THESIS

for the

DEGREE OF Ph.D.

submitted by

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A SERIES OF ELECTRO-MAGNETIC INVESTIGATIONS

(I) ON A GYRO MAGNETIC EFFECT;

(II) ON DIFFUSION IN FLAMES;

(III) ON AN INDUCTION COIL INTERRUPTER; AND

(IV) ON THE ELECTRICAL CONDUCTIVITY OF HOT SOLUTIONS.

C O N T E N T S .

The Record of Experimental Research carried out as Thomson Experimental Scholar in the Natural Philosophy Institute, Glasgow University; and later as Assistant Lecturer in the Natural Philosophy Department of the Royal Technical College, Glasgow.

PART I

THE INVESTIGATION OF A POSSIBLE GYRO-MAGNETIC EFFECT

SUMMARY.

A Gray-Ross magnetometer was used to obtain I-H curves for a steel rod under normal conditions and under the influence of a rotating magnetic field to find whether the effect of the latter would be to help in the process of producing longitudinal magnetisation of the rod. The rotation of a bar-magnet in a plane at right angles to the axis of the specimen, and near to the magnetising solenoid, was used to supply this field, which was therefore not very strong and decreased towards the end of the specimen distant from the rotating magnet. When the I-H curves for a given range, and under the different conditions, were compared, the curve obtained for either direction of rotation of the magnet differed but slightly from the curve for normal conditions. Sometimes it seemed that the rotating field helped, but in other experiments the opposite was indicated, and in other sets no difference was distinguishable, so it was concluded that a rotating magnetic field of the order used has no distinct effect on the longitudinal magnetisation of a specimen lying in the direction of the axis of rotation.

INTRODUCTION.

In 1908 O.W.Richardson(1) pointed out that since, on the electron theory, an atom of iron is itself a little magnet because of electrons revolving inside it, and since these electrons have mass, the process of magnetisation is accompanied by the creation of a proportional amount of angular momentum about the axis of magnetisation. Thus the term 'gyro-magnetic effect' came into use to denote the fact that magnetisation is accompanied by rotation, and that rotation may be used to produce magnetisation. This effect has been investigated by various workers, and S.J.Barnett(2) succeeded in magnetising a rod by rotating it, the resulting polarity being the same as would have been produced by an electric current flowing round the rod in a direction opposite to that of the rotation.

It was suggested that by rotating a magnetic field about the centre-line of a rod as axis, longitudinal magnetisation might be induced in the rod. This seemed reasonable according to the principle of precession which holds for gyroscopic motion. The atoms of a magnetic

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(1) O.W.Richardson: Phys. Rev., 26, 1908, P.248.

(2) S.J.Barnett: Phys. Rev., 6, 1915, P.239.

material, due to their spinning electrons, resemble gyrostats, and it was thought that a rotating magnetic field, rotating about an axis in line with the rod, would have an effect similar to that of a couple acting on a gyrostat, and would tend to turn the directions of the axes of electronic spin to be parallel to the axis of rotation of the field, and so induce longitudinal magnetisation in the rod.

To investigate this, the experiments now described were carried out in the Natural Philosophy Institute, Glasgow University, under the supervision of Professor J. G. Gray, D.Sc. and at his suggestion. They consisted in putting a specimen through a hysteresis cycle, by the deflection magnetometer method, with and without a rotating magnetic field, and in looking for differences in the I-H curves obtained.

APPARATUS.

The magnetometer used was of the improved form devised by Professors J.G.Gray and A.D.Ross (3), the general arrangement of which is shown diagrammatically in Fig.1. The base is a beam of mahogany about 12 feet long with a cross-beam about 4½ ft. long, both fitted with channels in which the stands for the various coils, etc., could be adjusted and readily clamped in any position. A is the solenoid for magnetising the specimen S. B, C, and D are the compensating coils which form a special feature of the magnetometer. B is the principal one, and by it the field at the magnetometer needle, E, due to coil A is approximately balanced. Coil C has only a few turns and is generally placed at a good distance from E, so that by its means a slight adjustment of the compensation may easily be effected, as may be necessary if the position of B is slightly altered in the process of clamping. A similar shift of C would have a negligible effect because of its few turns and large distance. In this way balance is made exact as far as the field in the direction of the long beam is concerned. Coil D is to allow for a lack of true alignment between the coils A, B, and C which would result in a component of field in the direction

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(3) Gray & Ross: Proc. Roy. Soc. Edin., Vol.29, 1909, P.182.

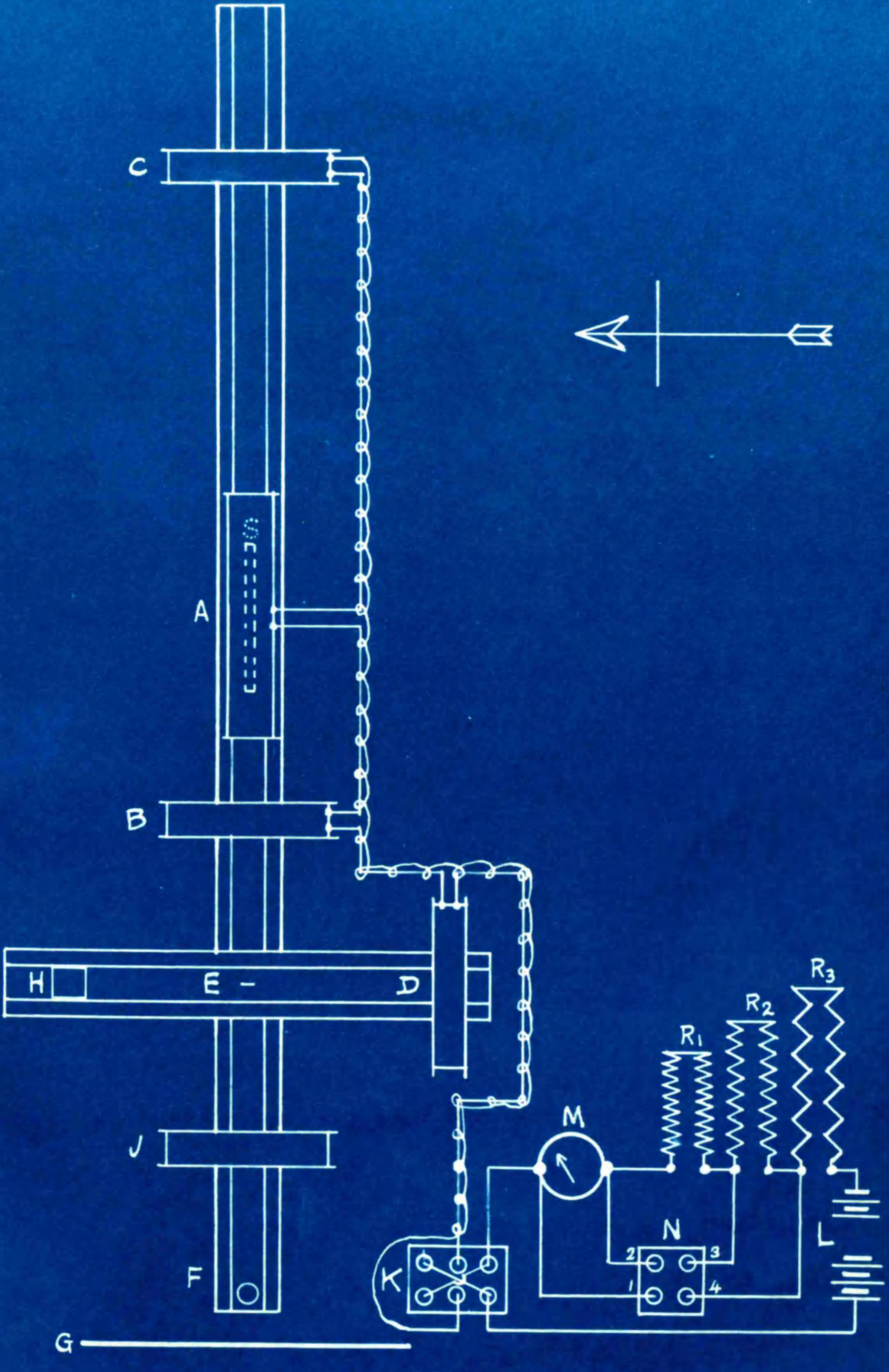

Fig. 1

Diagrammatic Sketch of Magnetometer Circuit of the cross-beam. A few turns of D may be used to counter-balance such a component. F and G are the lamp and scale for the magnetometer needle, E, which is of the suspended mirror type. (The distance between E and G was rather more than a metre.) H is a stand for a small permanent magnet used in testing whether coil D needs to be brought into the circuit. J is a damping coil. A pulse of current sent through it creates a temporary magnetic field at E, and may be used to bring the needle to rest more quickly. A small dry cell, a tapping key, and a resistance in series with J (but not shown) are used to provide the pulses of current.

K is a mercury-cup reversing-key to whose centre pair of terminals coils A, B, C, and D are connected in series. An outer pair of terminals is connected in series with L, a battery of storage cells, M an ammeter, and a set of three rheostats R_1, R_2, and R_3 wound non-inductively and capable of carrying currents of 0.25 amps, 1.5 amps, and 10 amps, respectively. N is a special four-hole mercury-cup key with terminals 1 and 2 connected to the terminals of M, terminal 3 to the join of R_1 and R_2, and terminal 4 to the join of R_2 and R_3. The function of N is as follows: Before running a cycle the specimen is first demagnetised by the method of reversals, and a link of copper is meanwhile used to connect up cups 1 and 2 and so short-circuit the ammeter M and protect it during the sudden fluctuations of the gradually reduced current. Then, when running a cycle, resistance R_1 is first reduced by stages to increase the current through the magnetising solenoid A, and when it is cut out completely - or supposed to be - the copper link is inserted in N between cups 2 and 3. In this way the last turn or so in the Rheostat R_1 is protected when heavier currents are sent through R_3 and R_2. Similarly when the second rheostat is fully cut out another link is inserted between cups 3 and 4.

It should be noted that the connecting-wires were everywhere intertwined to make them as non-inductive as possible.

The rotating field was supplied by rotating an ordinary bar magnet about an axis through its middle point and at right angles to its length, this axis being coincident with the axis of the solenoid. The attachment for holding the magnet was very simple, and is shown in Fig.2. It consisted of a horizontal spindle turning in a wooden base, which fitted into the channel in the long limb of the magnetometer, and was provided with the same kind of clamping arrangement as the bases of the coils. The spindle was kept in position by means of two small brass collars, and carried at one end a small brass pulley for a cord drive. The other end of the

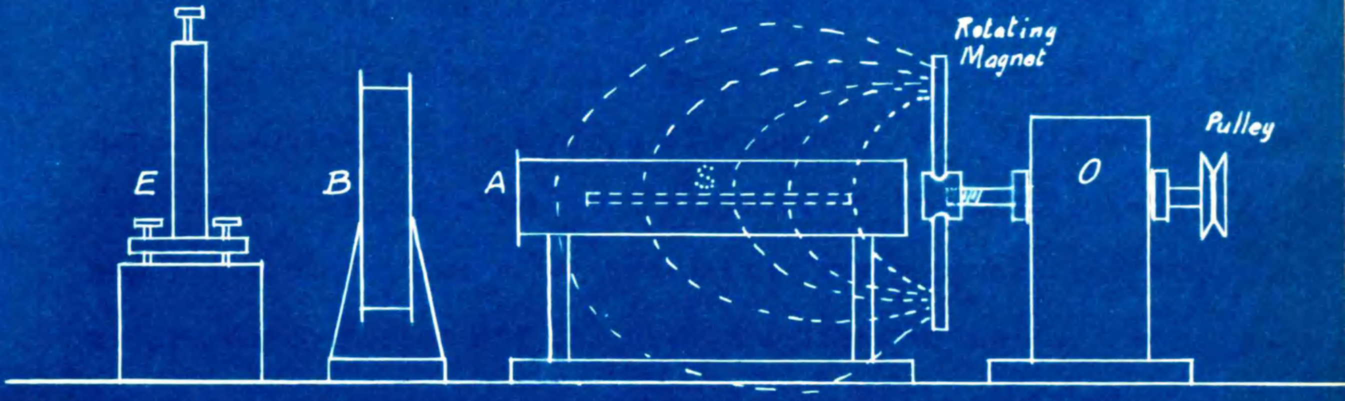

Fig. 2

Diagrammatic sketch showing arrangement for imposing a rotating magnetic field.

spindle was screwed to fit a special nut. This nut in addition to its screwed hole had a transverse hole bored in it to fit the magnet that was to be rotated. By sliding the nut along to the middle of the magnet and then screwing the nut tightly to the end of the spindle, it was easy to fix the magnet securely. This piece of apparatus was designed and made by Mr. Wm. Johnstone, the mechanic at the Institute. It was rotated by means of a cord-drive from a small electric motor, which worked off the electric lighting mains, the speed being controlled by means of a variable resistance.

PROCEDURE.

The sole control field for the magnetometer needle was to be the horizontal component of the earth's field, H_e, so the first step in setting up the apparatus was to lay out the magnetometer on a horizontal table and adjust it so that the long beam was accurately at right angles to the magnetic meridian. This adjustment was made by the method described in Gray's 'Absolute Measurements in Electricity and Magnetism' (2nd. Ed., P.124). The magnitude of H_e at the position occupied by the needle was then measured by the usual method involving the use of the equations

$$\frac{M}{He} = \frac{(d^2 - l^2)^2}{2.d} . \tan\theta \text{ --------------- } (1)$$

$$M. He = \frac{4 . \pi^2 . K}{T^2} \text{ ------------------- } (2)$$

To obtain a mean value three small cylindrical magnets were used, each in turn, at distance d from the needle due East and due West and reversed in each position, and the deflection δ of the magnetometer noted in each case. Then the needle was removed and replaced by a suspended aluminium stirrup and the period of oscillation, T, was accurately measured for each magnet when placed in the stirrup. The timing was done by means of a 'time switch' graduated to one-tenth of a second, and was repeated carefully three times. The results for the three magnets, A, B, and C, are summarised in Table I, and yield an average value of 0.1485 gauss for H_e.

Table I.

Results of Experiments for finding H_e
(Horizontal Component of Earth's Field).

Magnets.	A	B	C
Mean Length = L : cm.	10.10	10.14	10.14
Mean Diameter = 2r : cm.	.2375	.2375	.2385
Mass = m : gm.	3.536	3.548	3.564
$K = m. \left\{\frac{L^2}{12} + \frac{r^2}{4}\right\}$: c.g.s.u.	30.07	30.42	30.55
Period = T : sec.	6.891	6.587	6.779
Distance from needle = d : cm.	30.0	30.0	30.0
Half magnetic length = $\ell = \frac{5}{12}L$	4.21	4.23	4.23
Mean deflection = δ : cm.	18.74	20.67	19.75
Distance from Needle to scale = D	106.3	106.3	106.3
$2\theta = \mathrm{Tan}^{-1}\frac{\delta}{D}$	$9^{0}59^{1}$	$11^{0}2^{1}$	$10^{0}\ 32^{1}$
θ	$4^{0}59\frac{1}{2}'$	$5^{0}31^{1}$	$5^{0}\ 16^{1}$
$\frac{M}{H_e} = \frac{(d^2-\ell^2)^2}{2d}.\mathrm{Tan}\,\theta$	1134	1252	1195
$M.H_e = \frac{4\pi^2 K}{T^2}$	25.00	27.68	26.24
Hor.Comp.of earth's field: H_e	.1485	.1487	.1482

Mean value of H_e = .1485 c.g.s.u.

The arrangement of apparatus was then completed as in Fig.1 and readings for a number of I - H curves for a specimen of chromium steel (marked W.T.3, 4.05 % Cr.) were taken in the ordinary way, so as to determine its magnetic qualities and to become familiar with the method of working. In each case the magnetising solenoid was placed at such a distance from the magnetometer needle, that, when the current used was at the maximum value for the cycle, the deflection of the needle, due to the magnetism induced in the specimen, was almost the full length of the scale (25 cm.). Thus for maximum currents 1, 2, 3, 4, 5, 6 and 7 amps. the solenoid was placed at 53, 60, 80, 90, 100, 110, 120 cm. respectively from the needle and the process of compensation repeated in each case. It was never necessary to bring compensating coil D into the circuit which shows that the magnetometer and its fittings had been well made.

The effect of the rotating magnetic field was then tested as follows:

The stand with the rotating magnet was placed in position in the channel in the long limb of the magnetometer base and clamped with the magnet at a measured distance from the specimen in the magnetising solenoid. Readings for the magnetisation curve were taken first with the magnet rotating in one direction, with the cord from the motor arranged for open drive; then secondly, with the cord drive crossed and the magnet rotating with the same speed in the opposite direction; and thirdly, with the magnet removed but the motor still running, so that if any stray field from the driving motor had an effect at the magnetometer needle it would affect all three cycles equally.

This was done for different positions of the solenoid, and different distances of the rotating magnet, and different maximum currents through the solenoid.

Before the I - H curves could be drawn for the above experiments, however, a considerable amount of calculation was required. The evaluation of I - the magnetic moment per unit volume - was quite straightforward and dependent on the equation (1) given above. Thus:

$$I = \frac{H_e . (d^2 - l^2)^2 . \tan\theta}{2d} \times \frac{1}{\pi . r^2 . L}$$

$$\text{i.e. } I = k_1 . \tan\theta .$$

k_1 being a constant for a given position of the solenoid and θ being obtained from the equation

$\tan 2\theta = \frac{\delta}{D}$ where δ and D denote respectively the deflection of the magnetometer 'spot', and the distance between the scale and the magnetometer needle.

The evaluation of H^1 the <u>applied</u> field was also simple, depending on the solenoidal formula

$$H' = \frac{4 . \pi . n' . C}{10}$$

where n^1 is the number of turns per unit length of the solenoid, and C is the current in amperes. This gave 23.5 C for the applied field, but the <u>effective</u> field was smaller since the lines of force due to the induced magnetism run the opposite way to those of the applied field.

If, in the case of a cylindrical rod, the free poles were concentrated only at the end faces, the demagnetising field at the centre of the rod would obviously be given by

$$\frac{2.(\pi.\ r^2).I}{(\frac{1}{2}L)^2} \quad \text{i.e.} \quad \frac{2.\pi.I}{m^2}$$

where m is 'dimension-ratio' of length to diameter.

But the distribution of the free poles in a cylindrical specimen is never so simple as that. Indeed, it is not possible to predict it, and the self demagnetising effect of the induced magnetism has to be found empirically. It is generally assumed to be proportional to I and to depend also on the value of m , the dimension-ratio, and so the demagnetising field is generally expressed as N. I. In fact, N the 'demagnetising factor' is generally stated in text-books to depend <u>only</u> on the dimension ratio and is tabulated alongside the corresponding value of m. Shuddemagen (4), however, giving the results of his experiments on several series of rods, in which he kept to one diameter in one series and a different diameter in another series, shows that the actual diameter of a rod, as well as the ratio of the length to the

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(4) C.L.B. Shuddemagen: Proc. Amer. Acad. 43, 1907, P.185.

diameter, also influences the demagnetising factor. In his paper Shuddemagen gives a very thorough summary of the work which had previously been done in connection with demagnetising factors. He confirms the finding of Mann (5) that it is only for values of I less than about 800 c.g.s. units that the demagnetising factor may be considered constant. He emphasised, also, the findings of Benedicks (6) that for a ballistic experiment the value of the factor N for the range in which it is constant is smaller than for the same rod in a magnetometric experiment, becoming still smaller after the constant stage is past, whereas the factor for a magnetometric determination increases after $I = 800$.

The reason for this difference in the demagnetising factor lies in the fact that in the ballistic type of experiment, with a search-coil round the middle part of the rod, it is the <u>maximum</u> value of I which is measured, whereas in a magnetometric experiment it is the <u>mean</u> value of I for the whole rod, and due to the distribution of the free poles all over the curved surface the mean is considerably less than the maximum. It is generally the ballistic method of measurement that has been used by the different workers in this field of

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(5) R. Mann: Phys. Rev., 3, 1896, P.359.

(6) Benedicks: Wiedemann Ann., 6, 1901, P.726

research, and to obtain the correction factor for the present magnetometric experiments, the writer had to go back to the results of Mann in the paper just referred to. As m^2N varies less rapidly than N, a graph was drawn of m^2N against m, and from this the value of 0.0832 was obtained for N. Thus for each value of the applied field, given by $H' = 23.5C$, the value of the effective field was obtained from $H = H' - 0.0832.I$. For the few values of I greater than 800 the factor should be slightly higher than this, but the same slight error would equally affect the I-H curves with or without the rotation of the magnet, and it is therefore unimportant.

RESULTS.

The tables of results and the corresponding graphs are now given. In Table II the various steps in the calculation of I and H are shown for an ordinary hysteresis cycle with a maximum magnetising current of seven amperes, and in Fig.3 the intensity of the induced magnetism is plotted against the apparent magnetising field as well as against the corrected field. Tables III to VI give the values obtained for I and H in the experiments with the rotating magnet, and Figs. 4 to 7 give the corresponding graphs.

Fig. 8 is added to showthe curves originally obtained for the specimen under normal conditions and with maximum magnetising currents ranging from one to seven amperes.

TABLE II

Full Table of Results for Ordinary Hysteresis Cycle with 7 amperes maximum current.

Length of specimen = 20.4 cm.
Diameter .. .. = 0.97 cm.
Distance from needle to specimen = 120 cm.
.. .. scale = 106.7 cm.
Half magnetic length of specimen = 20.4 . (5/12) = 8.5 cm.

$$I = \frac{(120^2 - 8.5^2)^2 \, . \, 0.1485 \, . \tan\theta}{2 \, . \, 120 \, . \pi \, . \, (0.485)^2 \, . \, 20.4} = 8420 \, . \tan\theta$$

C amps.	δ cm.	2θ $\left(\tan^{-1}\frac{\delta}{106.7}\right)$	$\tan\theta$	I $(8420\tan\theta)$	H' $(23.5\,C)$	N.I $(.0832\ I)$	H $(H' - N.I)$
+1.36	+2.55	1° 22'	.0119	100	32.0	8.3	23.7
+2.14	+4.96	2° 40'	.0233	196	50.3	16.3	34.0
+2.90	+8.06	4° 20'	.0379	317	68.2	26.4	41.8
+3.44	+10.42	5° 34'	.0487	409	80.8	34.0	46.8
+4.06	+12.90	6° 54'	.0603	508	95.5	42.3	53.2
+4.76	+15.38	8° 12'	.0717	604	111.9	50.3	61.6
+5.98	+18.78	9° 58'	.0872	734	140.6	61.1	79.5
+7.17	+21.15	11° 12'	.0981	826	168.5	68.8	99.7
+3.06	+16.16	8° 36'	.0752	633	72.0	52.6	19.4
+0.70	+10.72	5° 44'	.0501	423	16.5	35.2	-18.7
- 0	+8.30	4° 2[illegible]'	.0389	327	0	27.2	-27.2
-0.97	+3.97	2° 8'	.0187	157	-22.8	13.1	-35.9
-1.69	-0.05	-0° 2'	-.0003	-3	-39.7	-.2	-39.5
-2.56	-5.00	-2° 40'	-.0233	-196	-60.2	-16.3	-43.9
-3.45	-9.90	-5° 18'	-.0463	-390	-81.2	-32.4	-48.8
-4.58	-14.90	-7° 56'	-.0694	-584	-107.6	-48.6	-59.0
-6.06	-18.98	-10° 6'	-.0884	-744	-142.5	-61.9	-80.6
-7.08	-20.96	-11° 6'	-.0972	-818	-166.5	-68.1	-98.4
-7.15	-21.15	-11° 12'	-.0981	-826	-168	-68.8	-99.2
-3.69	-17.35	-9° 14'	-.0808	-680	-86.8	-56.6	-30.2
-1.31	-12.75	-6° 49'	-.0596	-502	-30.8	-41.8	11.0
0	-8.65	-4° 38'	-.0405	-341	0	-28.4	28.4
+0.90	-4.52	-2° 26'	-.0212	-178	21.2	-14.8	36.0
+1.72	+0.15	+0° 5'	.0007	+6	40.4	.5	39.9
+2.73	+6.00	3° 13'	.0281	237	64.2	19.7	44.5
+3.51	+10.20	5° 28'	.0478	402	82.5	33.4	49.1
+4.64	+15.18	8° 6'	.0708	596	109	49.6	59.4
+6.00	+18.92	10° 4'	.0881	742	141	61.7	79.3
+7.22	+21.25	11° 16'	.0987	831	169.7	69.2	100.5

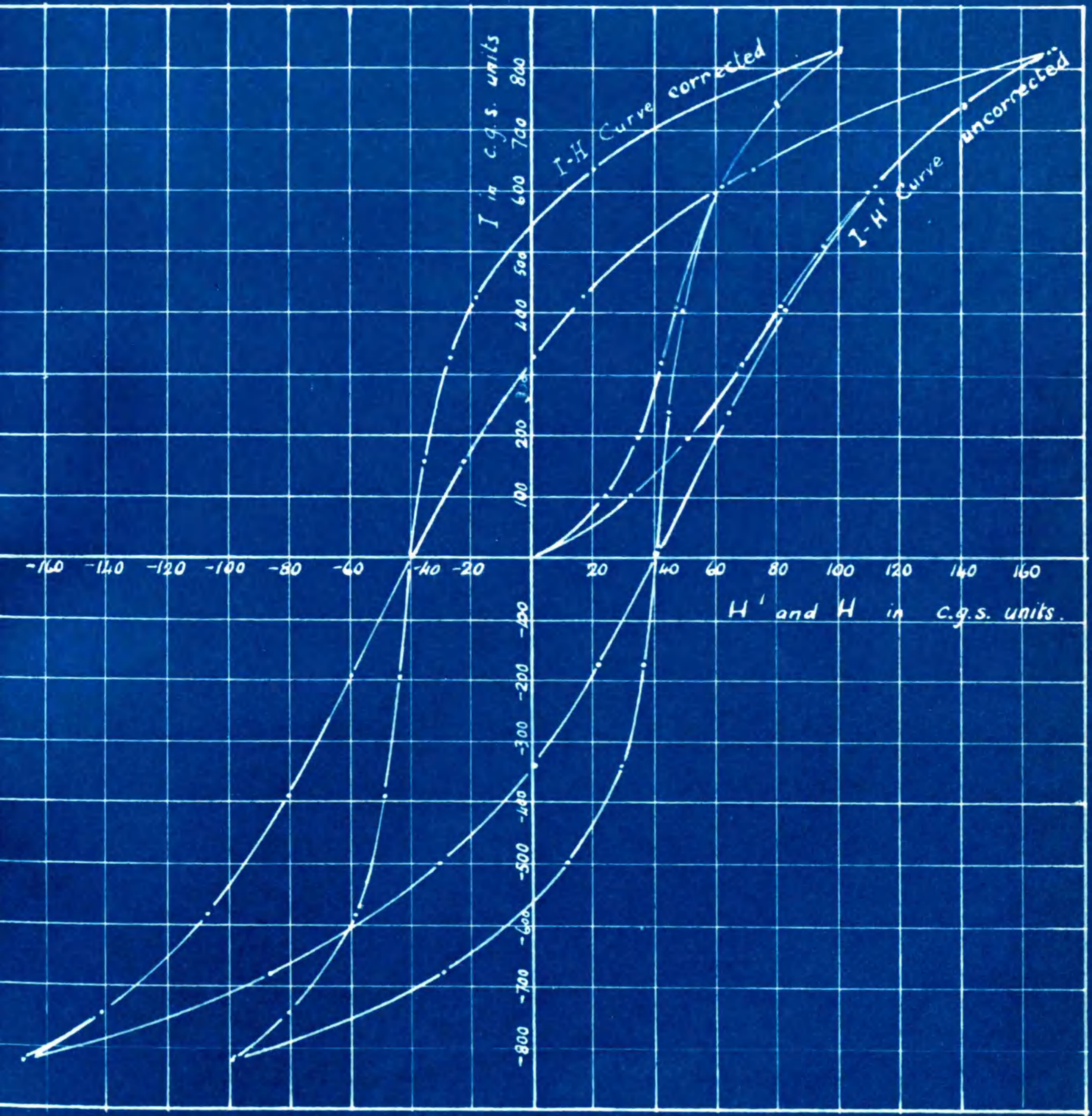

Fig. 3.

