005995 N	642.0	113.2	39.8
2	0.005995 N	642.0	113.2	39.8
3	0.002382 N	260.0	113.3	39.9
			Mean	39.8

FIGURE <u>XVIII</u>

Titration of 0·002417 N acetic acid with ammonia.

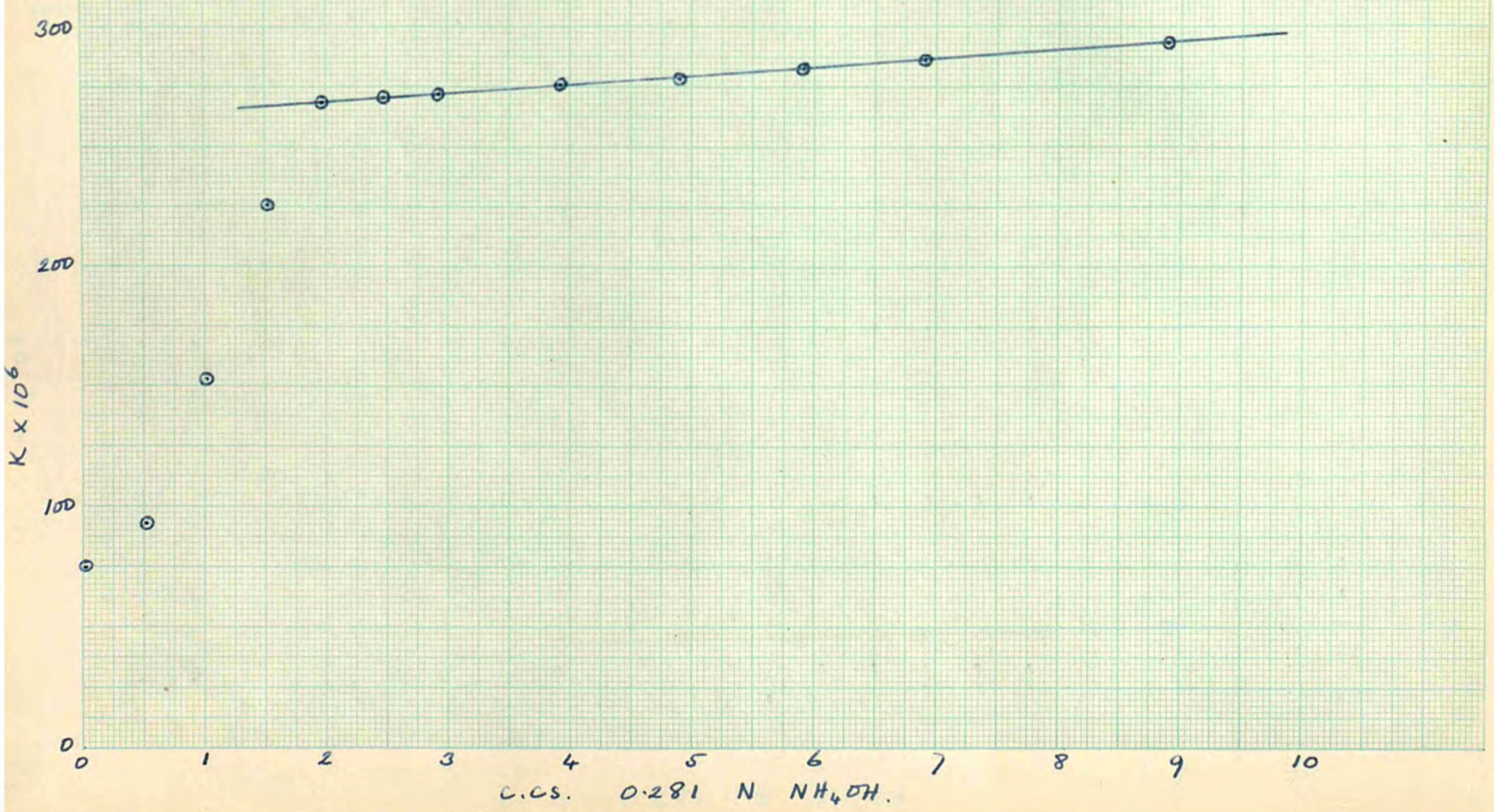
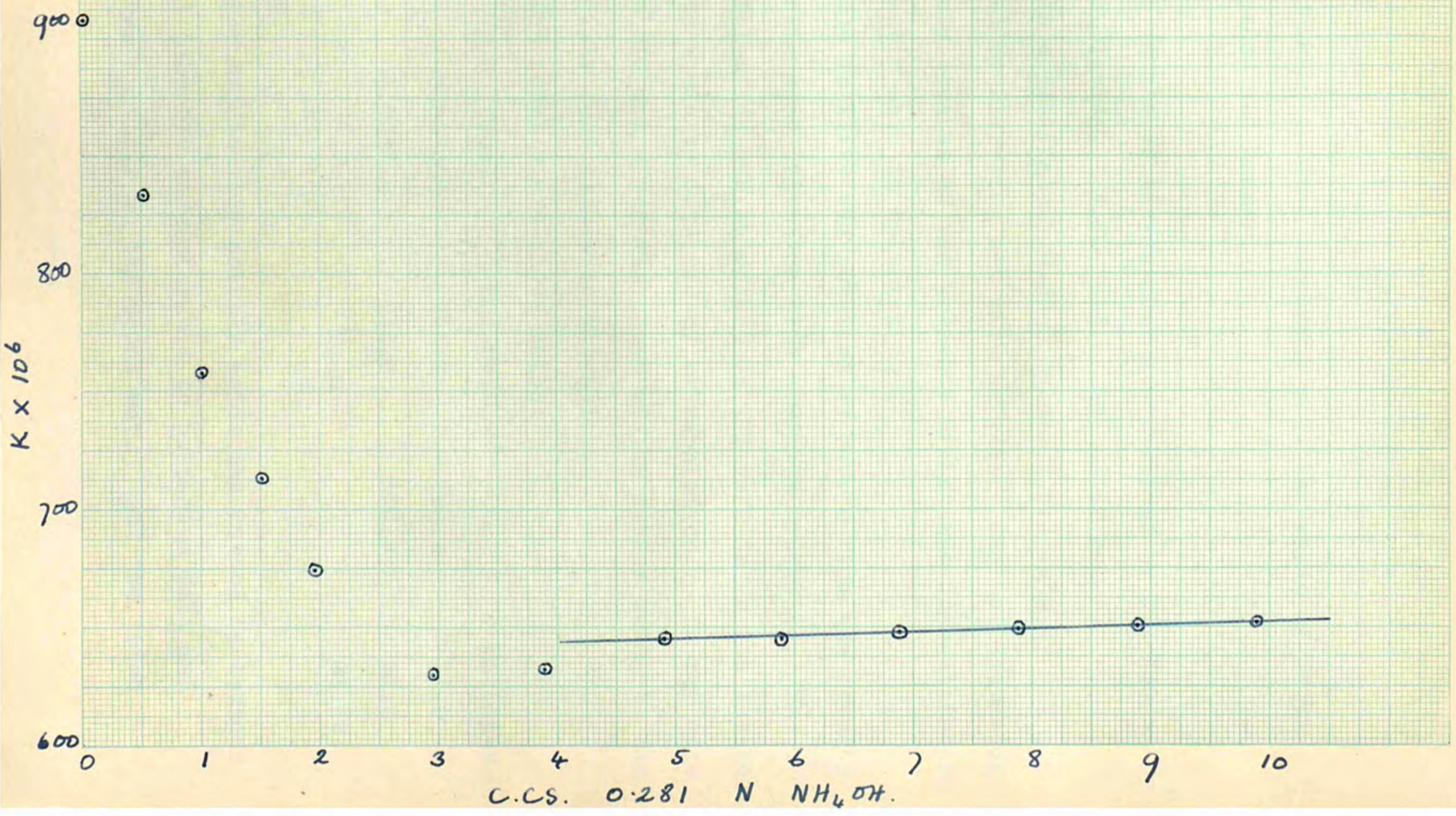