I-H Curves for Maximum Current of 7 Amperes,
With and without self-demagnetisation correction.

TABLE III

Results of Experiments with Rotating Magnet. **First Set.**

Maximum magnetising current ...... 9 amperes.
Distance of magnet from centre of specimen ...... 25.2 cm.
Distance of needle " " " " ......120 cm.
(giving I = 8420 . tan θ)
Speed of rotation of magnet about 150 revs. per minute.

Condensed Table of Results

Magnet Rotating with Open Drive		Magnet Rotating with Crossed Drive		Normal Conditions	
I	H	I	H	I	H
35	9.8	34	9.4	32	9.5
72	18.7	72	18.9	67	18.3
175	32.4	181	32.8	178	32.7
336	43.3	336	43.2	348	44.0
498	52.6	517	54.3	498	52.6
636	65.0	642	64.5	633	66.0
753	83.2	744	81.0	737	81.4
823	99.0	825	100.1	828	101.7
878	116.8	895	122.2	924	135.5
924	134.4	930	136.7	...	...

In this Set the points for the magnet rotating in either direction lie partly above the curve for Normal Conditions.

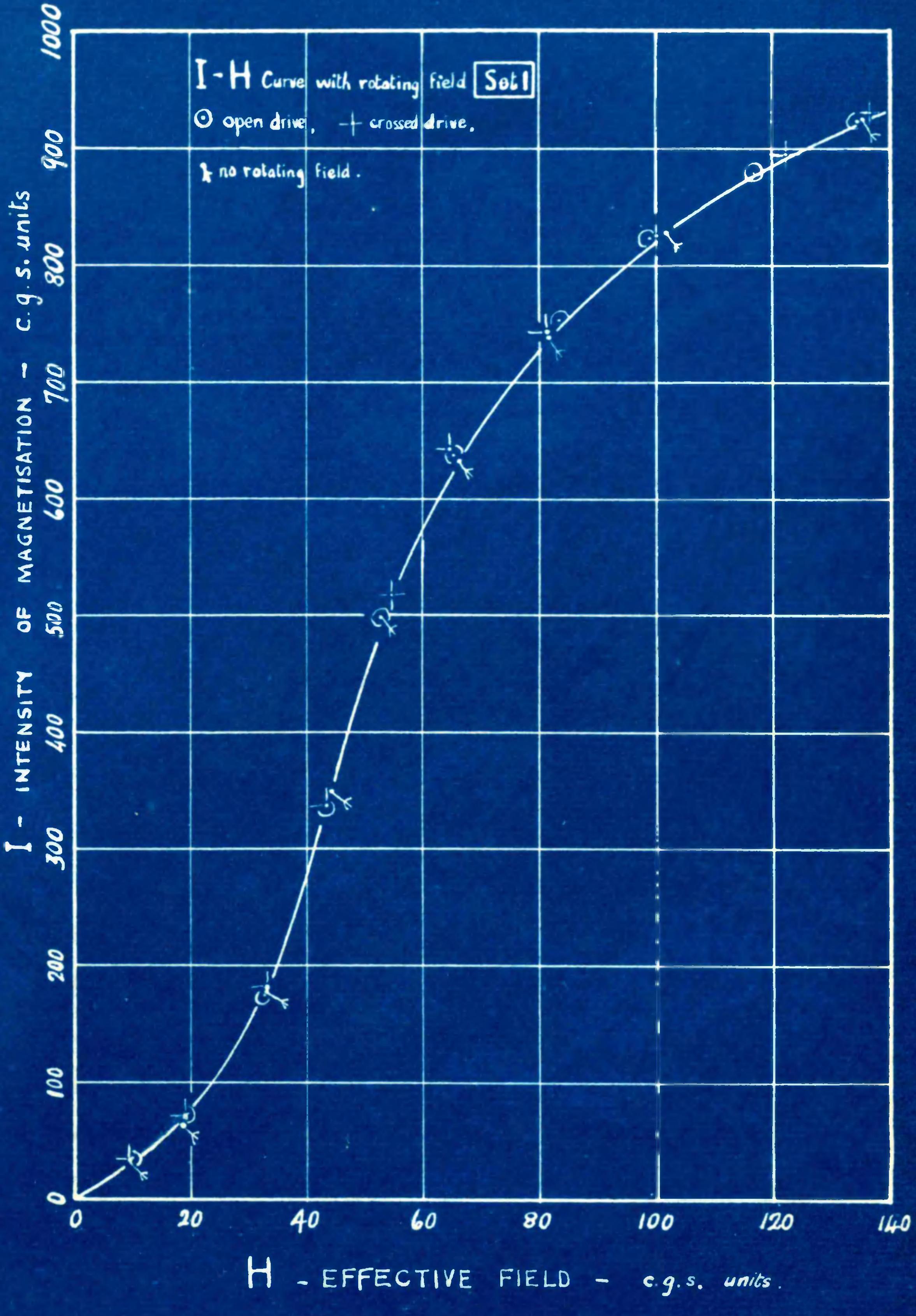
I - H Curve with rotating field
Set I
⊙ open drive, -+ crossed drive,
no rotating field.
I - INTENSITY OF MAGNETISATION - c.g.s. units
H - EFFECTIVE FIELD - c.g.s. units.
0
100
200
300
400
500
600
700
800
900
1000
0
20
40
60
80
100
120
140

Fig. 4.

TABLE IV

Results of Experiments withRotating Magnet. Second Set.

Solenoid moved much nearer to needle, to suit
Maximum magnetising current of 1.4 amperes.
Distance of magnet from centre of specimen ..... 25.2 cm.
Distance of needle " " " " ..... 60.0 cm.
(giving $I = 1021 \tan\theta$)
Speed of rotation of magnet..... 150 to 180 r.p.m.

Condensed Table of Results

Magnet Rotating with Open Drive		Magnet Rotating with Crossed Drive		Normal Conditions	
I	H	I	H	I	H
12.2	3.93	12.5	3.90	11.5	3.86
24.8	7.37	24.9	7.85	24.9	7.61
...	...	...	...	25.5	7.75
39.7	11.62	38.9	11.56	39.5	11.64
55.1	15.27	54.8	15.41	55.0	15.35
69.8	18.46	68.4	18.17	68.4	18.17
85.4	21.09	85.8	21.66	86.1	21.70
104.2	24.80	102.9	24.70	104.9	24.88

In this Set, save for occasional exceptions, the points for allthree conditions lie on the same curve.

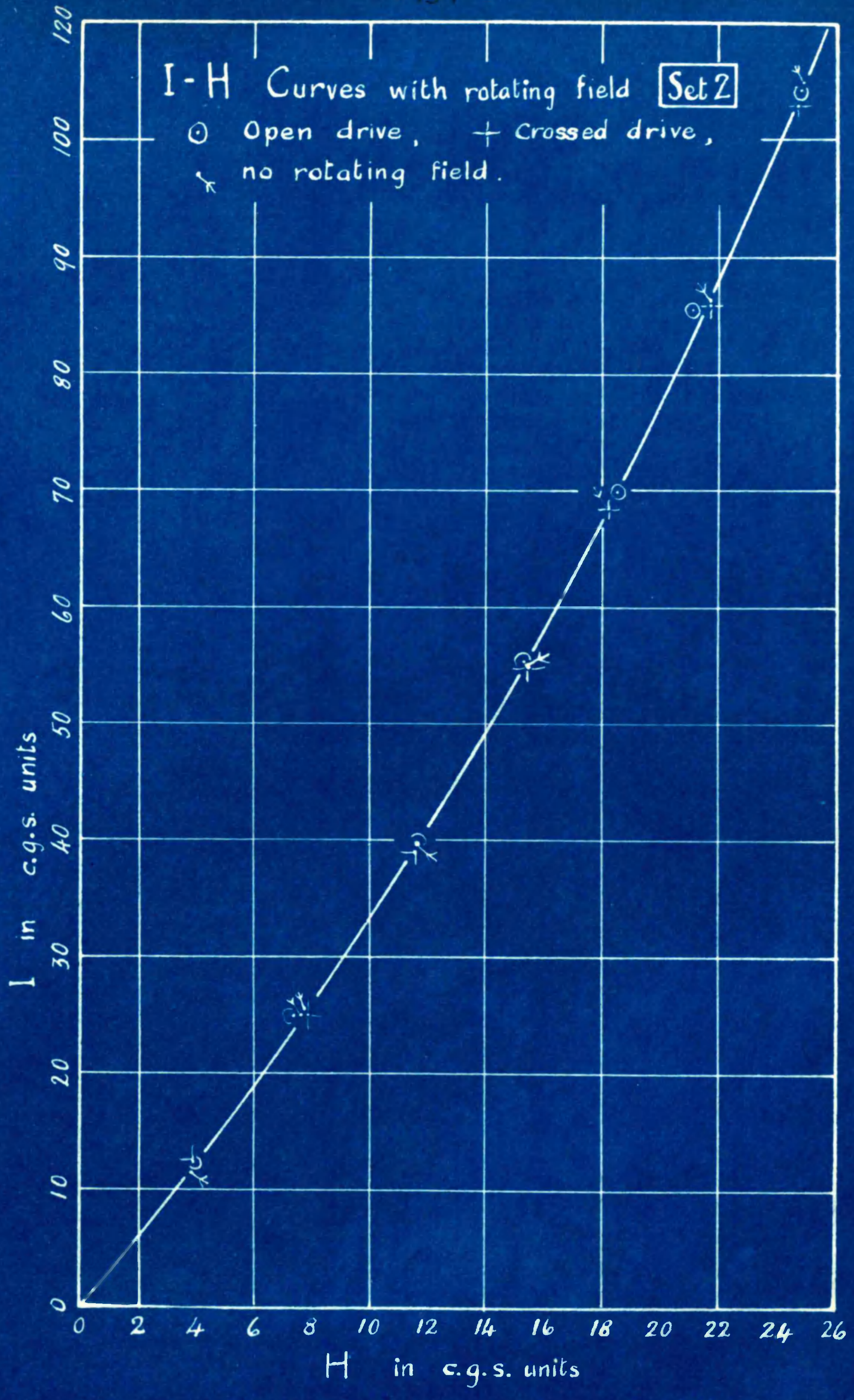
I-H Curves with rotating field
Set 2
⊙ Open drive, + Crossed drive,
no rotating field.
I in c.g.s. units
H in c.g.s. units
0
10
20
30
40
50
60
70
80
90
100
120
0
2
4
6
8
10
12
14
16
18
20
22
24
26

Fig. 5.

TABLE V

Results of Experiments with Rotating Magnet. Third Set.

Solenoid moved away from needle, to suit
Maximum magnetising current of 8.8 amperes.
Distance of magnet from centre of specimen ..... 16.5 cm.
(To attain this shorter distance, thespecimen was pushed along near to the end of the solenoid distant from the needle. Near the end of a solenoid the magnetising field is not quite uniform, but this condition is the same for each run.)
Distance of needle from centre of specimen .....129.0 cm.
(giving I = 10470 . tanθ).
Speed of rotation of magnet about 150 r.p.m.

Condensed Table of Results

Magnet Rotating with Open Drive		Magnet Rotating with Crossed Drive		Normal Conditions	
I	H	I	H	I	H
30	10.4	31	10.3	37	10.4
66	18.2	107	25.6	71	18.5
176	33.6	170	32.9	184	33.6
320	44.4	323	44.1	334	44.3
485	54.9	487	54.7	493	54.6
622	67.4	637	68.7	636	67.4
728	83.2	719	81.9	732	82.9
802	100.3	807	101.4	807	100.7
861	116.8	867	119.9	871	120.3
901	132.5	900	131.4	904	132.5

In this Set some of the points for the magnet rotating lie slightly below the normal curve.

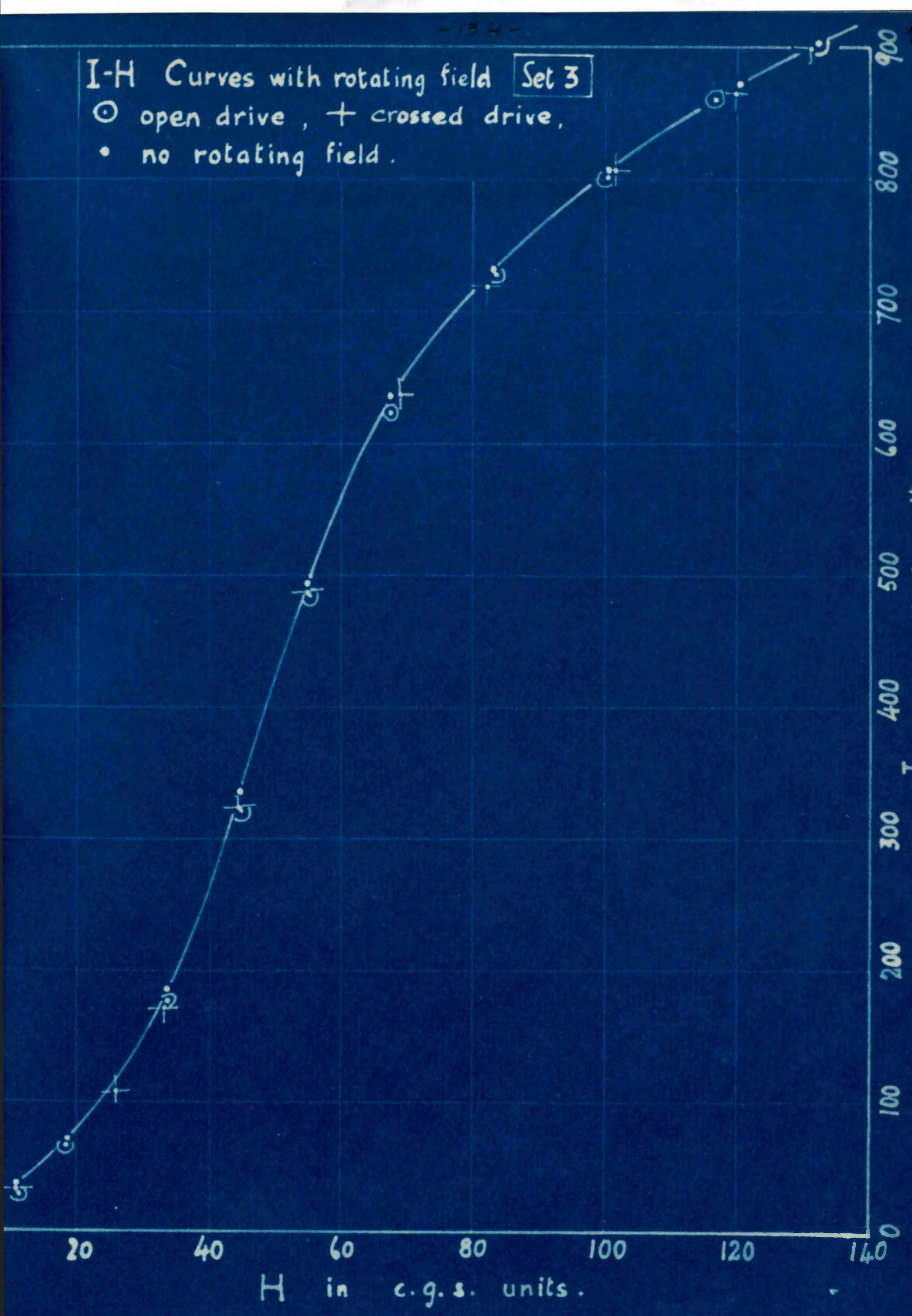
I-H Curves with rotating field
Set 3
⊙ open drive , + crossed drive ,
• no rotating field .
20
40
60
80
100
120
140
H in c.g.s. units .
0
100
200
300
400
500
600
700
800
900
I in c.g.s. units

Fig. 6.

TABLE VI

Results of Experiments with Rotating Magnet. Fourth Set.

Solenoid again moved closer to the needle, to suit Maximum current of 1.4 amperes.
Distance of needle from centre of specimen ..... 12.6 cm.
(The magnet was brought still nearerto the specimen by reversing the solenoid so that the end with the projecting tube for the cooling arrangement now faced towards the needle instead of towards the magnet.)
Distance of needle from centre of specimen ..... 72.0 cm.
giving I = 1787 . tan 0 .
Speed of rotation of magnet now about 300 revs. per minute.

Condensed Table of Results

Magnet Rotating with Open Drive		Magnet Rotating with Crossed Drive		Normal Conditions	
I	H	I	H	I	H
5.7	2.05	63	1.95	6.1	1.96
11.2	3.85	10.9	3.98	12.5	3.94
17.5	5.68	17.2	5.62	19.3	6.19
24.3	7.64	24.3	7.68	24.1	7.56
39.3	11.68	39.3	11.65	39.0	11.66
52.2	14.96	51.8	14.87	52.6	15.00
66.8	18.17	67.2	18.26	68.5	18.43
83.3	21.51	85.2	21.91	85.8	22.10
102.0	24.64	101.3	24.65	101.3	25.17

In this Set again all the points lie on one curve.

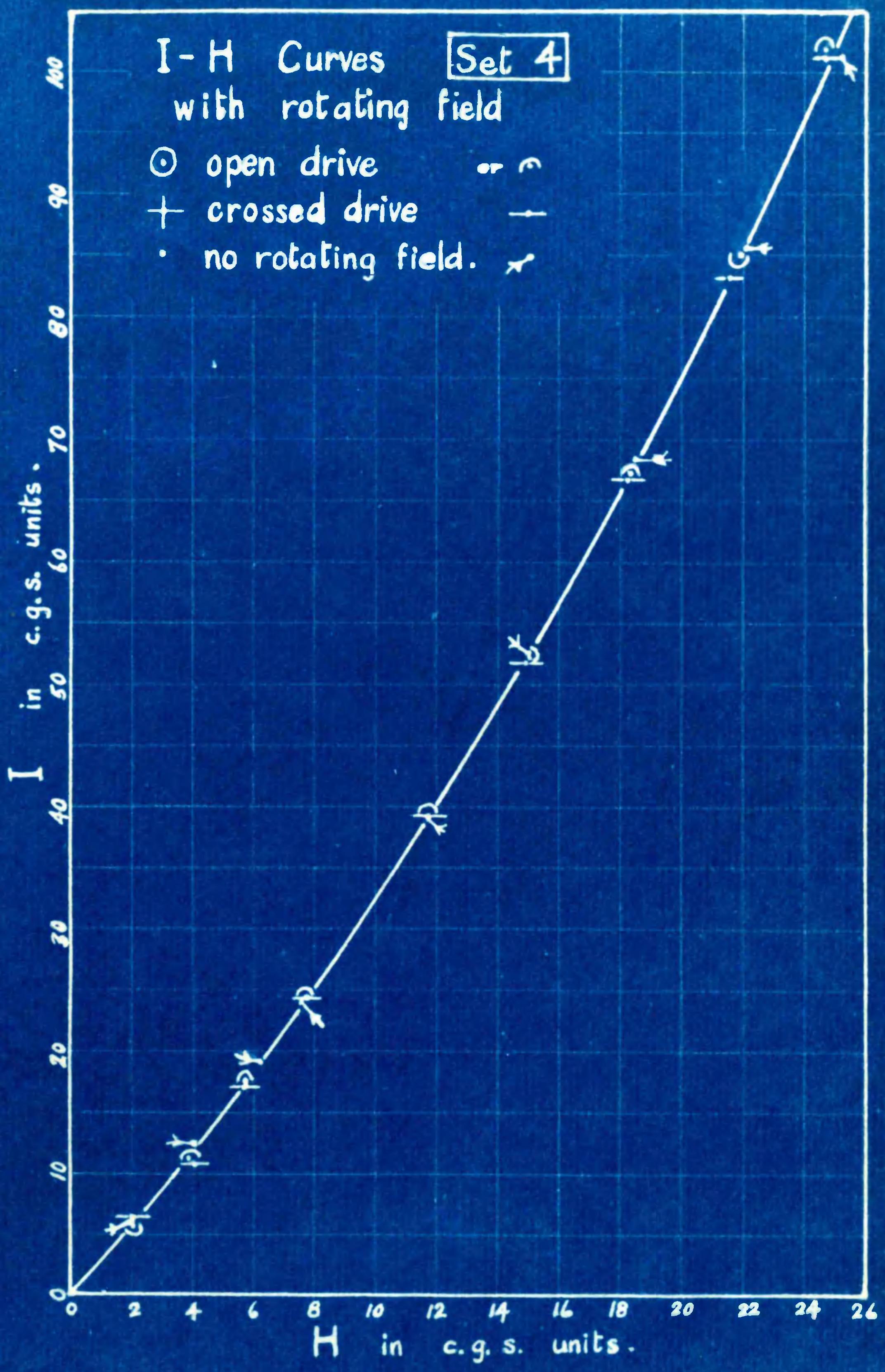
I - H Curves
Set 4
with rotating field
⊙ open drive
+ crossed drive
· no rotating field.
I in c.g.s. units.
H in c.g.s. units.
0
10
20
30
40
50
60
70
80
90
100
0
2
4
6
8
10
12
14
16
18
20
22
24
26

Fig. 7.

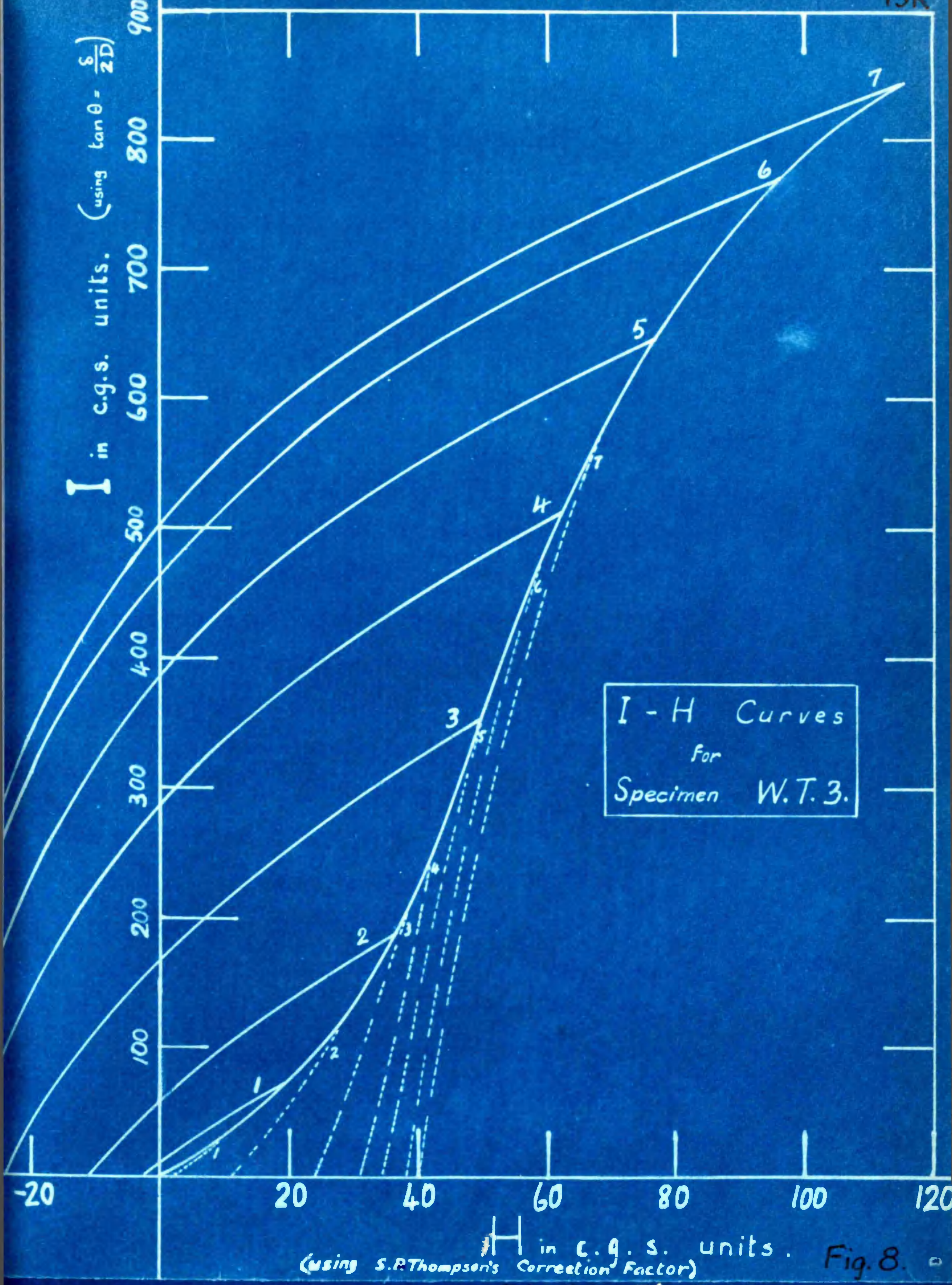
I - H Curves
for
Specimen W.T.3.
I in c.g.s. units. (using tan θ = δ/2D)
H in c.g.s. units.
(using S.P.Thompson's Correction Factor)
900
800
700
600
500
400
300
200
100
-20
20
40
60
80
100
120
1
2
3
4
5
6
7

Fig. 8.

Comment on the Results.

When the graphs for the experiments with the rotating field are examined it is seen that their evidence is conflicting. In set (1) the I - H curve obtained when the magnet was rotating clockwise seemed to coincide with the curve for counter clockwise rotation but to lie, in part, slightly above the normal curve. But in set (3) the opposite effect seemed to be shown, as the I - H curves for both directions of rotation again coincide but lie, in part, slightly below the normal curve. On the other hand, in sets (2) and (4) one curve seems to suit all the three sets of points, thus indicating that the rotating magnet makes no appreciable difference.

To investigate further, single spot readings were taken by bringing the specimen to a certain stage in the cycle of magnetisation and reading the deflection for (a) normal conditions, (b) magnet rotating clockwise, and (c) magnet rotating counter-clockwise, but the readings were not consistent on repetition. Readings (b) and (c) were sometimes a little greater than (a), and sometimes less.

The effect of the rotating magnet on the control field was tested by timing the swing of the needle for (a) normal conditions, (b) motor running without the magnet, and (c) motor running and magnet rotating. In all three cases the period of oscillation was found to be exactly the same - 3.00 seconds - so that it was assumed that the rotation of the magnet did not affect the control field at the needle.

Conclusion.

The results of these experiments may therefore be summed up as follows: The influence of the rotating magnet did not seem to be very appreciable. When an effect appeared to be detected it was not consistent. For one set of experiments, rotation in either direction seemed to help the magnetisation; for another to hinder it; and in other experiments it seemed to make no difference. Thus it is concluded that a rotating field of the order used produces no distinct effect on a specimen lying in the direction of the axis of rotation. It is to be noted that the field due to the magnet was not very great - a few gauss at most - nor was it uniform, being greatest at the end of the specimen nearest to the magnet, and decreasing towards the farther end. Also it should be noted that in a paper which was published a year after these experiments were carried out, J.W.Fisher(7) described experiments with more elaborate apparatus and a much stronger field, in which he also failed to obtain the looked-for effect.

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(7) Proc. Roy. Soc., Ser.A, Vol.109, 1925, P.7.
(The following is his summary of the investigation:
'Experiments are described in which it is sought to
'detect /

'detect a gyro-magnetic effect by magnetising a substance '(in most cases magnetite) by a rotating magnetic field, 'and looking for a component of magnetisation in a 'direction perpendicular to the plane of rotation of the 'field; such a component would be expected to arise if a 'rotation of the magnetic axes of the molecules is set up 'by a rotating field. Fields rotating at frequencies of '2 - 5.10^4 cycles per second were produced by valve 'generators, but no evidence of an effect of this kind was 'found, even for rotating fields of over 100 gauss. The 'magnitude of the effect has been calculated and the 'sensitivity of the apparatus was such that it should have 'been easily capable of detection if present.'

Acknowledgments.

The writer desires to express his thanks to Professor J. G. Gray for his supervision, and for the facilities he provided for carrying out the work; also for his recommendation which gained for the writer the Thomson Experimental Scholarship.

He is also grateful for the encouragement and advice given by Dr. R. C. Gray during the course of the work.

PART II

THE COEFFICIENTS OF DIFFUSION OF ALKALI VAPOURS IN FLAMES

SUMMARY.

Experiments are described in which the coefficients of diffusion of sodium and potassium vapours in a bunsen flame were measured by means of an electrical method. Electrodes of platinum wire, insulated by quartz tubes were connected to a battery and galvanometer and held in a flame in which a bead of salt was being vaporized. The cathode was moved about in the flame, and when the current in the galvanometer was the same for successive positions of the cathode it was assumed that the concentration of metallic vapour was the same at these points. By noting the positions of pairs of such points, and by measuring the velocity of the flame gases, the coefficients of diffusion were calculated. The values obtained are rather higher than those got previously by Professor H. A. Wilson from measurements of the maximum diameter of the coloured region in the flame.

INTRODUCTION.

When an alkali salt is vaporised in a bunsen flame the distinctive colour obtained seems to originate in atoms of the metal which are set free by the dissociation of the salt.(1) This would explain the familiar fact that the same coloration is produced by different salts of the same metal, and the less known observation that the same molecular concentration of different salts of the same metal imparts the same electrical conductivity to the flame (1'). On this assumption, that the spread of colour through the flame is due to the diffusion of the metal atoms, and on the further assumption that the boundary of the coloured region marks a surface over which the concentration of the metallic vapour is uniform, Professor H. A. Wilson calculated the coefficients of diffusion through a flame of a number of metallic vapours using measurements of the maximum diameter of the coloured region (2). The experiments here described were carried out at his suggestion in the hope that more accurate values of the coefficients might be obtained by an electrical method.

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(1) Thomson : 'Conduction of electricity through gases', 3rd Ed., P. 402.

(1') Ibid., P.413.

(2) H. A. Wilson : Phil.Mag., July 1912, P. 118.

THEORY.

The term 'Coefficient of Diffusions of a Substance' is best explained by reference to **F**ick's law of diffusion, which may be stated as follows:- 'Consider the substance to be distributed through a given medium so that layers of equal concentration are horizontal, less dense layers being uppermost; and let the concentration in the layer at a height x above a fixed plane be c gm. per c.c.; then through unit area of this layer $-K. \frac{dc}{dx}$ grams of the substance will pass in unit time from the side on which the substance is more concentrated to that on which it is less.' The constant factor, K, in this expression is termed the coefficient of diffusion of the substance through the given medium and under the given conditions. In such an arrangement, which is illustrated in Fig.1, since the concentration decreases as x increases, the concentration-gradient, $\frac{dc}{dx}$, is negative, and the mass of the substance, Q grams, diffusing upwards in time t seconds, through an area A sq. cm., at right angles to x, is given by the equation

$$Q = - K. A. t. \frac{dc}{dx} \quad - - - - - - - - - (1)$$

This equation fits the relatively simple case of the diffusion of a substance in solution from a concentrated layer at the foot of a vessel into the layers of weaker solution above,

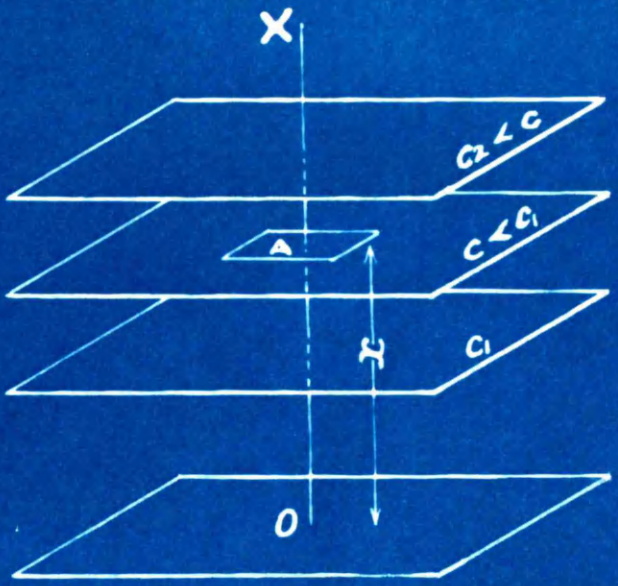

Fig. 1.

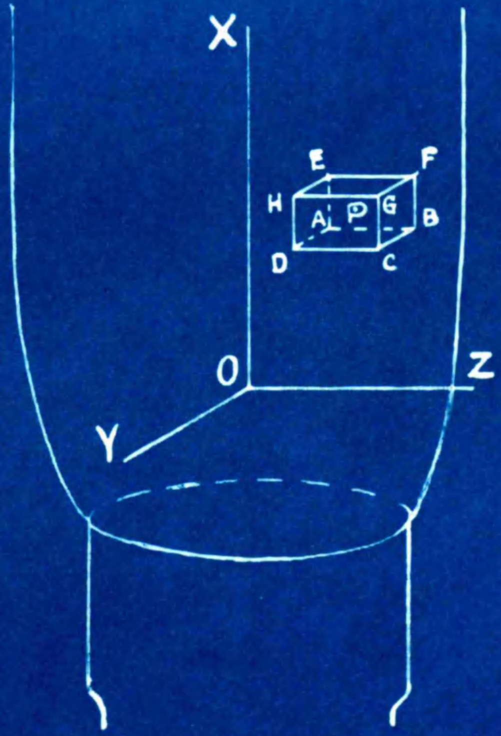

Fig. 2.

but the conditions of the present problem are more complicated. A bead of salt in a flame may be regarded as a source from which metallic vapour issues at an almost steady rate and diffuses in all directions, even downwards against the upward current of the flame, as the colouration of the flame shows. The above equation must therefore be extended to three dimensions, and allowance must be made for the velocity of the flame. It will be observed that the equation is closely analogous to the simple equation relating to thermal conduction (sometimes called 'diffusion of heat') and the following treatment is similar to the standard method of dealing with the problem of thermal conduction.

Let the origin of coordinates be taken at the centre of the bead of salt, with the axis O X vertically upwards, i.e. in the direction of motion of the flame. The axes O Y and O Z are thus in a horizontal plane, as shown in Fig.2. Consider the point P (x, y, z) at the centre of a very small parallelopiped ABCDEFGH whose sides AE, AD, AB are δx, δy, δz respectively. If c is the concentration of metallic vapour at P, $\left\{c - \frac{\partial c}{\partial x} \cdot \frac{\delta x}{2}\right\}$ may be taken as the average concentration over the face ABCD, and $\left\{\frac{\partial c}{\partial x} - \frac{\partial^2 c}{\partial x^2} \cdot \frac{\delta x}{2}\right\}$ the average concentration-gradient in the x-direction for the same face.

Thus, neglecting in the meantime, the upward velocity of the flame, the amount of metal entering the face ABCD per second would be $-K\left\{\frac{\partial c}{\partial x} - \frac{\partial^2 c}{\partial x^2}\cdot\frac{\delta x}{2}\right\}\delta y.\delta z$, and the amount passing out through the opposite face per second would be

$$-K\left\{\frac{\partial c}{\partial x} + \frac{\partial^2 c}{\partial x^2}\cdot\frac{\delta x}{2}\right\}\delta y.\delta z.$$

Hence the increase per second in the amount of metallic vapour inside the parallelopiped due to the component of the diffusion in the direction parallel to O X would be

$$+K\cdot\frac{\partial^2 c}{\partial x^2}\cdot\delta x.\delta y.\delta z.$$

The components of the diffusion parallel to OY and OZ would contribute similar increments, giving a total increment per second of

$$K\left\{\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2}\right\}\delta x.\delta y.\delta z.$$

But the velocity of the flame gases has still to be considered. This is found to be sensibly constant and may be denoted by V cm. per second parallel to O X. Due to this velocity alone, the amount of metallic vapour entering face ABCD per second would be $V.\left\{c - \frac{\partial c}{\partial x}\cdot\frac{\delta x}{2}\right\}.\delta y.\delta z$, and the amount leaving through face EFGH would be $V.\left\{c + \frac{\partial c}{\partial x}\cdot\frac{\delta x}{2}\right\}.\delta y.\delta z$. This would result in an increase in the amount of metal in the parallelopiped at the rate of

$-V.\frac{\partial c}{\partial x}.\delta x.\delta y.\delta z.$ gm. per second, and since, when steady conditions are reached, the net increase per second in amount of vapour in the elementary parallelopiped will be zero, we have for steady conditions,

$$K\left\{\frac{\partial^2 c}{\partial x^2}+\frac{\partial^2 c}{\partial y^2}+\frac{\partial^2 c}{\partial z^2}\right\}-V\cdot\frac{\partial c}{\partial x}=0\ \text{.......}\ (2)$$

Professor Wilson has shown that a solution for this equation takes the form $c = \frac{A}{r} \cdot e^{\alpha(x - r)}$, where A and α are constants, and r is the polar coordinate of the point (x, y, z), i.e. $r = \sqrt{x^2 + y^2 + z^2}$ (3)

By differentiating and substituting in equation (2), the value of α may be shown to be $\frac{V}{2K}$

(Thus:

$$\frac{\partial r}{\partial x} = \frac{1}{2}\cdot\frac{2x}{\sqrt{x^2+y^2+z^2}} = \frac{x}{r},$$

$$\frac{\partial c}{\partial x} = A\cdot e^{\alpha(x-r)}\left\{\frac{\alpha}{r}-\frac{\alpha x}{r^2}-\frac{x}{r^3}\right\},$$

$$\frac{\partial^2 c}{\partial x^2} = +A\cdot e^{\alpha(x-r)}\left\{\frac{\alpha^2}{r}-\frac{\alpha}{r^2}-\frac{2\alpha^2 x}{r^2}-\frac{1}{r^3}\overset{-\frac{2\alpha x}{r^3}}{\wedge}+\frac{\alpha^2 x^2}{r^3}+\frac{3\alpha x^2}{r^4}+\frac{3x^2}{r^5}\right\}$$

$$\frac{\partial c}{\partial y} = -A\cdot e^{\alpha(x-r)}\left\{\frac{\alpha . y}{r^2}+\frac{y}{r^3}\right\},$$

$$\frac{\partial^2 c}{\partial y^2} = +A\cdot e^{\alpha(x-r)}\left\{\frac{-\alpha}{r^2}-\frac{1}{r^3}+\frac{\alpha^2 y^2}{r^3}+\frac{3\alpha y^2}{r^4}+\frac{3y^2}{r^5}\right\}, \text{ and}$$

$$\frac{\partial^2 c}{\partial z^2} = +A\cdot e^{\alpha(x-r)}\left\{-\frac{\alpha}{r^2}-\frac{1}{r^3}+\frac{\alpha^2 z^2}{r^3}+\frac{3\alpha z^2}{r^4}+\frac{3z^2}{r^5}\right\}.$$

Hence, $\frac{\partial^2 c}{\partial x^2}+\frac{\partial^2 c}{\partial y^2}+\frac{\partial^2 c}{\partial z^2} =$

$$A . e^{\alpha(x-r)}\left\{\frac{\alpha^2}{r}-\frac{3\alpha}{r^2}-\frac{2\alpha^2 x}{r^2}-\frac{3}{r^3}-\frac{2\alpha x}{r^3}+\left(\frac{\alpha^2}{r^3}+\frac{3\alpha}{r^4}+\frac{3}{r^5}\right)(x^2+y^2+z^2)\right\}$$

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(3) Proc. Camb. Soc. Vol. XII, pt. 5 (1904)

and since $x^2 + y^2 + z^2 = r^2$

$$\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2} = A.e^{\alpha(x-r)}\left\{\frac{2\alpha^2}{r} - \frac{2\alpha^2 x}{r^2} - \frac{2\alpha x}{r^3}\right\} = 2\,\alpha.\frac{\partial c}{\partial x}.$$

Thus, from equation (2), $\alpha = \frac{V}{2K}$.)

To evaluate A, consider the special case when $V = 0$. For such a condition, the quantity of metallic vapour diffusing through a spherical surface of radius r and centre at the centre of the bead will be q the total amount issuing per second from the bead. Hence

$$q = -K \cdot \frac{dc}{dr} \cdot 4\pi . r^2$$

and for this case $c = \frac{A}{r} . e^{\frac{V}{2K}(x-r)} = \frac{A}{r}$, since $V = 0$,

and $\frac{dc}{dr} = -\frac{A}{r^2}$

i.e. $q = -K.\left(-\frac{A}{r^2}\right). 4\pi . r^2$

$\therefore$ $A = \frac{q}{4\pi K}$, and the full solution of equation (2) becomes

$$c = \frac{q}{4\pi . K . r} \cdot e^{\frac{V}{2K}(x-r)}$$

This equation gives the distribution of metallic vapour in the flame and from it, using the coordinates (x_1, r_1), (x_2, r_2) of two points at which the concentration is the same, a simple equation for K may be derived.

Thus:-

$$\frac{q}{4\pi K . r_1} \cdot e^{\frac{V}{2K}(x_1 - r_1)} = \frac{q}{4\pi K r_2} \cdot e^{\frac{V}{2K}(x_2 - r_2)}$$

giving $$\frac{r_2}{r_1} = e^{\frac{V}{2K}(x_2 - r_2 - x_1 + r_1)}$$

or $$K = \frac{V(x_2 - r_2 - x_1 + r_1)}{2 \log_e \frac{r_2}{r_1}}$$

That an electrical method might be used for locating points where the concentration is the same was suggested by the results of an investigation of the electrical properties of flames by Prof. H.A.Wilson (4). He found that when two electrodes of platinum were held in a flame, and a current of electricity passed between them, practically all the resistance to the current was in the part of the flame close to the negative electrode. Further, when salt vapour was introduced into the flame, provided the vapour came into contact with the cathode, a large increase in the current was observed, this being greater the nearer the cathode was moved to the source of salt vapour. The position of the anode seemed to be unimportant, provided it was kept red-hot, whereas a slight change in the position of the cathode made all the difference in the current obtained, and it was concluded that the magnitude of the current was due to the number of metallic ions present in the region of the cathode.

In such an arrangement, therefore, when the same current is obtained for two different positions of the cathode, it seems reasonable to assume that the concentration of metallic vapour at these points is the same. This assumption was the basis of the experiments now described.

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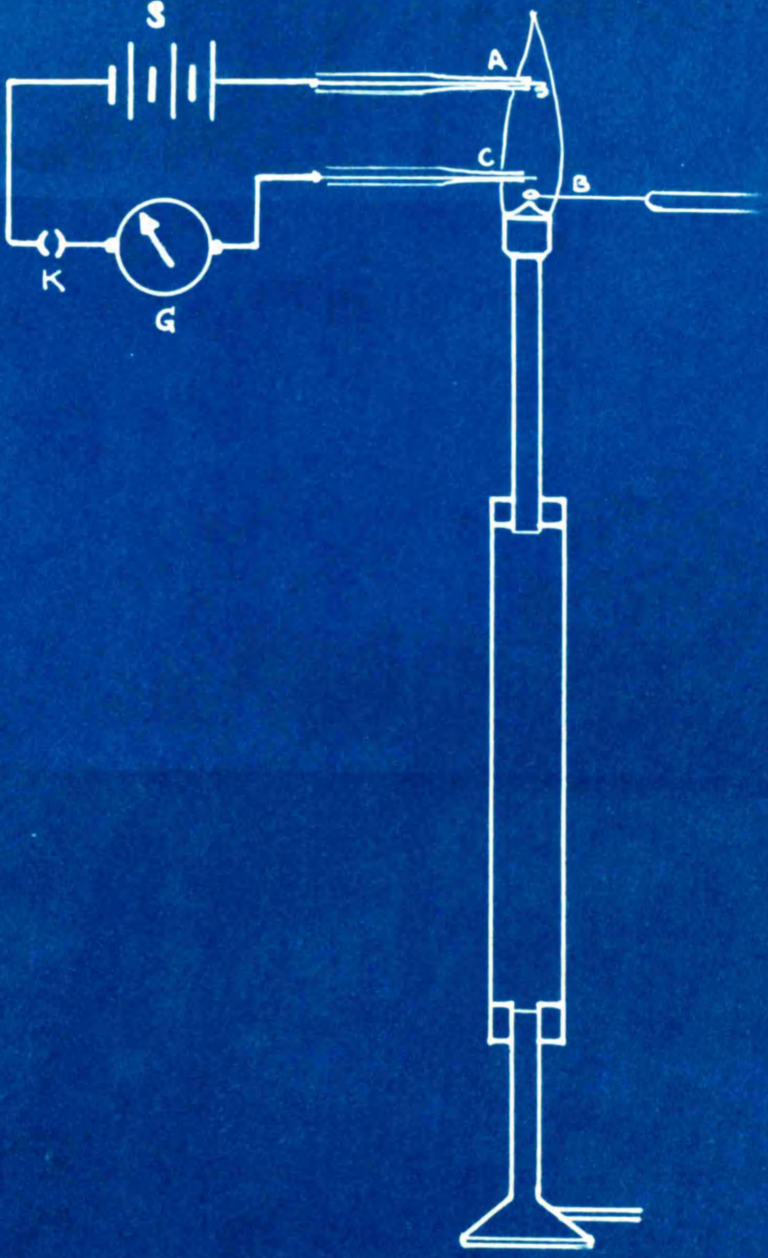
(4) H.A.Wilson: 'Electrical Properties of Flames'.
or : 'Modern Physics', 1st.Ed., Pp. 250 - 267.

APPARATUS.

The apparatus used is shown diagrammatically in Fig.3. An ordinary bunsen with wire gauze top had its chimney extended by the addition of two lengths of brass tubing. The purpose of this was to allow the gas and air to be well mixed and so produce a steadier flame. A loop of platinum wire for the salt-bead, B, was supported on an iron stand. The current was taken from a 6-volt storage battery, S, and measured by G, a microammeter in some experiments, and a more sensitive reflecting galvanometer in others. The lead from the positive terminal of the battery was fused to one end of a platinum wire which was insulated by being sheathed in a drawn-out tube of quartz, the other end of the platinum wire, A, being twisted into a little spiral to form the anode. The negative electrode, C, was similarly formed but the platinum wire used was thinner and projected from the quartz tube only about two millimetres. A vernier microscope, equipped with three racking movements, proved to be a very suitable support for the cathode once the optical parts were removed. This is seen in Fig.4.

The apparatus for measuring the velocity of the flame is described later.



Diagrammatic Sketch of Apparatus.

Fig. 3.