FIGURE XIX

Titration of 0·005995 N monochloracetic acid with ammonia.



This is in good agreement with the value of 39.92 given by Saxton and Langer[11].

Lactic acid.

A sample of lactic acid was purified by Dr. Kenyon by vacuum distillation. B.P. 119 - 120° at 13 mm.

An approximately 0.05 N solution was made up and standardised by titrating hot with baryta; the hot titration was necessary because of the presence of lactide in equilibrium with the lactic acid in solution.

The mobility was obtained as before from the results of a conductimetric titration with ammonium hydroxide. The presence of lactide had no effect on the results as the end-point conductivity could be obtained by extrapolation. In any case the lactide did not alter the shape of the curves owing to the slowness of the conductimetric titration.

The results are shown below:

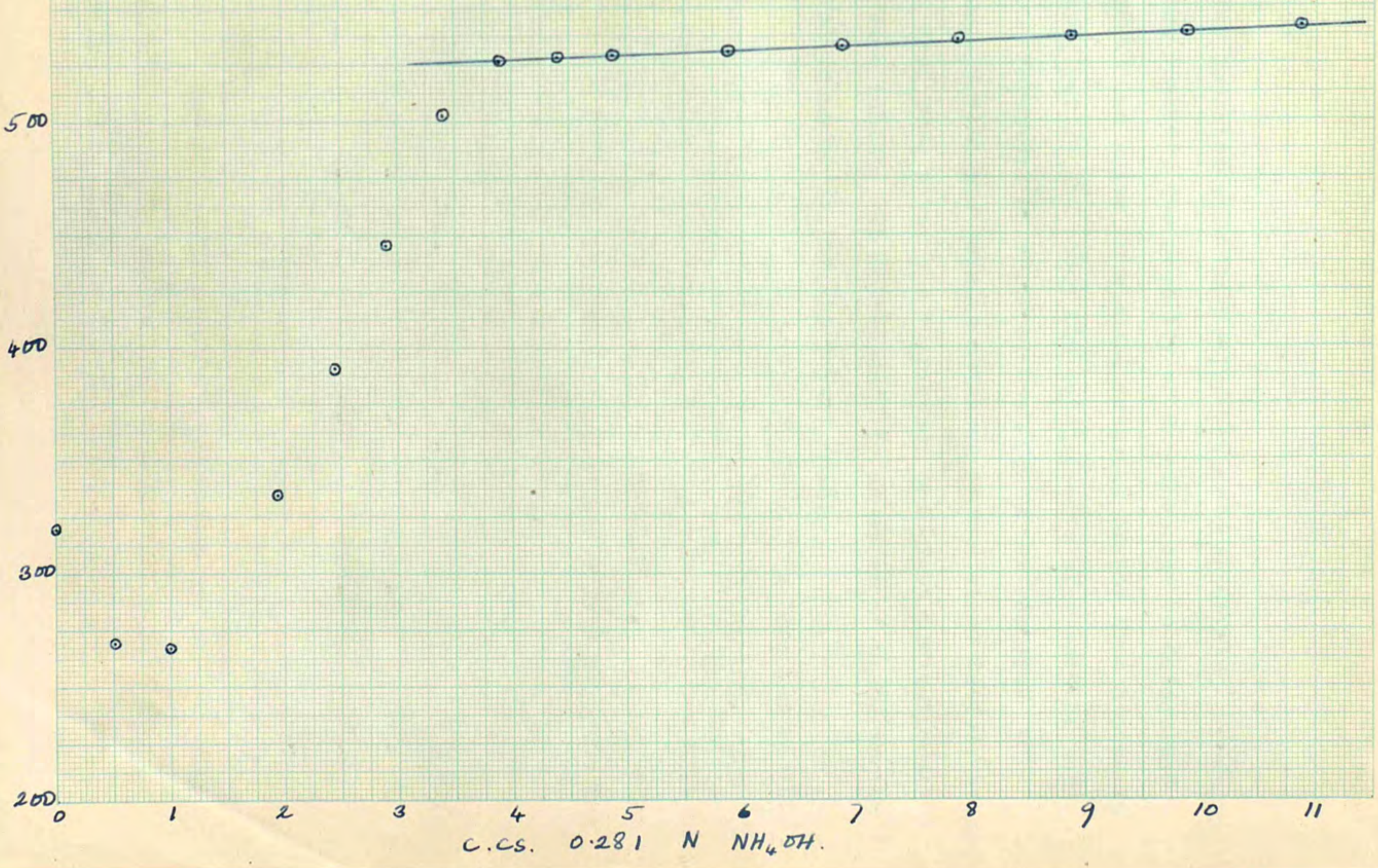
Run	Conc.	End-pt.K $\times 10^6$	Λ_o	Mobility
1	0.005306	524.0	104.4	31.0
2	0.002412	243.0	104.7	31.3
		Mean		31.15

Conclusions

For difficultly soluble acids the method is tedious and it will probably be preferable to prepare a salt and determine the mobility in the usual way. But the later

FIGURE XX

Titration of 0.005306 N lactic acid with ammonia.



results reported show that using proper precautions, and water of good quality, the mobility of an anion can be determined to within 0.2 units in a small fraction of the time needed to prepare, purify and study the conductivity of a salt of the acid. Moreover, an error of even 0.2 units compares favourably with the results obtained by the older method, except where very pure water has been used, and great precautions have been taken; it corresponds to an error of 0.05% in the derived value for Λ_0 of the parent acid.

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