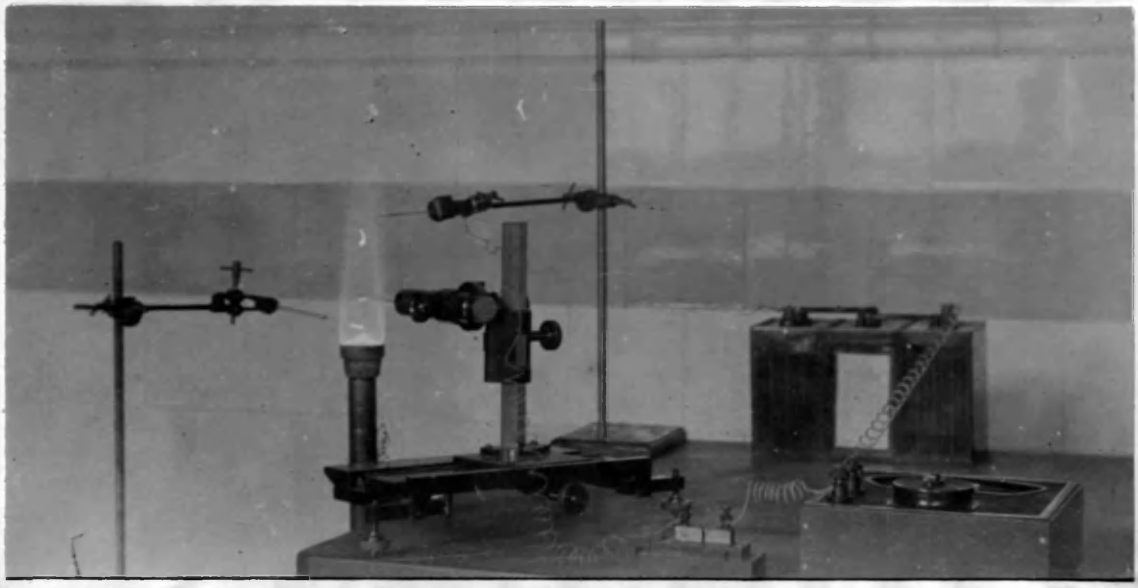


Fig. 4.

Photograph of Apparatus.

PROCEDURE.

To keep conditions as far as possible the same throughout the experiments, the gas supply was always regulated so that the tip of the blue inner cone was the same height (1 cm.) above the top of the burner, and bead of salt was adjusted so as to be on the axis of the flame at the regular distance 2 cm. above the top of the burner. The anode, also, was kept in the one position fairly high in the flame. With the three different movements of the microscope it was easy, first of all, to adjust the cathode to be directly above the salt bead, and thereafter, to move it about in a vertical plane ($z = o$) and read off its vertical and horizontal distances from the bead (i.e. its x and y co-ordinates) for any particular position.

Various potassium salts were tried, and potassium phosphate was found to be most suitable, as it burned off most slowly. It was found, too, that when the cathode was kept fixed in one position, the current slowly increased as the bead of salt evaporated, being greatest just before the colouration of the flame disappeared. To allow for this, in locating different positions of the cathode which gave the same current, the cathode was first raised to be one centimetre above the bead, then moved across the flame, and readings of the horizontal vernier were taken for the positions

A and B (Fig.5) which corresponded to a certain current. Then, the cathode was raised to be three centimetres above the bead, and the readings taken for C and D, which gave the same current. Finally, the cathode was again lowered to the former level and the readings repeated for A and B. The mean of the two values for the distance AB was taken as corresponding to the state of the bead when the observations were made for the distance CD. These readings allowed the coordinates of A and D to be determined as follows:-

For A,
$x_1 = OE = 1$,
$y_1 = EA = \frac{1}{2} . (BA)$
$z_1 = 0$,
$r_1 = OA = (x_1^2 + y_1^2)^{\frac{1}{2}}$.

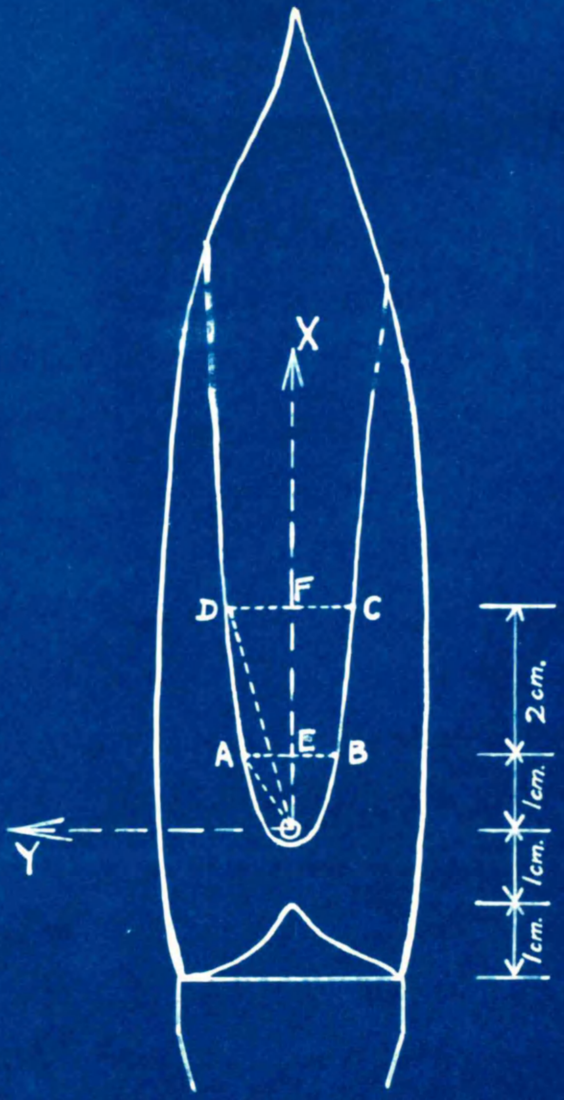
For D,
$x_2 = OF = 3$
$y_2 = FD = \frac{1}{2} . (CD)$,
$z_2 = 0$,
$r_2 = OD = (x_2^2 + y_2^2)^{\frac{1}{2}}$.

The readings were repeated for several beads, and different values were used for the constant current.

Before K could be evaluated, however, from

$$K = \frac{V(x_2 - x_1 - r_2 + r_1)}{2 \log_e \frac{r_2}{r_1}}$$

V, the velocity of the flame gases, had to be determined.



Full Scale Diagram of Flame
showing
Surface of Uniform Concentration
and
Method of Measurement.

Fig. 5.

Measurement of the Flame-velocity.

A photograph of the apparatus used in measuring the velocity of the flame is shown in Fig.6. A small electric motor was fitted at one end of its shaft with a disc having four equally spaced radial slots through which the flame could be observed, and at the other end with a special stop-cock which opened and closed four times during one revolution of the motor. A foot-pump was connected through the stopcock to a small quartz tube held in the flame. Into this tube was introduced a little sodium chloride in the form of a powder, and when the motor was running little puffs of salt were blown into the flame at the rate of four per revolution by applying pressure to the foot-pump. When the flame was then viewed through the rotating disc the puffs in the flame appeared to be stationary(like the teeth of a saw)as the time interval between two puffs was just the same as the time between two successive glimpses of the flame through a slit. The apparent vertical distance between two puffs was observed by means of a cathetometer, and this gave the distance the flame travelled upwards in the time of one quarter of a revolution of the motor. The speed of the motor was measured with the help of a revolution-counter, and by running the motor at different speeds several estimates of the velocity of the flame were made.

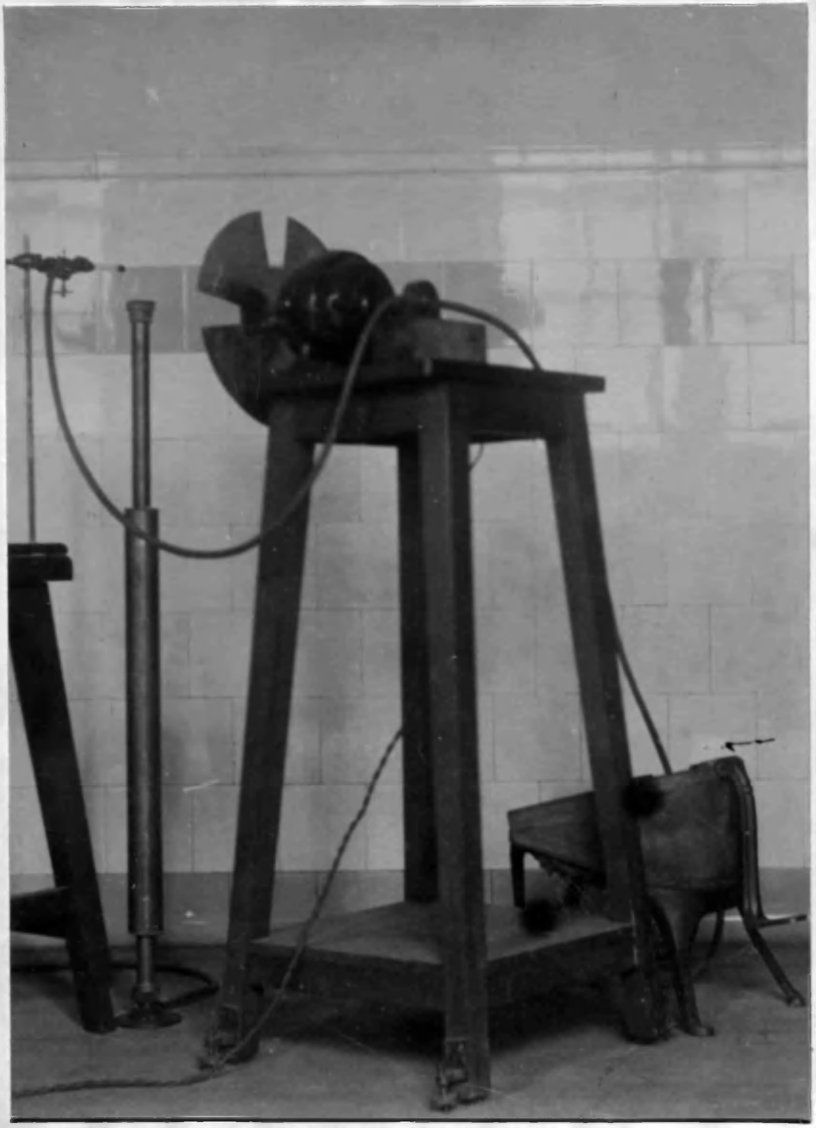


Fig. 6.

Photograph of Apparatus for measuring Velocity of Flame.

RESULTS.

The following data were obtained in the first experiment to measure the velocity of the flame:-

Voltage applied to motor = $42\frac{1}{2}$ volts.

Average speed of motor = 1450 revs. per min. (mean of 3 readings).

Average vertical distance between puffs = 2.69 cm. (mean of 5 readings)

$\therefore$ Average velocity of flame = $\frac{2.69 \times 4 \times 1450}{60}$ cm. per sec.

= 260 cm. per sec.

By applying different voltages in turn the motor was run at different speeds and similar readings taken, so that the following additional results were obtained for the flame-velocity:-

310, 210, 300, 310, 260, 280, 310 cm. per sec., giving an average value for flame-velocity of 280 cm. per sec.

The curve DABC in Fig.4, giving the shape of a region of uniform concentration was plotted from the following table of results obtained from a series of beads of potassium sulphate, each value of y being the mean for several beads.

Common current 5 microamps. (Potassium Sulphate)

x	0	1	2	3	4	5	6
y	.35	.635	.75	.84	.92	1.00	1.10

Due to the rapid evaporation of potassium sulphate these values are only approximate.

Results for Potassium Phosphate.

With beads of Potassium Phosphate the following table of results was obtained, the values of K being derived from the expression

$$K \approx \frac{V\,(x_2 - x - r_2 + r_1}{2 \times 2.303 \times \log_{10}\left(\frac{r_2}{r_1}\right)}$$

using the average value of 280 cm. per sec. for V.

Current in Micro-amps	x cm.	y cm.	r cm.	K cm ^{2}/sec
5	1 3	0.295 0.0	1.04_2 3.00^2	5.4
10	1 3	0.325 0.14	1.05_1 3.00_2	6.4
10	1 3	0.33 0.14_5	1.05_3 3.00_4	6.7
5	1 3	0.31 0.17_5	1.04_7 3.00_5	5.6
5	1 3	0.38 0.44	1.07_1 3.03_3	5.2

This gives an average value of K for potassium of 5.8 cm ^{2} per sec.

Results for Sodium Phosphate.

As the conductivity of the flame for sodium salts is much less than for the corresponding potassium salts a sensitive mirror galvanometer was substituted for the micro-ammeter. Again the phosphate proved to be the most suitable salt, and the results obtained are given below.

x cm.	y cm.	r cm.	K cm.^{2}/sec.
1	0.85	1.31_3	15.6
3	1.15	3.21_3	
1	0.75	1.25_0	14.4
3	0.97	3.15_3	
1	0.78	1.27_0	15.4
3	1.02	3.16_9	
1	0.705	1.22_4	10.8
3	0.965	3.15_1	
1	0.745	1.24_7	11.3
3	1.03	3.17_2	
1	0.74	1.24_4	11.3
3	1.02	3.16_9	
1	0.73	1.23_8	13.5
3	0.95_5	3.14_8	

This gives 13.2 as the average value of K for sodium.

Comment on the Results.

The final values of 5.8 for Potassium, and 13.2 for Sodium are rather higher than the corresponding results, 4.7 and 11.5, previously obtained by Professor Wilson. The latter values were based on the assumption that the boundary of the coloured region of the flame was a surface over which the concentration of metallic vapour had a small constant value, and that the shape of this region was approximately an *ellipsoid* of revolution. The values were worked out from measurements of its greatest horizontal diameter and the corresponding value of r. Bateman(5), on the other hand, in discussing the solution

$$c = \frac{q}{4\pi K r} \cdot e^{\frac{V}{2K}(x-r)}$$

for the differential equation of the present problem, suggests that when K is small and V large the shape of the coloured region approximates to the form of a *paraboloid* of revolution.

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(5) Differential Equations of Mathematical Physics: Bateman, P. 343.

Acknowledgements.

The experiments just described were carried out in the Natural Philosophy Institute of Glasgow University, under the supervision of Professor H.A.Wilson, F.R.S., and the writer desires to express his thanks for all the guidance, and help which he received during the course of the work, and for the use of the apparatus so freely put at his disposal; also for the fact that on his supervisor's recommendation a short account of the experiments was communicated to the RoyalSociety of Edinburgh, and was published in their Proceedings (Vol.46, 1925-26, P.15).

PART III

THE MERCURY DIPPER INTERRUPTER OF AN INDUCTION COIL

SUMMARY.

In various ways an investigation was made of the relative merits of different shapes of dipper for the interrupter of an induction coil, and of different speeds of withdrawal of the dipper from the mercury. This was first done by photographing different forms of dipper in action, and it was discovered that when a dipper is jerked out of the mercury a column of mercury is drawn up with it, and that interruption is caused by the parting asunder of this column in mid-air. The efficiency of the break, it is argued, depends upon the rapidity of the collapse of the column, and the photographs seem to show that a more efficient break is produced when the dipper is jerked out than when it is pulled out gently; that a pointed tip gives a better break than a blunt one; and that probably a dipper with several pointed tips is more efficient than a simple pointed rod. These conclusions were supported by the results obtained in the other methods of comparison.

INTRODUCTION.

The Foucault Interrupter, or Mercury Dipper Break, though one of the earliest types of interrupter to be used in the Ruhmkorff Induction Coil, is still used today in some types of modern induction coils. It consists essentially of a metal rod which is passed in and out of a dish containing mercury, so that the primary circuit of the coil is complete when the rod is immersed in the mercury, and interrupted when the rod breaks contact with the mercury.

It was thought that the efficiency of this form of interrupter might depend on the shape of the dipper, and the experiments about to be described were carried out to see if one particular shape of dipper is better than another.

APPARATUS.

The experiments were performed in the Natural Philosophy Institute at Glasgow University using a fairly large Apps coil made by Newton & Co. The experimental interrupter was made from a piece of copper rod about 3½ inches long and ¼ inch in diameter. This was attached to a small brass weight by a cord passing over a pulley. Instead of the usual metal dish or a dish with metal bottom, a glass dish was used to hold the mercury, and connection was made to the mercury by means of a thick copper wire reaching down to the bottom of the dish. Connection was made to the dipper by a piece of flexible copper wire soldered to the rod.

On the base of the induction coil there were twelve terminals lettered as shown in Fig. (1). The connections between these terminals by wires inside the base were found to be as shown by the dotted lines. (These connections had to be traced by measuring the resistance and capacity between each terminal and all the others in turn.) It was judged that the proper place to put the interrupter was between the right hand terminal 'COIL' and terminal '2', and a condenser between right hand terminals 'C_1' and 'C_2' to be in parallel with this. A battery of cells was connected to terminals 'N' and 'P', and an ammeter and rheostat were connected in series /

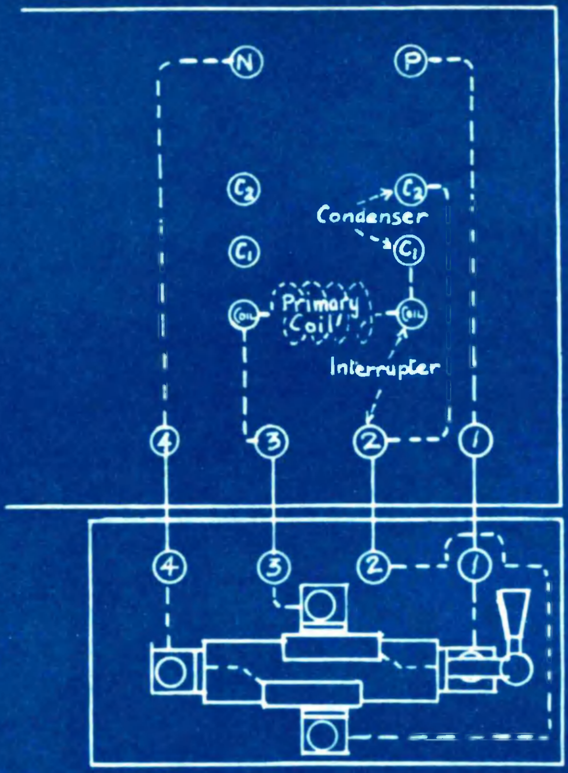

Fig. 1. Diagram of Connections in base of Induction Coil.

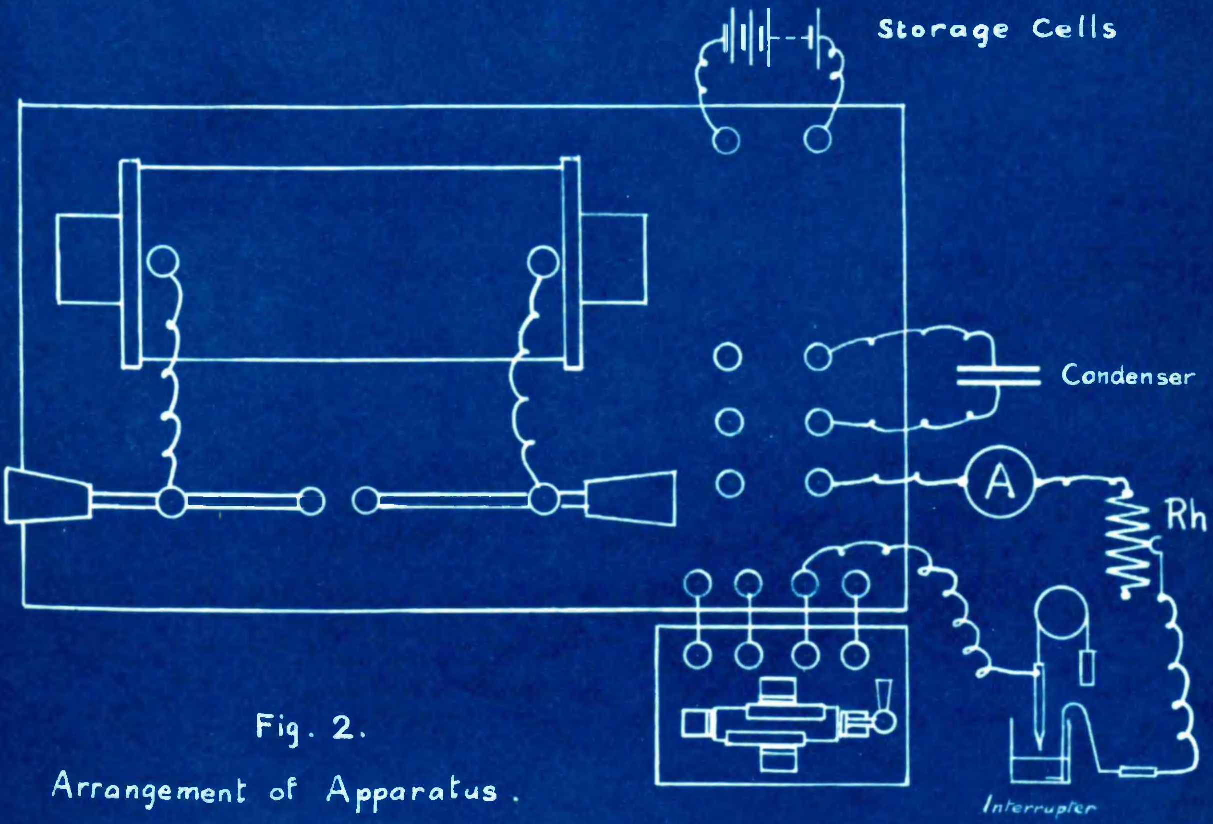

Fig. 2.
Arrangement of Apparatus.

in which he gives photographs of splashes at different stages in their rise and fall. His photographs were obtained by means of suitably timed electric sparks produced at a spark gap connected to Leyden jars which were charged by means of an electrical machine. In the present instance, however, there seemed to be no need for the elaborate arrangement previously used for timing the spark as it was intended to use the light of the secondary spark of the induction coil to illuminate the dipper in action, as this occurs almost immediately after the interruption of the primary current. Thus the arrangement for photographing the break was quite simple, as shown in Fig. (3). The experimental interrupter was placed near to the secondary spark gap so that the light of the spark could illuminate it, and the camera was placed so that no direct light from the spark could enter the lens. The diagram shows the arrangement finally adopted with tips of magnesium wire for the spark gap, a concave mirror supported behind it so as to concentrate the light on the dipper, and a background of white paper placed behind the dipper. The camera was a half-plate one, but cardboard adapters were made so that small plates (3½" x 2½") might be used.

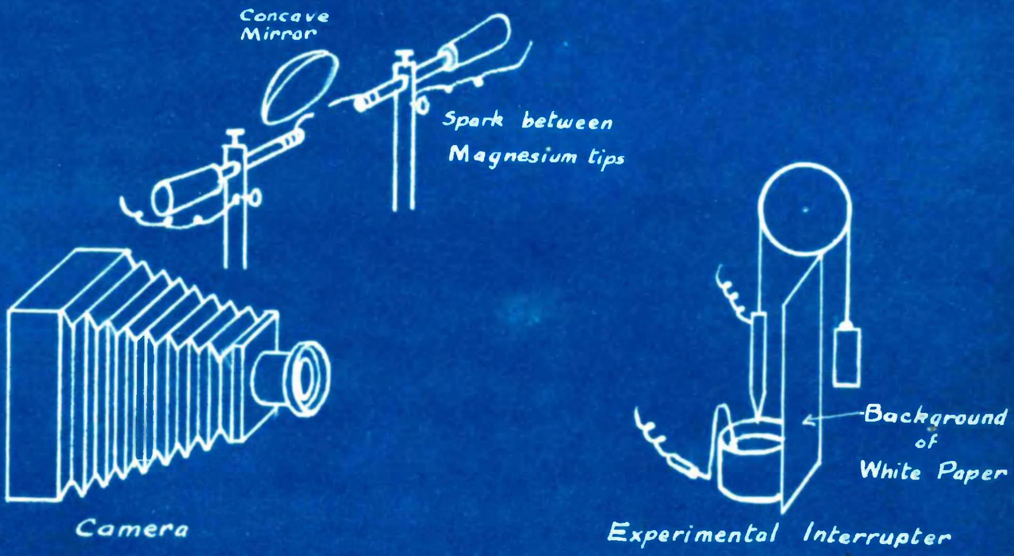

Fig. 3.

Arrangement for Photographing Interrupter in Action.

PROCEDURE.

Before any photographs were taken, experiments were made to determine the 'optimum' (3) value for the capacity of the condenser connected in parallel with the interrupter. By using a 'subdivided microfarad' different capacities from 0.05 to 1 microfarad were tried in turn, and the least primary current required at break to produce a secondary spark 1 cm. long was found for each. The graph of the results obtained is given in Fig. (4), and shows that the optimum capacity lay between 0.2 and 0.3 microfarad. The condenser, 'E 43', supplied with the coil was tested and found to have a capacity about 2.1 microfarads, and therefore not likely to be most suitable. Two new condensers were therefore obtained of marked capacity, 0.2 and 0.1 microfarad, and these were tried singly and in parallel for secondary spark gaps ranging from 1 to 10 cm. and in each case the smallest primary current was required by the condenser of marked capacity 0.2 microfarad.

Since there may be more than one optimum (4) primary capacity, the behaviour of the latter condenser was compared with that of condenser 'E 43' by obtaining

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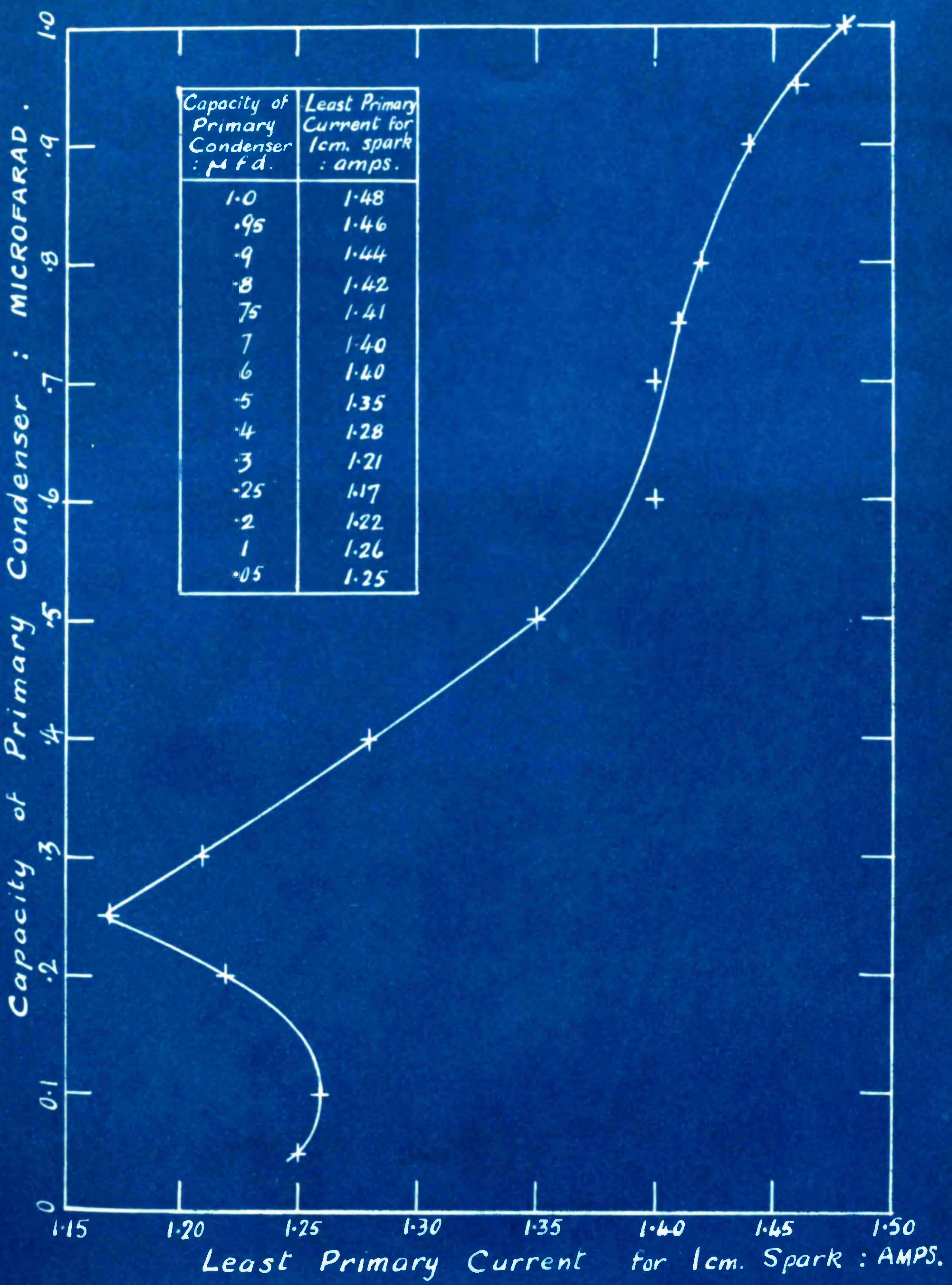
(3) Induction Coils: E.T.Jones, 1932. P.26.

(4) Ibid. P.40.

the /



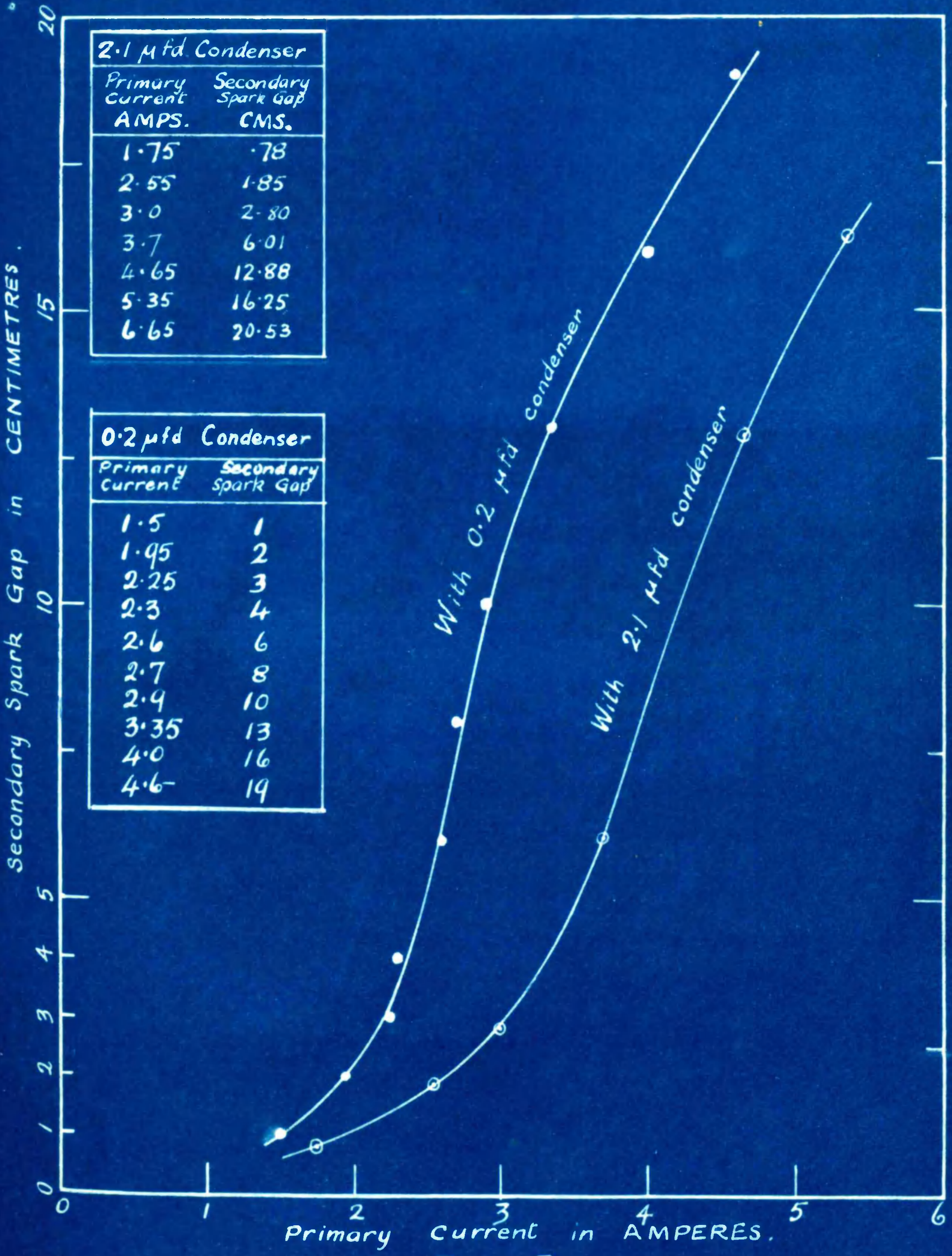
Capacity of Primary Condenser : μ f d.	Least Primary Current for 1cm. spark : amps.
1·0	1·48
·95	1·46
·9	1·44
·8	1·42
75	1·41
7	1·40
6	1·40
·5	1·35
·4	1·28
·3	1·21
·25	1·17
·2	1·22
1	1·26
·05	1·25

Fig 4.

the minimum primary current corresponding to various secondary spark gaps when each in turn was put in parallel with the break. The graphs obtained are given in Fig. (5). They show how important it is that the primary condenser should have the proper capacity, for throughout the range the least primary current required was much greater with condenser 'E 43' than with the 0.2 microfarad condenser. The latter condenser was therefore substituted for condenser 'E 43' and used with the coil throughout the experiments in which the photographs were taken.

The manner of taking a photograph was as follows: The windows of the room were darkened, and the camera was set up and focussed by means of electric light. The electric light was then switched off, the cover removed from the dark slide in the camera, and the dipper pulled out so that the exposure was made partly by the light of the spark at the dipper, but chiefly by the light of the secondary spark if there was one. The cover was then replaced on the dark slide and the plate taken to the dark room, where the development was carried out under cover because of the high speed of the plates, the time being observed occasionally by means of a faint green light.

The exposure was so brief that even fast plates yielded but thin negatives. After a few trials, however, and by making certain improvements in the arrangement, fairly



2.1 µfd Condenser	
Primary Current AMPS.	Secondary Spark Gap CMS.
1.75	.78
2.55	1.85
3.0	2.80
3.7	6.01
4.65	12.88
5.35	16.25
6.65	20.53

0.2 µfd Condenser	
Primary Current	Secondary Spark Gap
1.5	1
1.95	2
2.25	3
2.3	4
2.6	6
2.7	8
2.9	10
3.35	13
4.0	16
4.6	19

Fig. 5.

satisfactory negatives were obtained on Imperial Eclipse Plates of speed 650 H. and D. These were developed in Standard Pyro-Soda Developer, generally for seven minutes, but in some cases for a longer time.

The secondary spark was the chief source of light and its effect was improved by making it take place between points of mag~~k~~esium wire, by supporting a concave mirror behind it to concentrate its light on the dipper, by putting a Leyden Jar in parallel with it to 'fatten' the spark, by using a bigger primary current than the minimum, and by fixing a sheet of white paper behind the interrupter to act as a background.

n/

The sheet of white paper was perhaps the best improvement, as it helped to show up the outline of the dipper even when there was no secondary spark, and the only illumination was the light of the spark at the dipper.

In general, for each form of tip used, a photograph was taken when the dipper was pulled out slowly, and when it was jerked out, and in order to identify them, a letter of the alphabet was scratched on each negative in the order in which they were taken. A selection of the photographs follows.

1

2

A

C

F

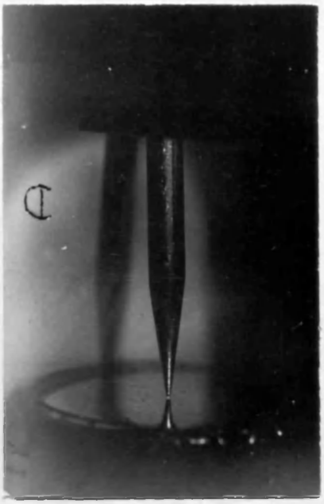
H

COMMENTS ON THE PHOTOGRAPHS.

The photographs which are now given are referred to by the letters originally scratched on them, and their seemingly haphazard arrangement is due to their being placed here in the order in which the comments are made, and not in the order in which they were taken.

Photographs 1 and 2 are from the first negatives which showed any image at all. They were taken before the introduction of any of the improvements mentioned overleaf. For No.1, the dipper was pulled out gently, and no secondary spark occurred. For No.2, the dipper was jerked out, and this time there was a secondary spark. In both cases, the negative was developed for half an hour. After this, most of the improvements, except the addition of the background of white paper, were made and Photograph A. was taken. Then the white background was added, and, from the photographs which follow, it is seen to be a very important addition. Thus, when Photograph C. is compared with A, the dipper in C. can be made out as a black shape against the background, whereas in A. it cannot be distinguished at all. In neither of these cases was there a secondary spark, but in most of the photographs which follow, witness Photographs F. and H, the fact of the secondary spark is established by the shadow it /

B



D

it casts of the dipper on the white background, and by the lines of reflected light seen on the dipper.

Photographs B. and D. show what generally happened when the dipper was pulled out gently. The interruption of the primary current produced a small spark which is just visible between the tip of the dipper and its image in the flat surface of the mercury below, and a break of this nature is what one might have expected would occur even when the dipper was jerked out. The Photographs 2, A, C, F, H, etc., however, demonstrate the interesting fact that when the dipper is raised quickly out of the mercury in the dish, a column of mercury is pulled up by it, and the interruption of the primary current takes place when this column breaks away from the dipper, or parts asunder in mid-air.

It has been pointed out by Plateau that if a cylinder of liquid is suddenly formed and left to itself, it cannot retain that form when its length is greater than its circumference. It is then unstable, and when a tremor of any kind causes the slightest depression at some point a 'waist' starts there, which rapidly develops so as to cause a complete break in the column. If the column is very long several waists develop, and the column breaks into a number of drops. A theoretical proof of Plateau's proposition, based on the different methods of treatment given in two standard text-books /

Y

AE

AF

text-books(5), is reserved for an appendix (Page 63), but several of the photographs furnish a striking confirmation of it. In Photograph Y, for example, or any photograph of the seven-pointed dipper, such as AE or AF, the columns which were approximately cylindrical when unbroken are seen to have parted in several places, and the small portions resulting have been caught by the camera in the act of forming into the familiar spherical globules which one associates with mercury in fine subdivision.

The collapse of a column is due to surface tension, aided, probably, by the upward motion of the dipper, but hindered by viscosity, and one would expect that, once a waist had started, the time of collapse would depend also on the diameter of the column, being probably greater for a thicker column. The method of dimensions may be used to gain some information on this point. Thus, let t denote the time taken for collapse once a waist starts, D the diameter of the column, S its surface tension, E its viscosity coefficient and V the velocity of the dipper. Then, if these are all the controlling factors,

$$t \text{ varies as } D^w \; S^x \; V^y \; E^z$$

$$\text{i.e. } T^1 = K.\; L^w.\; \left\{\frac{M}{T^2}\right\}^x.\; \left\{\frac{L}{T}\right\}^y.\; \left\{\frac{M}{L.T}\right\}^z ,$$

where K is a constant.

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(5) Poynting & Thomson: 'Properties of Matter', P.147.

Newman & Searle: 'The General Properties of Matter, P.150.

Hence $$1 = -2x - y - z$$

$$0 = w + y - z$$

$$0 = x + z \;;$$

giving $$z = -x\,,$$

$$y = -1 - x\,,$$

$$w = 1$$

Hence $$t = K.\ D^{1}.\ S^{x}.\ V^{-1-x}.\ E^{-x}$$

i.e. $$t = K.\ \frac{D}{V}.\ \left(\frac{S}{V.E.}\right)^{x}$$

The value of x in this expression is indeterminate without further data, but it is pretty certain to be negative and numerically less than unity. This may be demonstrated by means of experiments with a viscous liquid like treacle. One finds that on dipping a spoon into a jar of treacle and withdrawing it a considerable time elapses before the column of treacle, dripping from the spoon, is severed - much longer than in the case of a less viscous liquid such as water. The breaking of the column may be helped either by twisting the spoon, which serves to wind the column round it and in so doing reduce its diameter, or by jerking the spoon upwards. From this it is seen that a greater value of V means a smaller value of t, so that the index of V, $-1-x$, in the equation for t must be negative, and since a greater value of viscosity evidently increases the value of t the index for E must obviously be positive, so that x is negative.

For $(- 1 - x)$ to be negative when x is negative, x must be smaller numerically than 1. The simplest form of the expression for t would correspond to $x = -\frac{1}{2}$, and would then be $t = K.D.\sqrt{\frac{E}{V.S.}}$, but further evidence would need to be forthcoming before this could be established. Independent of the value of x, however, the result obtained is that t varies as D, so that if a rapid collapse of the column is desired, the thinner the column is made before a waist starts the better the break will be.

That a more rapid collapse of the column is desirable seems fairly obvious. It is now recognised that due to the self-inductances and the mutual inductance of the coupled circuits there is a combination of two oscillations in both primary and secondary circuits (6). Yet there is so much damping due to various factors, that after the first maximum is past the oscillations have much smaller amplitudes, so that the older form of the theory gives a fairly adequate explanation. According to it, the magnitude of the secondary potential determined by the rate at which the lines of magnetic force cease to be linked with the turns of the secondary coil, and if the flux can be made to disappear more quickly the secondary potential will be greater. The decay of the magnetic flux is caused by the breaking of the primary

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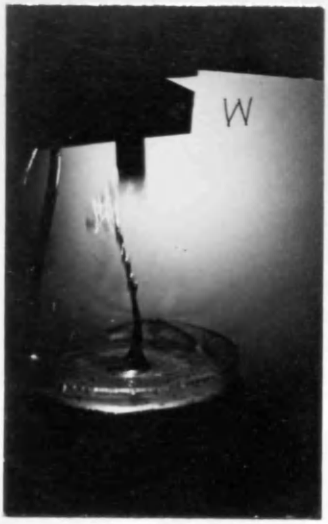
(6) E.T.Jones: Induction Coils. P.26 et passim.

V



W

AC

G

circuit, i.e. by the sudden introduction of an infinite resistance, after which inductance effects in the circuit carry the current on for a fraction of a second longer, into the condenser connected across the interrupter and out again. Once the resistance has become infinite, however, the time interval is very short before the current becomes zero. It is the introduction of the resistance that has to be rapid, and, as the photographs show, this is brought about by the formation of waists in the columns of mercury drawn up by the dipper. In the coil used the primary winding has a resistance of only 0.28 ohm, and a column of mercury ½ cm. long and ½ mm. in diameter adds more than six per cent to this, and waists developing cause a rapid increase up to practically infinity at severance. As the time of collapse is shorter for a column of smaller diameter the rate at which the resistance is increased to infinity is greater, with the result that a greater secondary potential is produced.

The thickness of the column at the start of collapse is probably determined by several factors - the diameter of the dipper itself, the speed with which it is jerked out, and the instant at which a tremor is imparted to it. The column drawn up starts as an envelope to the dipper, and is therefore thicker for a tip of wider diameter, such as the blunt form shown in Photographs V and W , or the ring-shaped one

N

P

S

seen in Photograph AC. The columns of mercury raised up by these dippers were much thicker than for the pointed dipper, and in consequence they were much taller before interruption than in the case of a pointed dipper. (Even when gently raised out of the mercury, the blunt form of dipper had to be raised higher above the dish before breaking contact. This is clearly seen when photographs V and G are examined. The distance between the dipper and its image in the mercury surface is greater for V than for G, and half of this distance may be taken as a measure of the height the dipper has been raised above the level of the mercury.) But not only has the length of the column to be greater than its circumference, a slight tremor of some kind has to be imparted to it, and one would expect that when a dipper is jerked up more smartly the column may be thinned down further before the necessary tremor is received. Confirmation of this seems to be given by Photographs N, P, and S which were taken of the pointed dipper when the mercury was covered by a layer of liquid paraffin. In these cases the column of mercury drawn up is surrounded by a sheath of the liquid paraffin and the spark at 'break' is 'quenched' by the paraffin and less contamination of the dipper and the mercury takes place. For N the dipper was pulled out slowly; for P it was jerked out, and for S it was jerked out more

AJ

AK

violently. The power of the paraffin to quench the spark is shown in P. The mercury column is seen to be broken up into a number of globules inside the sheath of paraffin, but the primary spark was too faint for one to say at which part of the column it occurred. (It should be mentioned that in this particular case the primary current interrupted was 4 amperes instead of the usual 5 amperes. The result was that the secondary spark was not so bright as usual and the photograph obtained was poorer than usual). In S the jerk was so vigorous that the column of mercury and its surrounding sheath of paraffin were both thinned down so much before interruption that the layer of paraffin was so thin as to be hardly effective in quenching the spark.

Even with a pointed dipper, due to its taper, deeper immersion in the mercury would mean that the initial diameter of the mercury column drawn up would be greater than for less deep immersion, and consequently the column would be longer before collapse. Photographs AJ and AK are interesting in this connection, for the tips were immersed to a depth of 4 mm. in AJ and 7 mm. in AK, and in the latter case the dipper is seen to have been raised higher. Photograph AJ is also interesting as showing, rather clearly, different columns in different stages of collapse.

One thing which the photographs show up very clearly is /

I

X

AA

is the time-lag between the interruption of the primary current and occurrence of the secondary spark - a time interval which is large compared with the duration of the secondary spark. In Photographs I and X, for example, the spark at the dipper was bright enough to illuminate the dipper so that its position at break is registered on the photograph by a paler image bordering on the patch of light which marks the spark. Then, by the time the secondary spark occurred, the dipper had been raised a fraction of an inch (say $^3/16"$) and the light of the secondary spark produced a fainter image on the negative giving the darker and higher image of the dipper in the print. The sharpness of the upper image and the clearness of the reflections on it show that the illumination produced by the secondary spark is for practical purposes instantaneous, whereas if the speed of upward jerk of the dipper had been measured - as could be done by some mechanical cam arrangement - the time-lag between the primary and secondary sparks could have been measured. That the double image is not due to two secondary sparks may be established by an examination of a photograph of a multipointed dipper. In photograph AA, for example, the primary spark taking place at the right hand tip is seen to have caused patches of reflection on the right-hand side of the other two tips in the lower images of these tips, whereas the patches of reflection in the upper images of the tips /

M

AD

tips are all placed centrally due to the illumination by the secondary spark when it occurred later.

Due to the self-inductance of the primary and secondary coils, and their mutual inductance, the interruption of the primary current is followed by oscillations in both circuits. The investigation of this both mathematically and experimentally is gone into very fully by Professor E. Taylor Jones in his books on the induction coil (7), and the reason for the time-lag between the primary and secondary sparks is that the oscillatory potential produced at the terminals of the secondary coil takes some time - of the order of one thousandth of a second, say,- to reach its first maximum, after which later maxima are generally much reduced by damping so that if a second spark is produced it is much less bright. Occasionally a double secondary spark was heard and its occurrence may be distinguished in certain photographs, such as M and AD, in which the lines of reflection on the dipper due to the spark at the secondary terminals are seen to be repeated.

Another thing that the photographs reveal is that a better break is produced when the dipper is jerked out than when it is pulled out slowly. This is shown by the further

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(7) 'Induction Coil Theory and Applications': Pitman 1932, and previously 'Theory of Induction Coil': Pitman 1921.

V – Slow Exit

X – Quick Exit

Z – Slow Exit

AA – Quick Exit

AB – Slow Exit

AC – Quick Exit

prints given opposite of the negatives V, X, Z, AA, AB, and AC. The efficiency of the behaviour of an induction coil is determined by the energy dissipated in the secondary spark. The more energy in the spark the brighter is its light, and, in the present arrangement, the better is the photograph obtained of the dipper. Because of the very brief duration of the secondary spark the negatives were always under-exposed. Except for the parts of the negative corresponding to the spark at the interrupter, and the lines of reflection on the mercury and on the dipper, the negatives were all very thin, yielding dark prints. The better the illumination of the dipper, the better were the prints. In order to compare the behaviour of the different dippers, the conditions were made as far as possible the same in each case. The primary current regularly used was five amperes, and the standard time of development of the negatives was seven minutes in the same strength of developer. Generally in making prints, however, the writer adjusted time of exposure and development etc., to produce as clear a print as possible, but in order to obtain some sort of comparison between different dippers and between slow-exit and quick-exit breaks the prints shown opposite were made under standard conditions. Care was taken to give each print the same exposure (30 seconds at 2 feet from a 25-Watt lamp) and the same /

same development (45 seconds in normal Rytol developer) so that they might give a fair comparison. When the prints V and X, et cetera, are examined, looking chiefly at the whiteness of the background and at the detail in the dipper and its rod, it is at once apparent that in each pair the better print is for the quick-exit break. It may be pointed out that it is not really obvious that when the dipper is jerked out of the mercury it will produce a better break than when it is gently removed. The rate of cutting lines of induction for the secondary coil is not related directly to the upward speed of the dipper but to the rate of collapse of the primary current, and since an electric spark takes place at either type of break one might well expect the operation to be as instantaneous and effective in the one case as in the other. The evidence of the photographs, however, cannot be disallowed, and the reason for the greater efficiency of the 'quick-exit' break may be connected with the formation and collapse of the mercury columns as already considered.

Further, if the prints X, AA, and AC of the quick-exit breaks of the three different dippers are compared, that of the three pointed dipper seems to give clearest detail of the rod and dipper (part of the whiteness of the background of X is evidently due to the primary spark as this has obliterated the bottom of the shadow of the dipper.)/

AF
Spark at far
right-hand tip

AG
Spark at near
right-hand tip

AH
Spark at near
left-hand tip

AJ
Spark at Centre tip

That the best photograph is that of the dipper with pointed tips supports the argument given above that the dipper pulling up a thinner column is likely to give a more efficient break than one which pulls up a thicker one, because in the latter case the time of collapse of the column, once a tremor starts a waist, is longer than in the former case, and the resulting secondary E.M.F. is not so high.

Another important fact that the photographs reveal is in connection with the dippers having several pointed tips. It had been thought that this form of dipper with two or more columns breaking simultaneously would allow a greater current to be interrupted than in the case of a single tip. But the photographs of the multipointed dippers, e.g. AF, AG, AH, AJ, seem to show that the primary spark always takes place at one tip only, though not always the same tip. Sparks may seem to occur at several tips as they enter the mercury together, yet when the dipper is jerked out there is generally one tip which breaks its connection with the mercury slightly later than all the others, and the real interruption of the primary current takes place only at it. Thus as regards the magnitude of the current that can be interrupted, the multipointed form does not seem to be any better than a single pointed dipper. Yet the photographs show that it may be worth while to employ several tips. For, since only one spark /

spark is produced for each interruption, a multipointed dipper may not produce any more pollution of the mercury than a single tip, and since the spark is seen to take place at different tips in turn, a multipointed dipper may be expected to keep in good working condition longer than a single-pointed.

Some numerical observations were next tried to further compare the different forms of dipper, and the results obtained support the conclusions reached from a study of the photographs. These experiments are now described.

FURTHER METHODS OF COMPARISON.

Comparison by least primary currents for different spark gaps.

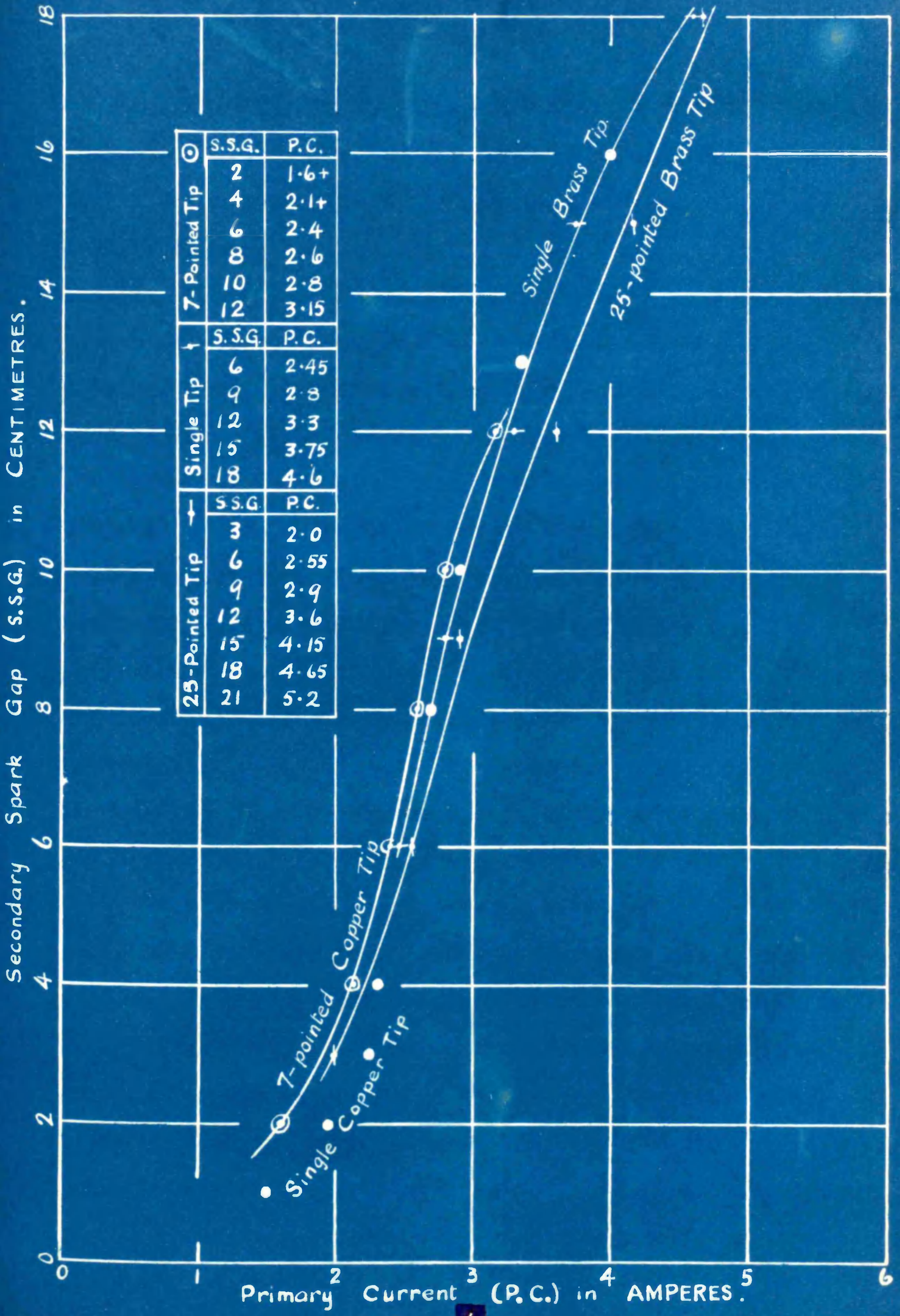
Experiments were carried out, with different tips in turn, to determine the least primary current to produce different lengths of secondary spark. The tables of results obtained, and the corresponding graphs are given in Fig.6. These seem to show that the seven-pointed dipper is best, as according to the graphs a smaller primary current is necessary for any particular length of secondary spark with the seven-pointed dipper of copper than with the single brass tip or the twenty-five-pointed. It should be noted that the graph for the single brass tip agrees very well with the graph for the original pointed copper rod, the points for the latter being plotted as prominent dots in Fig.6.

But the readings were taken on different days, and the condition of the mercury alters with use, and it was thought that these graphs might not give a fair comparison between the tips.

Figure of Merit Experiments.

Another method tried for comparing the tips was that

of /



7-Pointed Tip ⊙	S.S.G.	P.C.
	2	1·6+
	4	2·1+
	6	2·4
	8	2·6
	10	2·8
	12	3·15

Single Tip +	S.S.G.	P.C.
	6	2·45
	9	2·8
	12	3·3
	15	3·75
	18	4·6

25-Pointed Tip +	S.S.G.	P.C.
	3	2·0
	6	2·55
	9	2·9
	12	3·6
	15	4·15
	18	4·65
	21	5·2

Fig. 6.

of finding a 'figure of merit' for each. When a big enough current is interrupted in the primary circuit, a secondary spark of given length can be obtained regularly, but when a smaller current is used the spark may only take place occasionally. The term 'FIGURE OF MERIT' is here used to signify the number of times a secondary spark of certain length was obtained when a given primary current was interrupted a hundred times, i.e. the figure of merit means the percentage of primary breaks which produced a secondary spark. Four forms of tip were compared in this way - the seven-pointed, the twenty-five-pointed, the single-pointed and single-blunt tips, all amalgamated with mercury. Of these the former pair, the seven-pointed and the twenty-five-pointed, were the original ones which were photographed, the single blunt and pointed tips were made afresh. The investigation was continued at a later date, and with a different induction coil, since the first one was not available.

The results obtained from the figure-of-merit experiments were very erratic. In a set of experiments the secondary spark gap and the primary current were kept the same for each tip. In all, seven sets were tried with various lengths of spark gap and with different covering liquids above the mercury. In the first, sixth and seventh sets where the seven-pointed tip was used before the twenty-five pointed, the former had a bigger figure of merit than the /

the latter. In the second, third, and fourth sets, where the twenty-five-pointed tip was used before the seven-pointed, the order of merit was reversed.

Again, when the seven-pointed tip was used before and after the twenty-five-pointed in the same set, the first figure of merit obtained for the seven-pointed dipper was greater than that obtained for the twenty-five-pointed, but the one obtained afterwards was not. It is obvious to the eye that the condition of the mercury alters with use - it becomes polluted with the sparking - and this may be what gives rise to the phenomenon observed above, viz., that it is the tip used first that shows up best. The order in which the tips were used seemed to make all the difference. In the third set. for example, three tips were used in the order 25-, 7-, and 1-pointed, and their figures of merit came out in that order; and in the sixth set they were used in the reverse order , and the order of merit was reversed.

In all these figure-of-merit experiments, the dipper was jerked out of the mercury, because an initial test seemed to show that 'quick-exit' breaks were better than 'slow-exit' breaks. In this test only the seven-pointed dipper was used for two different lengths of secondary spark in turn.

In each set it was jerked out for a hundred times ('quick exit' break) and then pulled out gently for a hundred times ('slow exit break') and in the first set the figures of merit were 17 for quick exit breaks, and 11 for the slow-exit breaks, and in the second set 15 and 1 respectively. These figures seem to indicate that a better break is produced when the dipper is jerked out than when it is pulled out gently, but they are open to the same objection as the other figure of merit results: the jerked breaks in each set were done before the slow-exit breaks, and may therefore correspond to a better condition of the mercury.

Minimum primary current for different tips and same gap.

It was thought that a better comparison would be obtained by finding the minimum primary current necessary to give occasional secondary sparks of some definite length, using each tip in turn when the mercury was in the same condition. A low value of primary current was tried and when more than six breaks in succession failed to cause a secondary spark it was counted too low, and a slightly higher current was tried, and so on, till a value of current was reached that gave a secondary spark for one or more of the first seven breaks. This was done for both 'slow exit' and 'quick exit' breaks. Then the tip was unscrewed and replaced by another one, and the process repeated immediately for the same spark gap with the new tip. In this way the condition of the mercury was practically the same for all the tips for the same spark gap. Especially was this true since very little adjustment of the current was required for succeeding tips, once the minimum current had been found for one tip. The following table gives the results obtained for spark gaps ranging from one to five centimetres, the letters Q and S denoting quick-exit, and slow-exit breaks respectively.

Length of Secondary Spark : cm.	Least Primary Current: amperes.							
	Blunt Tip		1-pointed		7-pointed		25-pointed	
	Q.	S.	Q.	S.	Q.	S.	Q.	S.
1	(1st.)		(2nd.)		(3rd.)		(4th.)	
	1.53	1.53	1.48	1.50	1.48	1.50	1.48	1.50
2	(4th.)		(3rd.)		(2nd.)		(1st.)	
	2.22	2.23	2.22	2.23	2.22	2.22	2.22	2.25
3	(1st.)		(2nd.)		(3rd.)		(4th.)	
	2.63	2.68	2.67	2.68	2.65	2.65	2.65	2.67
4	(4th.)		(3rd.)		(2nd.)		(1st.)	
	2.88	2.90	2.87	2.87	2.87	2.87	2.87	2.90
5	(4th.)		(3rd.)		(2nd.)		(1st.)	
	3.08	3.10	3.07	3.07	3.05	3.05	3.07	3.10

The covering liquid above the mercury was absolute alcohol, and the numbers given in brackets give the order in which the different tips were used in any set.

This table of results confirms the conclusion already reached in different ways, viz:- that a quick-exit break is better than a slow-exit break. In a few cases the primary current interrupted to produce a certain length of secondary spark was the same when the dipper was jerked out as when it was pulled out gently, but in most cases it was found that a quick-exit break required a smaller primary current than a slow-exit break which produced the same length of secondary spark.

Further, when the quick-exit breaks for the different tips are compared, it is seen that the blunt tip required a rather greater current than the others in three cases out of five, though in one case it required less than the others. This latter case, however, was the very first break in a series of trials, and frequently, after the coil and interrupter had had a rest, the first break was found to give better results than succeeding breaks. This would explain the exception, and allow the conclusion to be drawn that a blunt tip is less efficient than a pointed one.

Finally, when the behaviour of the seven-pointed dipper is compared with the others, it is seen that whereas it required the same primary current as the single-pointed in three cases out of five, ~~but~~ in the other two cases it required less. This is another indication that a dipper with several tips may be more efficient than a single-pointed one.

CONCLUSION.

The outstanding fact brought to light by the above research seems to be that when the dipper is jerked out, the break of contact at the interrupter is not due simply to the dipper leaving the mercury surface, but due to a column of mercury drawn up by the dipper parting asunder in mid-air; and bound up with this fact are probably to be found the reasons for the following conclusions which seem to be fairly well established:

(a) That the interruption of the primary current is mofe efficient when the dipper is jerked out quickly than when it is pulled out slowly,

(b) That the pointed form gives a better break than one with a blunt end, and

(c) That probably a dipper with several pointed tips is better than a single-pointed rod.

APPENDIX.

A Proof that a long cylindrical liquid column is unstable.

The general behaviour of liquids under surface tension is easily investigated experimentally by the use of films of soap-solution, in which, of course, there are two liquid-air surfaces, so that the formula obtained for them differ from those for a single liquid-air surface simply by the factor two. It is found experimentally that a nearly cylindrical soap film, formed between two equal circular end-pieces, corresponds to the revolution about the axis of symmetry of part of a curve of the form A B C D E (Fig.7.) If the length of the soap film exceeds the semi-circumference of the end-pieces, there are two points of inflexion in the tracing curve corresponding to B and C in A B C D (Fig. 7.a.) when the diameter of the soap-bubble is greatest in the middle, or to C and E in L C E M (Fig.7.c.) when the diameter of the bubble is least in the middle. The curvature of a nearly cylindrical soap film is given by the usual equation:

$$\frac{p}{2S} = \frac{1}{r'} + \frac{1}{r''}$$

where p is the excess of pressure inside the bubble, S is the surface tension, and r" and r' are respectively the

Diagrams to prove that a long cylinder of liquid is unstable

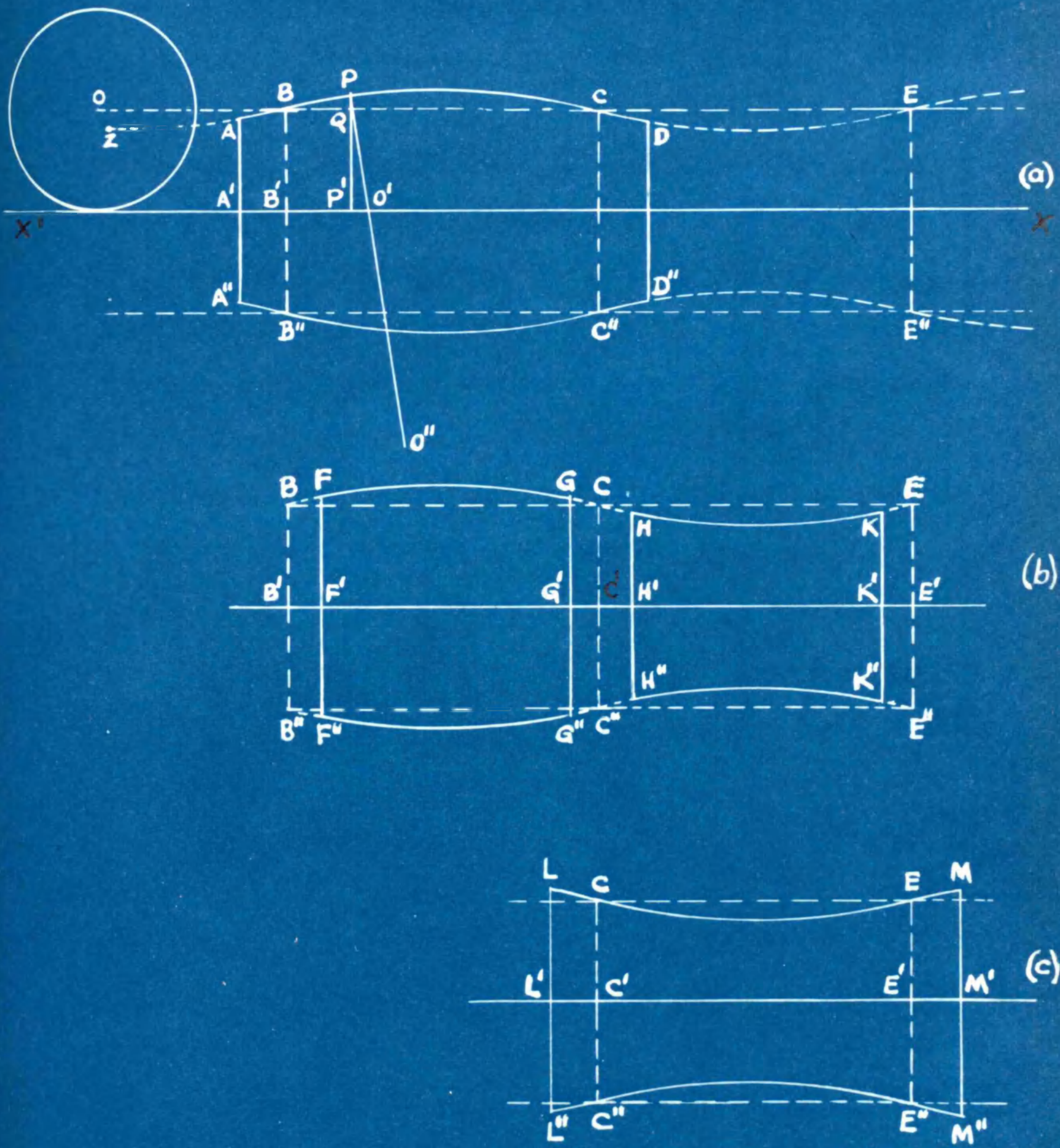


Fig 7

the curve A P C is proportional to its distance from a fixed straight line, and the further condition that the point is never very far from the straight line are fulfilled by one particular member of the family of 'elastic curves'. It is the curve traced out by a point near to the centre of a circle, when the circle rolls, without slipping, along a straight line, the fixed straight line in the above statement being the path traced out the centre of the circle. In the present case the rolling circle (shown in Fig.7.a.) has radius a equal to B'B, and the distance of the tracing point, Z, from the centre of the circle, O, is equal to the maximum height of the curve above B C. The centre of the rolling circle traces out the straight line O E, and the curve traced out by Z cuts this line in B, C, E----, such that B C $\doteq$ C E $\doteq$ $\pi . a$, the half-circumference of the rolling circle.

It is the rotation of this curve, therefore, about the axis X'X which gives the shape of the surface of a soap film which is very nearly cylindrical, the excess pressure inside the soap film being given by $p = \frac{2.S}{a}$ where a is the distance from the axis to a point of inflexion. Now, for an almost cylindrical bubble whose length F G (Fig. 7.b.) is *less* than B C (the distance between two adjacent points of inflexion in the curve under consideration) if the surface bulges *out* slightly, the excess of pressure inside the bubble is given by

$$p = \frac{2.S}{a} = \frac{2.S}{B'B}$$

This is greater than the pressure-excess $\frac{2.S}{F'F}$ which would obtain if the surface were truly cylindrical between the ends F"F and G"G.

Again, for an almost cylindrical bubble whose length H K (Fig. 7.b.) is less than B C, if the surface bulges in slightly, the excess of pressure inside the bubble is given by

$$p = \frac{2.S}{a} = \frac{2.S}{C'C}$$

and this is less than the pressure-excess would be if the surface were exactly cylindrical between H and K i.e. $\frac{2.S}{H'H}$.

The result, thus established, is that an almost cylindrical bubble whose length is less than half its circumference has a pressure greater or less than a truly cylindrical bubble of the same end-faces according as it bulges out or in.

On the other hand, a bubble almost cylindrical and of length greater than B C, if bulging out in the middle would resemble A D (Fig.7.a.) and the excess of pressure inside, i.e. $\frac{2.S}{B'B}$, would be less than $\frac{2.S}{A'A}$ which it would have if it were truly cylindrical between its ends A"A and

D"D, and similarly if it bulged in (See L.M. Fig.7.c.) the pressure excess inside would be greater than for a truly cylindrical bubble with the same end-faces.

As a result, a soap film which is cylindrical is stable when its length is less than the circumference of its ends. For, if a disturbance causes one half to bulge out at the expense of a slight waist in the other half the pressure increase in the bulging half over the pressure in the other half would automatically remedy matters by causing a flow of air from the bulging half to the other until the pressures were the same and the cylindrical form was restored.

On the contrary, if a bubble is initially cylindrical and has a length greater than its circumference, and a tremor of some kind causes a depression in one half, the change in shape will be accompanied by an increase in the pressure in that region causing a flow of air to the other end so that a bulge is produced there, and a lowering of pressure which aggravates the condition, with the result that the 'waist' and the bulge both develop until eventually complete severance occurs. Thus a cylindrical bubble is unstable when its length is greater than its circumference.

A similar line of reasoning could be used for liquid columns instead of soap films, but it ignores the effect of gravity, and this is only justified when the effect of gravity is so small as to be negligible. Thus Plateau carried out experiments on the surface tension of olive oil by working with it in an 'atmosphere' consisting of a mixture of alcohol and water which had been adjusted to have the same specific gravity as the oil. Again it is well known that when the volume of mercury in a drop is reduced the shape of the drop becomes more and more truly spherical showing that in spite of the great density of mercury the effect of surface tension predominates making the effect of gravity almost negligible when the dimensions of the drop of mercury are made small. In a similar way when one is dealing with thin columns of mercury drawn up by a dipper the surface tension effect again predominates and of them it may be said that they become unstable when the length exceeds the circumference.

ACKNOWLEDGEMENT.

The writer desires to record his grateful thanks to Professor E. Taylor Jones, D.Sc., Professor of Natural Philosophy, The University, Glasgow, who suggested the line of research, provided the apparatus, and continually gave help and encouragement.

PART IV

THE ELECTRICAL CONDUCTIVITY OF CERTAIN SOLUTIONS AT DIFFERENT TEMPERATURES

SUMMARY.

In this paper an account is given of two sets of experiments in which the electric~~it~~al conductivity at different temperatures was measured for -

(a) A number of fairly weak aqueous solutions of sodium chloride up to about one per cent strength, and

(b) Several concentrated solutions of sulphuric acid ranging from 94 to 99 per cent.

In the latter case the range in temperature was from 15°C to 50°C, and no great difficulty was involved, but in the former set the temperature had to be carried up to 230°C, at which the pressure developed inside the conductivity-cell was nearly 400 lb. per sq.in., and a special cell had to be devised to suit the abnormal conditions.

In both cases the work was undertakem at the request of a commercial firm in need of information in connection with the design of instruments.

SECTION (a). SODIUM CHLORIDE.

INTRODUCTION.

The research work described in this section was carried out in order to obtain information for the design of an 'electrical salinometer' to indicate the amount of dissolved impurity in the water in a boiler working at pressures up to 375 lb. per sq. inch.

In the past, the method of controlling the accumulation of salt in a boiler, when there was a trace of it in the feed-water, has been to draw off frequent samples of the boiler-water or of the feed-water, and determine the amount of salt present by titration or by using a hydrometer. With a modern electrical salinometer (1), however, the drawing-off of samples is done away with, and the condition of the water in boiler, or in feed-pipe, may be read directly on a dial at any time.

The visible part of such an instrument is really a milliammeter which gives the current passing between two platinum electrodes held in the water when a definite potential difference is applied to the circuit, but instead of the dial registering the current it is calibrated so as

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(1) Kempe's Engineer's Year Book, 1930, P.1624.

to give the concentration of salt directly. Any variation in temperature, however, is accompanied by a change in the electrical conductivity of a given salt solution, so that an instrument of this kind must be fitted with a proper 'temperature-compensation', and in order to provide this it is necessary to know the electrical conductivity, over a considerable range of temperature, of a number of salt solutions within the range of concentration to be dealt with.

The particular instrument in question was required to deal with solutions stronger than usual - up to about 800 grains of common salt per gallon of water in the boiler, i.e. a 1.13 per cent solution, as against the maximum of 0.001 per cent for an instrument designed to be used in the feed-line of an Admiralty boiler. Further, it had to deal with unusually high temperatures, as the temperature of saturated steam at 375 lb. per sq. inch pressure is about 230°C.

Search of Published Tables for data required.

When published tables were consulted for the necessary data, it was found that the results available were insufficient and not in a form directly suitable for practical purposes. The most recent authoritative table (2), from which the first two columns of Table No.1 were obtained, gave the equivalent conductivity at different temperatures for various concentrations expressed in milliformula-weights per litre of solution at the temperature concerned, both of which quantities required adaptation. In the first place, the specific conductivity (k), i.e. the reciprocal of the resistance between opposite faces of a centimetre cube, is more directly useful than the equivalent conductivity (λ), which is the specific conductivity per gram-equivalent per cubic centimetre. For an x-Normal solution, however, k is obtained at once from λ using the simple formula $k = \lambda \cdot \frac{x}{1000}$. In the second place, the above method of specifying the concentration is both misleading and inconvenient for temperatures higher than the standard. A solution which is decinormal at a temperature above 18°C is really more concentrated than one which is decinormal at that temperature, for if it were cooled to 18°C it would contract to a smaller volume, and

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(2) Int. Crit. Tables, Vol.VI, 1929, P.230.

TABLE N°1

Specific Conductivities at 18°C of Sodium Chloride Solutions.

[Strength of re-expressed as grains per gallon and as per cent by weight]

Concentration x-Normal ($x = 1000\,c$) gm.eqt. per litre	Equivalent Conductivity, Λ ($\Lambda = k/c$) $ohm^{-1}\cdot cm^{-1}$ per gm. eqt. per litre	Specific Conductivity, k ($k = \Lambda . c$) $ohm^{-1}\cdot cm^{-1}$	Density d gm. per c.c.	Concentration	
				($W = \frac{5846 . c}{d}$) W per cent	($4101200 . c$) grains per gallon
1·0	74·19	·07419	1·0391 +	5·626	4101·
0·5	80·76	·04038	1·0192 −	2·868	2051·
0·2	87·53	$\cdot01750_{6}$	1·0069+	1·161	820·2
0·1	91·82	·009182	1·0028 −	0·5830	410·1
0·05	95·51	·004776	1·0007 −	0·2921	205·1
0·02	99·40	·001988	0·9994 +	0·1170	$82\cdot0_{2}$
0·01	101·72	$\cdot001017_{2}$	0·9990	0·05852	41·01
0·005	103·54	$\cdot000517_{7}$	0·9988 −	0·02927	20·51
0·002	105·31	·0002106	0·9987	0·01171	$8\cdot20_{2}$
0·001	106·27	$\cdot0001062_{7}$	0·9986	0·005854	4·101
0·0005	106·95	·00005348	0·9986	0·002927	2·051

would contain more than a tenth of a gram-equivalent per litre. Thus a solution which is decinormal at 218°C, if cooled to 18°C would be found to be 18.45 per cent stronger than a solution decinormal at 18°. This means that each entry in the original table (2) giving the equivalent conductivity of a 'deci-normal solution' really refers to a different solution. On the other hand, a solution containing one gram of salt per hundred grams of solution would be a 'one per cent' solution at any temperature, provided always there was no evaporation. This latter method of specifying concentration is therefore much more desirable when changes of temperature are involved, as in the case of the present problem, and the values of concentration in the given table were converted from 'x-Normal' to the form 'W per cent' by bringing in the density of the solution - d grams per C.C. Thus: 'x gram-equivalents per litre'

$=$ 58.46 x gm. of sodium chloride in 1000 c.c. of solution,

$=$ 58.46 x gm. in 1000 d gm. of solution,

and if this strength is the same as 'W per cent', i.e. as W. 10 d gm. in 1000 d gm. of solution, then

$$W. 10\, d = 58.46\, x ,$$

i.e.
$$W = \frac{5.846\, x}{d} \quad \text{.............} (1)$$

As no table could be found giving the values of d corresponding to the various values of x, they had to be obtained indirectly from a table of densities of solutions of sodium chloride one per cent and upwards (3). Each value of 'W' in the latter table was converted into the corresponding value of 'x' by means of equation (1), and a graph was plotted of 'd' against 'x'. Then from this graph, shown reduced in Fig.1, the required values of 'd' were read off and equation (1) was again used to obtain the value of 'W' corresponding to each value of 'x' in Table No.1.

The values of concentration in grains per gallon given in the last column of Table No.1 were obtained from the straightforward relation between the British and metric units, and were inserted in the table in order to abstract values of specific conductivity at 18°C for a set of solutions worked with.

Large scale graphs were then drawn for 'percentage' solutions (and for 'grains per gallon' solutions) and from these the specific conductivity at 18°C was read off for a series of 'round-number' concentrations and set down in Table No.2. In this way the required data at 18°C were derived for solutions weaker than five per cent. For

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(3) Bousfield & Bousfield: Proc. Roy. Soc. 103 (A), 1923, P.429.

(4) Landolt-Bornstein Tabellen, 3rd.Ed., 1905, P.735.

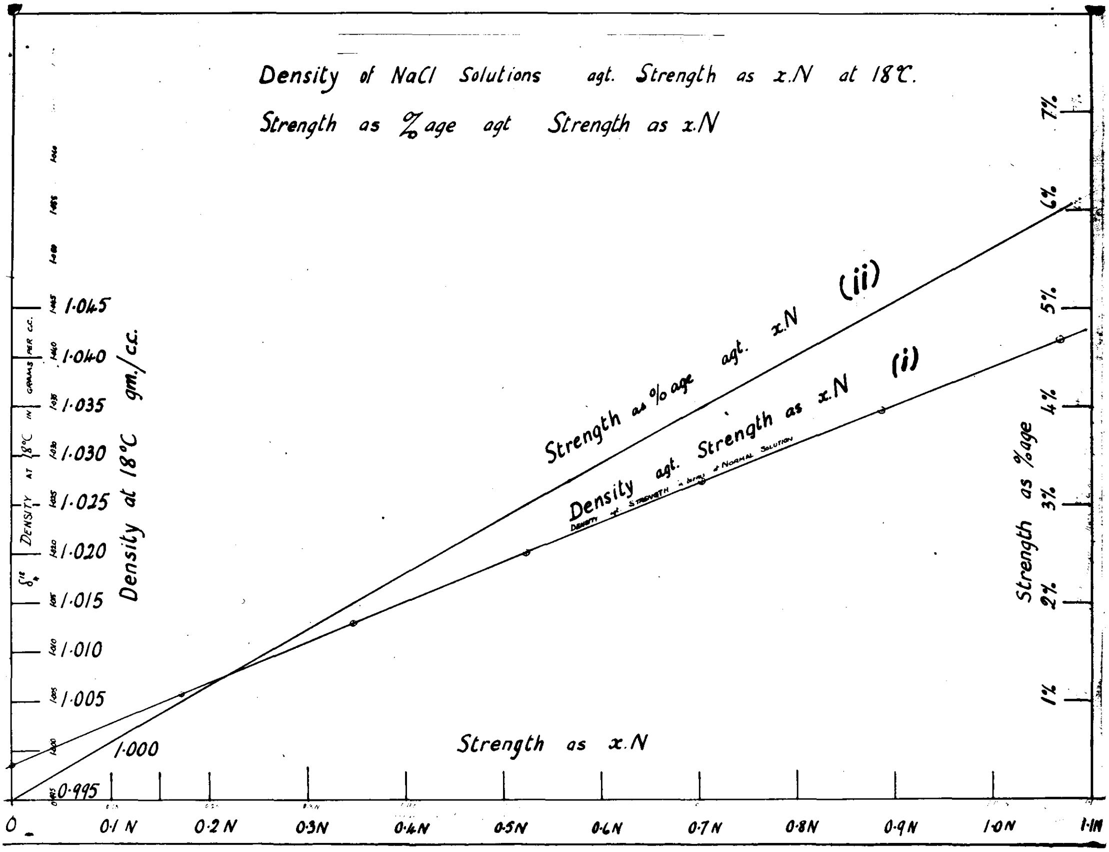

Fig. 1.

(Graph (ii) was used merely as a check on the calculations, as the values of x obtained by the use of graph (i) were more accurate due to the large scale permissable for density.)

Table No.2.

Derived Values of Specific Conductivity at 18° (k_{18})

of

Sodium Chloride Solutions, W gm per 100 gm. of solution.

Concentration W per cent.	k 18 $ohm^{-1}. cm^{-1}$
.001	.0000183
.002	.0000365
.005	.0000908
.010	.000181
.02	.000356
.05	.000872
0.1	.00171
0.2	.00333
0.5	.00794
1.0	.0153
2.0	.0291
3.0	.0423
4.0	.0550

solutions five per cent and upwards a suitable table had been prepared by Kohlrausch and Grotrian.(4)

For temperatures other than 18°C, but not far removed from it, a temperature coefficient of increase in conductivity, $(dk/dt)/k_{18}$, may be used to derive the specific conductivity from the known value at 18°. The mean temperature coefficient for a small specified range, e.g. $\frac{1}{k18}\left(\frac{k26 - k\,18}{26-18}\right)$, is sometimes given in tables and as this varies appreciably - from about 0.021 to more than 0.023 - for different strengths of common salt solutions, values were collected from different sources (4) (5), and graphed as shown in Fig.2. From this graph the temperature-coefficient near 18° can be read off for any solution up to saturated (26.4 per cent at 18°), and by its use in experimental work the tedium of adjusting the temperature to exactly 18° may be avoided.

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(4) Landolt-Bornstein Tabellen, 3rd.Ed., 1905, P.735, gave $\frac{1}{k18}\left\{\frac{k26 - k18}{26 - 18}\right\}$ directly of solutions 5 per cent and upwards.

(5) Bray and Hunt in Jour. Amer. Chem. Soc. 33, 1911, P.781 gave $\frac{k\,25}{k\,18}$ for solutions 0.001 Normal to 0.1 Normal at 25°C. The concentrations had to be transformed to 'percentages', and the mean temp. coeffts. bet. 18°C and 25°C were obtained from the formula

$$\frac{1}{k18} \cdot \frac{1}{7} \cdot \left\{\frac{k25}{k18} - 1\right\}$$

Graph of Mean Temperature Coefficient of Increase of Conductivity
between 18°C and 26°C (or 25°C) for Sodium Chloride Solutions

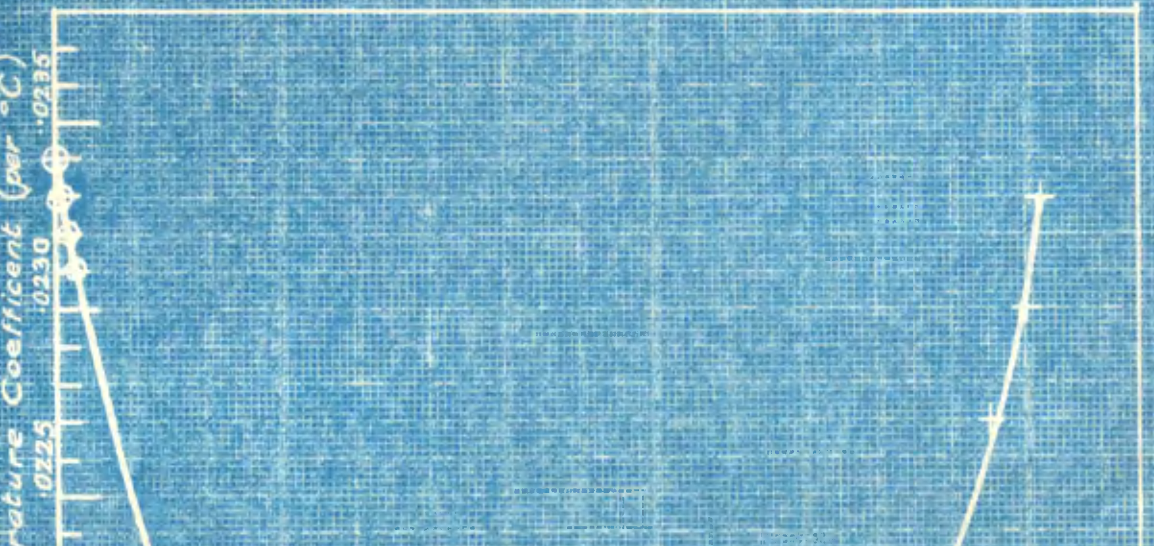

Fig. 2

For temperatures far removed from 18°C the only results available seemed to be those of Noyes and Coolidge (6) who found the conductivity of four common salt solutions at steady vapour-bath temperatures of 140°, 218°, 281° and 306°C using a conductivity-cell of unusual and costly design. Of these four solutions, the two strongest are of most use for the present purpose, as they were approximately centi-normal and deci-normal at 4°C. In addition to the resistance, the specific volume had been measured for each solution at each temperature, so that the new value of the weight-normal concentration could be calculated, and by graphing the results, the equivalent conductivity for the 'round-number' concentrations at each temperature had been tabulated. This meant that the final tabulated values were in a form very unsuitable for the present purpose, but from the values used in preparing them the following useful results were worked out.

Table No.3.

Concentration.	k_{140}	k_{218}	k_{281}	k_{306}
0.0584 per cent.	.00429	.00583	.00627	.00627
0.598 per cent.	.0386	.0509	.0524	.0488

These constitute all the useful results that could be readily abstracted from published tables, and further values had to be obtained by direct experiment. A description of the experiments is now given.

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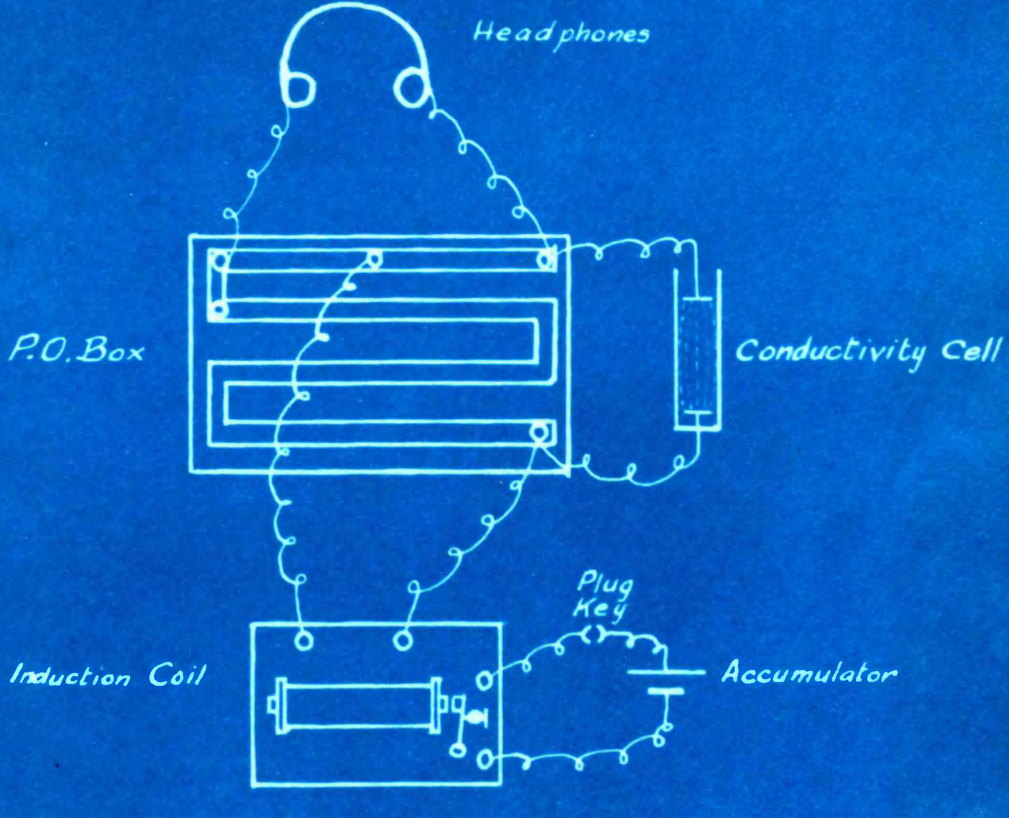
(6) Jour. Amer. Chem. Soc. 26, 1904, P.134.

Experiments at temperatures less than 100°C.

Apparatus:

The apparatus used in the experiments was such as is required for the classical Kohlrausch method of measuring a fluid resistance. The electrical circuit is shown in Fig.3. Instead of the usual wire-bridge with extension-coils, a Post-Office-Resistance-Box was used, the source of alternating current being a small induction-coil operated by means of a two-volt accumulator, and the detector a pair of telephone receivers. At first experiments were made at temperatures up to about 90°C only, and a conductivity-cell of standard type was used - a glass 'test-tube' of wide bore fitted with a vulcanite cap from which two parallel horizontal electrodes of platinum were suspended by glass tubes, the tubes serving at the same time to insulate the leads. This cell is shown in Fig.4. It was held in a thin brass tube with tripod base, shown also in Fig.4, the two being placed in a large copper can which served as a water-bath, and the water heated by a bunsen burner and kept stirred by means of a little propeller driven by an electric motor. Mercury thermometers were suspended in the water-bath and in the conductivity-cell to measure the temperatures, approximate correction graphs for these having first been obtained by checking the fixed points.



Sketch of Apparatus

for

Conductivity Measurements

Fig. 3

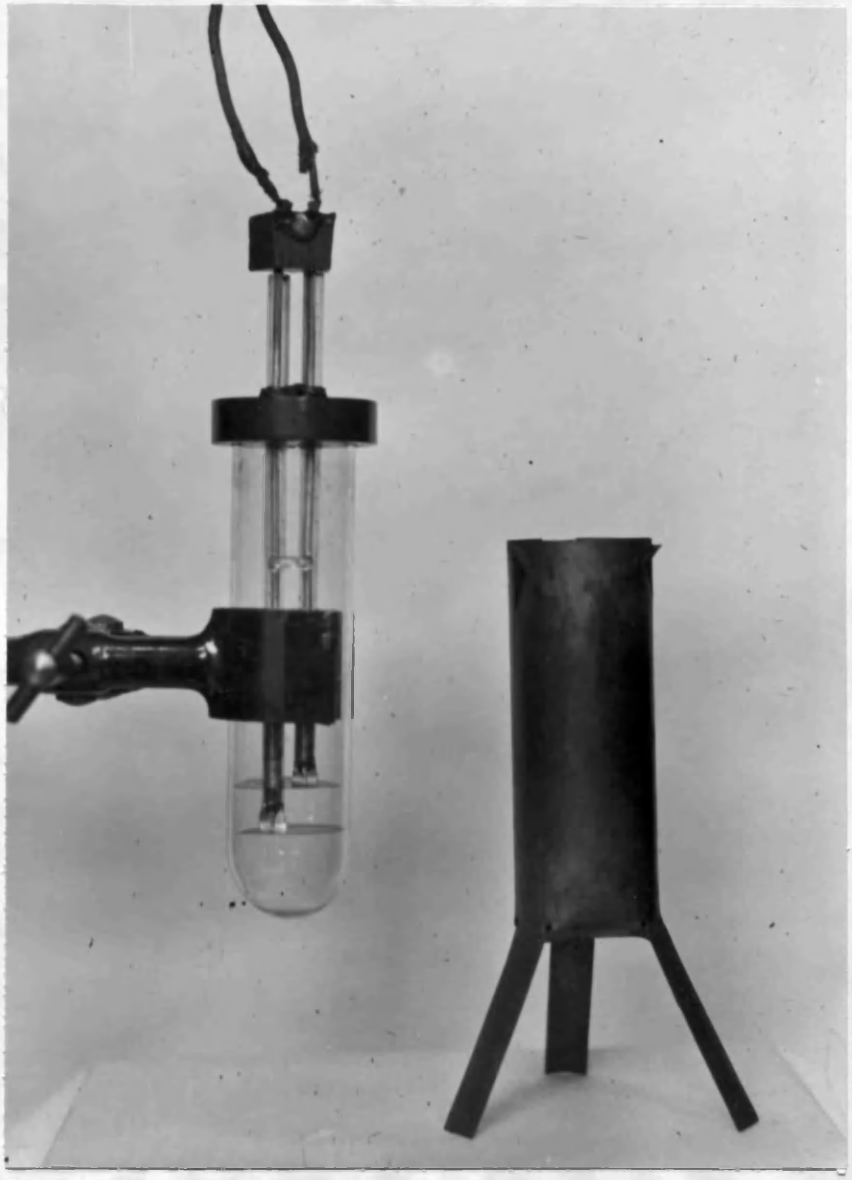


Fig. 4.

Standard Conductivity Cell.

Procedure:

Before putting the cell into use, the electrodes were given a coating of platinum-black by the usual method(7). A 'stock solution' was then prepared of pure sodium chloride of strength 800 grains per gallon at 18°C. Part of this was diluted to 80, 160, 320, 480, and 640 grains per gallon, and each solution in turn was used in the standard conductivity-cell.

The 'constant' of a conductivity-cell is the factor by means of which the specific conductivity, k, of a solution is obtained from the measured resistance, R. Thus, if R is the resistance of a column of solution of length ℓ and cross-section A, the specific conductivity is given by $\frac{1}{R} \times \frac{\ell}{A}$. But, since the cross-section of a cell is not generally the same as the area of the electrodes, nor is it uniform, the flow of the current is not in straight lines ([redacted]) and $\frac{'\ell'}{A}$ is not given accurately by the distance between the electrodes divided by their area. An effective value has to be found by experiment using a solution of known conductivity. In the present instance the resistance of each solution at exactly 18°C was determined, and using the value of specific conductivity obtained by means of Table No.1, the corresponding value of $\frac{\ell}{A}$ was calculated. It was never possible to obtain

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(7) Watson's Practical Physics, 1917, P.479.

complete silence in the 'phones and the resistance could only be measured with an accuracy of about one half per cent. The results obtained are set down in Table No.4, and yield a mean value of 0.201 cm for the cell-constant.

Table No.4.

Concentration: grains per gallon at 18°C.	R_{18} : ohm	K_{18} : ohm^{-1} cm^{-1}	$\frac{\ell}{A}$: cm^{-1}
80	104.5	$.00194_1$	.203
160	53.0	.00377	.200
320	27.7_5	.00727	.202
480	18.8	.01065	.200
640	14.5_5	.01391	.202
800	11.7	.01711	.200

The resistance of each solution was also found at various temperatures up to 90°C. by heating the water bath gradually up to this temperature, and steadying the heating at intervals till the reading of the thermometers, in the bath and in the solution, agreed to a fraction of a degree for several minutes. The resistance was noted at each steady temperature, and similarly for several temperatures as the solution cooled. The specific conductivity corresponding to each reading of resistance was then calculated, using the value of '$\frac{\ell}{A}$' derived above, and large scale graphs were drawn of specific conductivity against temperature. These are shown (to a reduced scale) in Fig.5, and in Table No.5 are noted the values of specific conductivity derived from them for the even temperatures 20, 30, - - - 90°C.

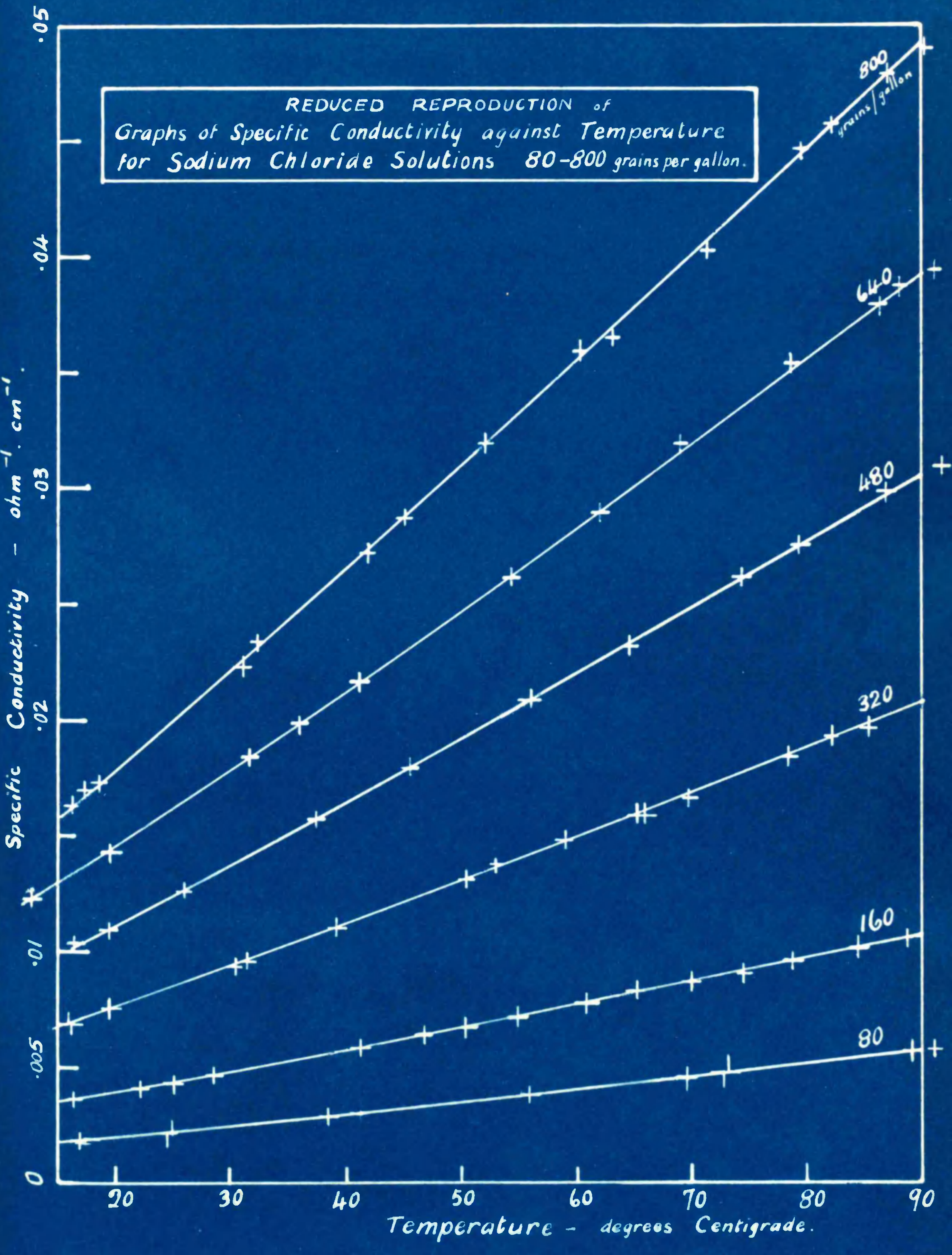

REDUCED REPRODUCTION of
Graphs of Specific Conductivity against Temperature
for Sodium Chloride Solutions 80-800 grains per gallon.
Specific Conductivity - ohm⁻¹. cm⁻¹
.05
.04
.03
.02
.01
.005
0
20
30
40
50
60
70
80
90
Temperature - degrees Centigrade.
800 grains/gallon
640
480
320
160
80

Fig. 5.

Table No.5.

Interpolated values of specific conductivity (k_t) at different temperatures for sodium chloride solutions

(80 - 800 grains per gallon; 18° - 90° C)

Concentration grains/gall. at 18° C.	80	160	320	480	640	800
k at 10°C	.00161	.00308	.0058	.0087	.0113	$.0137_5$
k at 18°C	$.00194_1$	.00377	$.0072_7$	.01065	$.0139_1$	$.0171_1$
k at 20°C	.00203	.00394	.0076	$.0111_5$	$.0145_5$	.0179
k at 30°C	.00248	$.0048_3$	.0094	.0137	$.0178_5$	.0222
k at 40°C	.00295	$.0057_4$	.0112	.0164	$.0212_5$	$.0265_5$
k at 50°C	.00344	$.0066_6$	.0130	$.0191_5$	.0247	.0310
k at 60°C	.00396	$.0076_1$	.0149	$.0219_5$	$.0282_5$	.0355
k at 70°C	$.0045_0$	$.0085_9$	.0168	.0248	.0319	$.040_1$
k at 80°C	$.0050_6$	$.0096_0$	$.0187_5$	$.0276_5$	$.0355_5$	.0447
k at 90°C	$.0056_2$	$.0106_3$	.0207	.0305	$.0392_5$	$.049_3$
Ratio $k_{50}:k_{18}$	1.77	1.77	1.78	1.80	1.78	1.81
Ratio $k_{90}:k_{18}$	2.89	2.82	2.84	2.87	2.82	2.88
Concentration W per cent	0.114%	0.23%	0.46%	0.68%	0.91%	1.13%

Experiments at temperatures above 100°C.

For temperatures above 100°C a different cell and heating bath were necessary. The cell had to be steam tight and the electrodes insulated from one another at the high pressures and temperatures corresponding to boiler conditions. The first designs tried were after the pattern of a water-gauge, such as is used for steam boilers. One electrode of platinum foil was held down by the lower end of a gauge-glass, and the other electrode was insulated from the first by being fixed to the central pin of a motor sparking-plug which was screwed into the upper part of the fitting. Two of these cells are shown in Fig.6. They were heated inside an electric furnace, but did not prove successful. The space inside the furnace was so small that it limited the size of the fittings for a cell, and it was difficult to prevent a leak at the joints between glass and metal. Also the sparking plugs proved leaky when put to this unwonted use.

Eventually a fairly satisfactory cell was evolved, the construction of which is shown in Fig.7. G, the cell proper, was a special 'test tube' of pyrex-glass for holding the solution under test. The lower electrode was of platinum and was inclined at about 45° to the horizontal so as to allow an easy way of escape upwards for any bubbles of air or

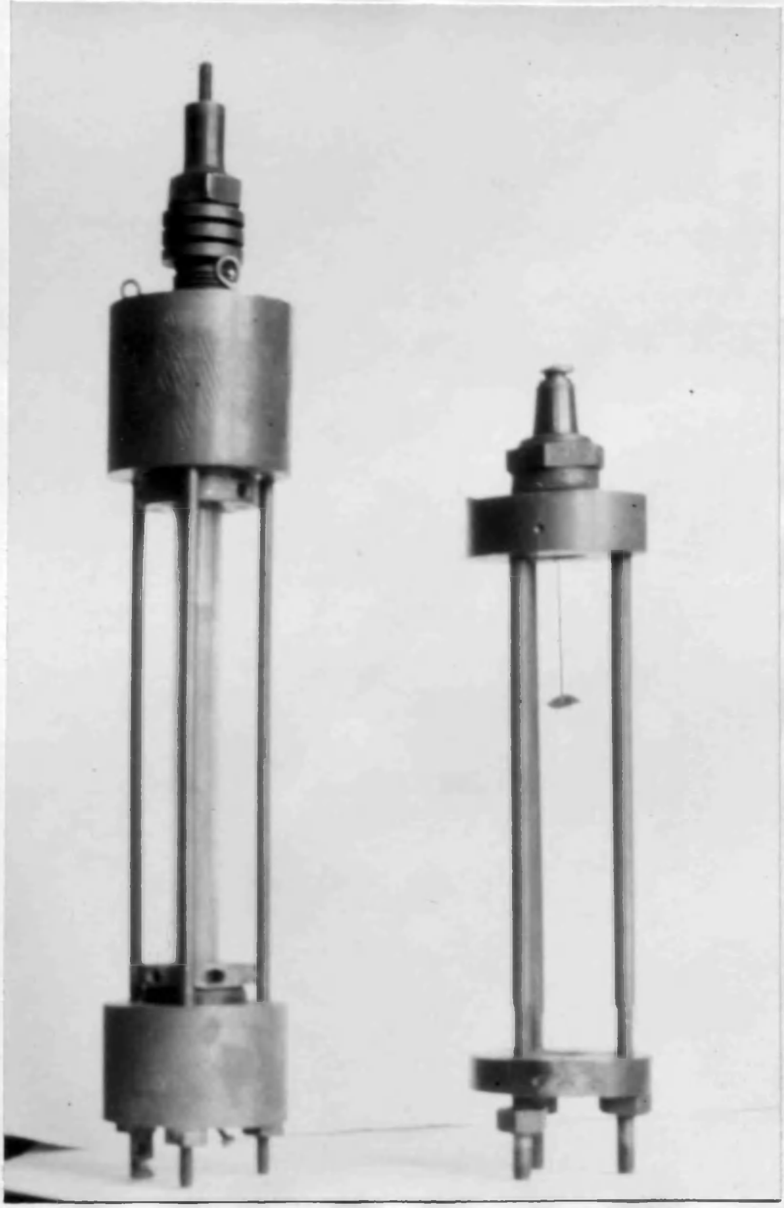


Fig. 6.

Unsuccessful forms of Conductivity Cell.

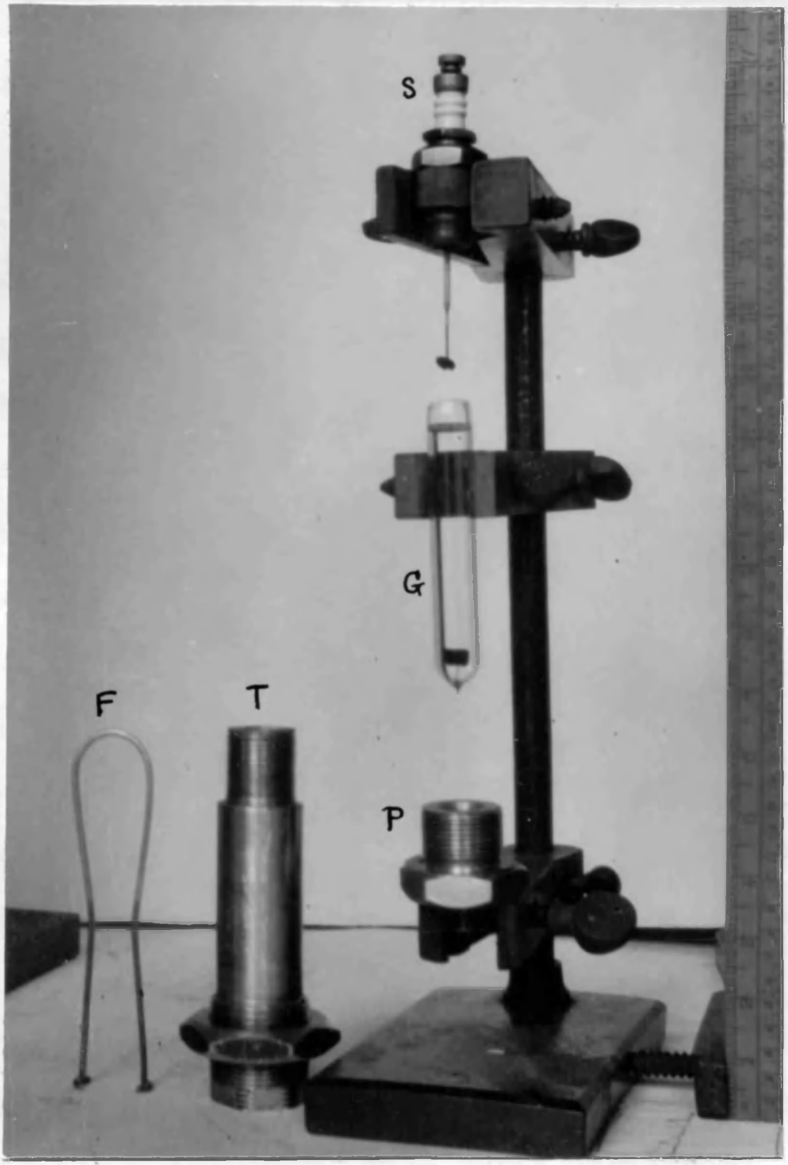


Fig. 7.

Conductivity Cell used for high temperatures.

steam that might be formed beneath it. This electrode was supported by a short piece of platinum wire fused through the bottom of G, and projecting a little so as to dip into a small hole in the steel plug P, which was also turned out a little to take the end of tube G. Mercury filled into the hollow in plug P served to complete the electrical circuit between the electrode and P. The upper electrode, also of platinum and also inclined, was attached by a platinum wire to the central pin of a sparking plug, S, specially made by Lodge Plugs Ltd. To prevent contamination of the solution, a glass sleeve was fitted over this central (steel) pin, long enough to cover its junction with the platinum; and a little 'umbrella' of mycalex was fitted to this, large enough to overlap the top of tube G and prevent any condensed steam from the water jacket, or impurity from the making of the screwed joint above, from dropping into the solution.

The steel tube, T, completed the cell. It was screwed inside at the bottom to take plug P, and at the top to take the sparking plug S. When these parts were properly fitted together they formed a compact unit which could be heated in different ways. Two types of heater were used - a steam-chamber in the first experiments, and in the later ones an oil-bath.

The steam-box used in the first experiments is seen in Fig.8. It was supplied with steam from a large experimental

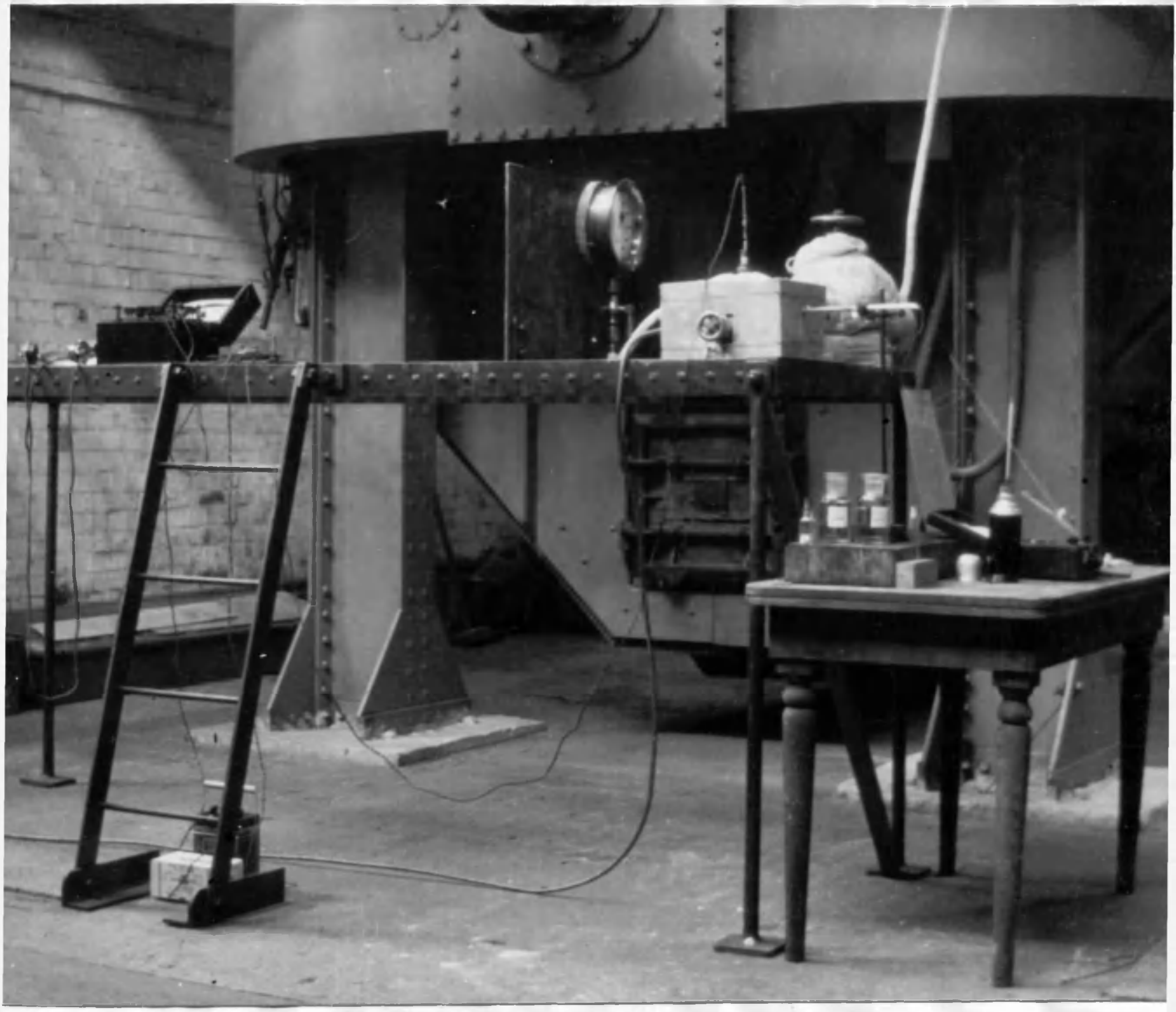


Fig. 8.

Photograph of Apparatus used at the works of Yarrow & Co. Ltd.

boiler at the works of Messrs. Yarrow & Co. Ltd., who granted the great privilege of carrying out the experiments there. The whole steam-box, with its delivery pipe and regulating valves, was well lagged, and a pressure gauge was connected to it to help in regulating the temperature to which the solution was raised. This temperature was measured by means of a copper-constantin thermo-couple and a micro-voltmeter, the hot-junction being thrust into a special thermometer pocket in the steam-box so that it was in metallic contact with tube T, while the cold junction was maintained at a steady temperature in water in a thermos flask.

Procedure:

The procedure in running an experiment was as follows. Tube T having been fitted into its place in the steam-box, and plug P screwed on, a little mercury was dropped into the hollow in P, and a measured quantity of water filled into the steel tube to help in the transmission of heat from the steam to the solution. The pyrex test-tube G was filled to the proper depth with the solution under test, and lowered into the steel tube by means of the special forceps F (Fig.7), and the sparking plug was tightly screwed into position, a soft copper washer smeared with red lead being used to make the joint steam-tight. The electrical connections were then completed as in Fig.2.

From the lay-out of the apparatus two observers were necessary to take readings of resistance and temperature. The writer made the measurements of resistance, while the readings of thermo-couple and steam-gauge were taken by Professor Muir, under whose supervision these experiments were carried out. Both observers noted the time at each reading, and afterwards, on the same sheet and against the same time-base, graphs were plotted of the three following variables: (i) conductance of the solution, (ii) temperature given by thermo-couple, (iii) temperature of saturated steam corresponding to gauge-pressure. By adjusting the steam valves at intervals the pressure of the steam admitted to the steam box was gradually raised, and at each stage conditions were allowed to steady until the measured resistance remained the same for several minutes. The pressure was reduced by the same stages so that the temperature of the solution was allowed to steady again at practically the same values. The experiments had to be repeated several times because of leaks developing in the sparking plug at the porcelain-to-metal joints, but eventually consistent results were obtained.

The time chart for one experiment is shown in Fig.9. Except for some irregularities in the conductance curve between B and D, the three graphs are seen to vary together fairly well. The changes in curve (iii) corres-

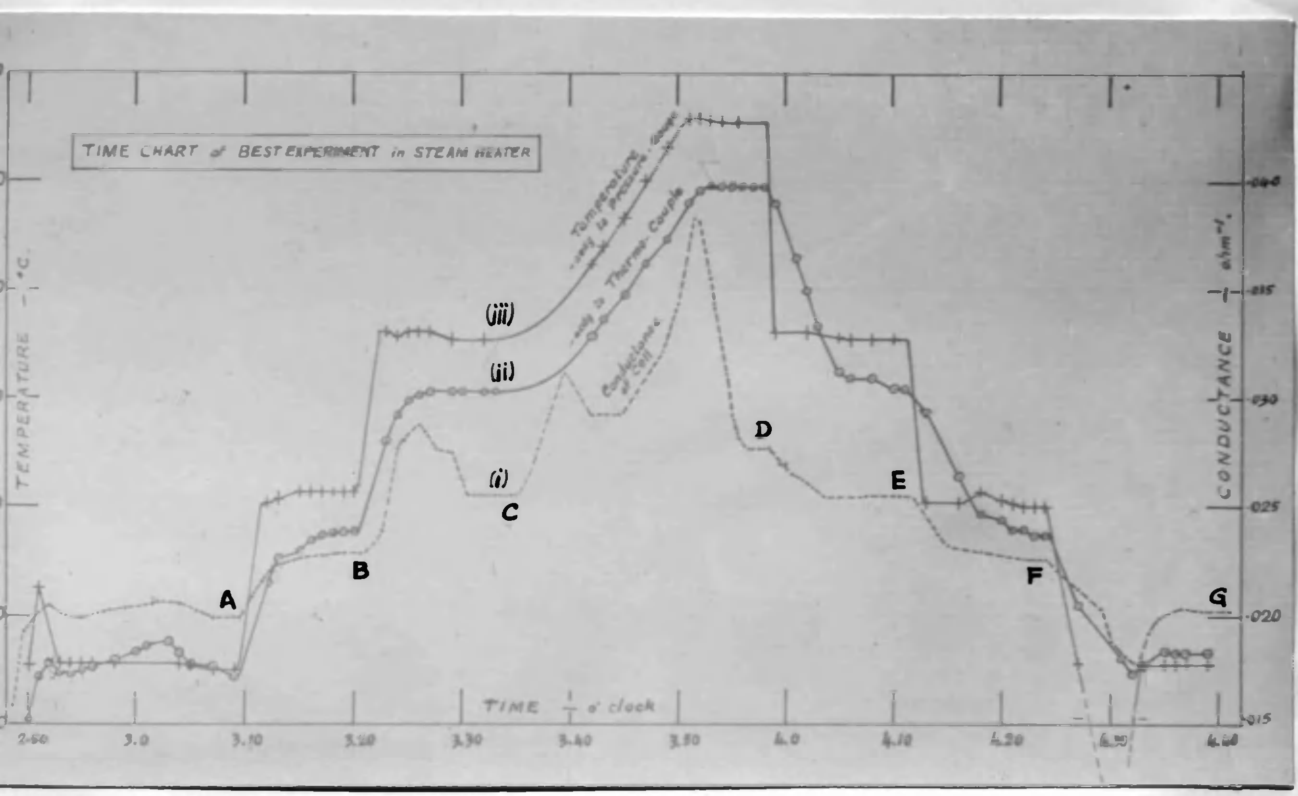


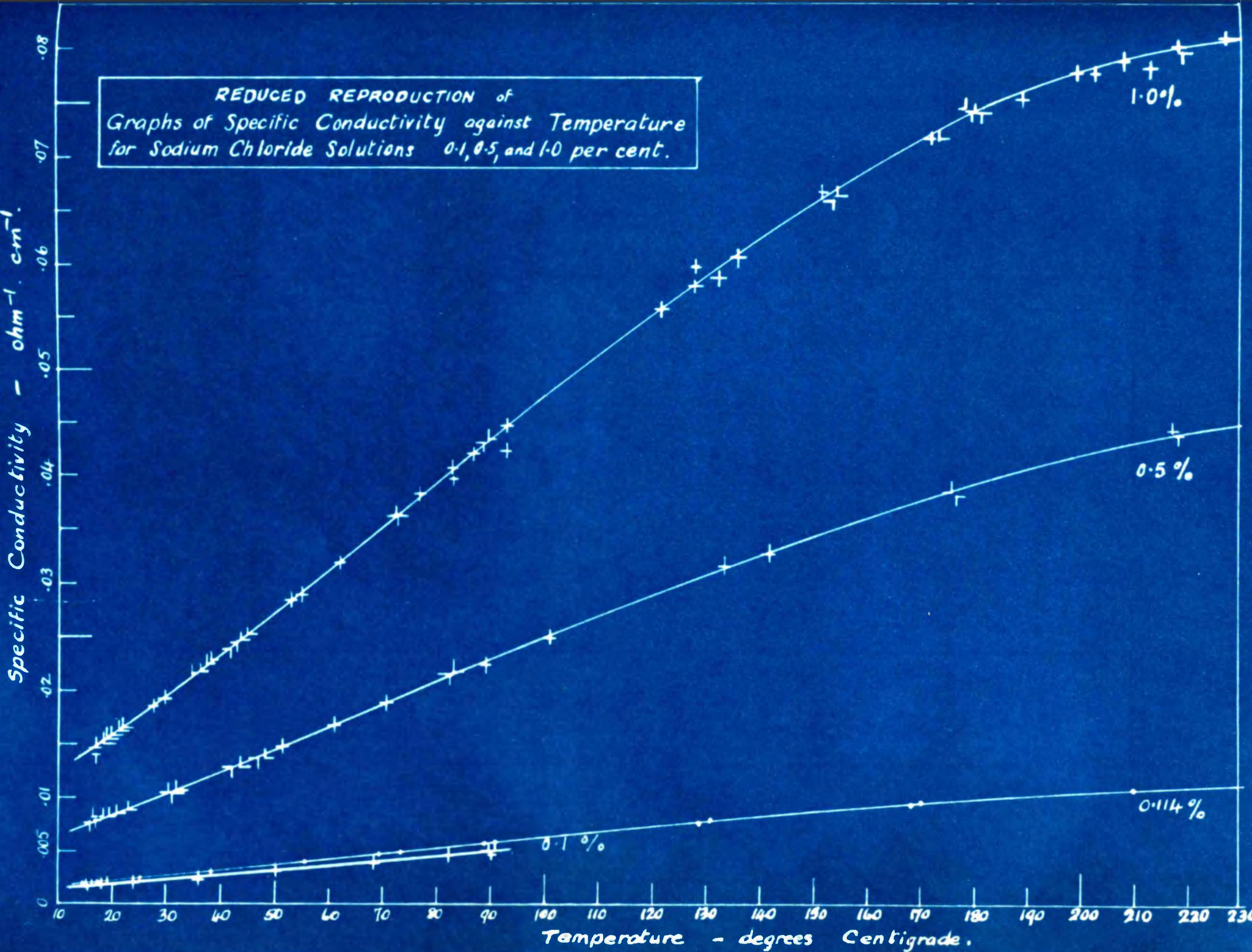
Fig. 9.

Sample Time Chart for Experiment in Steam Heater.

ponding to the pressure-gauge are naturally more abrupt than the others since these were effected in most cases by merely altering the inlet and outlet valves of the steam-box. The exception was at 3-33 p.m. when additional heat had to be supplied at the boiler. The break in the curve at 4-30 p.m. was due to the pressure in the steam-box being allowed to fall to atmospheric for a short interval before steadying it at the desired value of 25 lb. per sq. inch. It was assumed that the temperature measured by the thermo-couple, though generally lower than that corresponding to saturated steam at gauge-pressure, gave, with sufficient accuracy, the temperature of the solution, for the thermo-couple was in metallic contact with the steel tube and readings were taken at the same stages in cooling as in heating. The fact that the thermo-couple readings gave higher temperatures when the pressure was being steadied at 25 lb. per sq. in. was due to the steam being superheated, whereas the temperature corresponding to the pressure-gauge was for saturated steam. (The steam was produced in a boiler of exceptional power).

The irregularities in the conductance curve after B and C require some explanation. The sudden jumps of conductance took place when the regulating valve was altered, and seem to have been caused by sudden ebullition taking place inside the cell, followed by condensation of steam, or, indeed, the lodging of drops of solution, inside the sparking plug which from its exposed position would not attain to the new steady temperature till the steam had been passing for some time. Drops of water forming in this way and evaporating again as the contents of the cell settled down to a new state of equilibrium would temporarily form a parallel path for the current through the cell and thus cause such a variation in conductance as the graph shows. The steady value of the conductance eventually reached at C is seen to agree with that obtained at E for almost similar conditions, just as the values at G and F agree with those at A and B. Further, the steady value of conductance reached for a minute of two at D after the erratic variation, was confirmed next day when the solution was reheated to the same temperature before the application of steam at the exceptionally high pressure of 600 lb. per sq. in. and then 1000 lb. per sq. in. Under these abnormal pressures the sparking plug leaked, but the agreement among the values of conductivity just mentioned shows that there had been no leak in the experiment for which Fig.9 is the graph, and that the results it yielded could be relied on. This gave seven points in the final curve of k against t for temperatures about 130°, 155°, 180° and 220°C.

For these experiments with the steam-heater, besides the two observers taking readings, there were two men looking after the steam plant, and so whenever an experiment failed because of the development of a leak in the apparatus, the time of four men was wasted. In later experiments, therefore, the heating was carried out more simply. The steel tube was immersed in liquid paraffin in a rectangular copper vessel about 12" x 3" x 15". This bath was heated by a bunsen burner, and kept stirred by a little propeller driven by an electric motor. The temperature was still measured by the same thermo-couple, and also by a mercury thermometer, both immersed in the oil-bath, and the mean of the two values obtained was taken as the true one. With this arrangement the writer, working alone, was able to control the heating and take all the readings, though occasionally some were taken by his supervisor, notably in the case of the 0.114 per cent solution. Further values were thus obtained for the two solutions already used in the steam heater, i.e. ½ per cent, and 1 per cent and in addition for a solution of strength 80 grains of salt per gallon at 18°C, i.e. 0.114 per cent, and these values were plotted in the same graphs as those from the steam-heater experiments. The graphs are shown, reduced in Fig.10, and from them the specific conductivity at 'round' temperatures was read off for each solution and set down in Table No.6. It is thought that the values thus tabulated are accurate to about one per cent. By replotting them in



REDUCED REPRODUCTION of
Graphs of Specific Conductivity against Temperature
for Sodium Chloride Solutions 0·1, 0·5, and 1·0 per cent.

Table No.6.

Interpolated Values of Specific Conductivity of NaCl.

Concentration Percentage by weight:	0.1%	0.114%	0.5%	1.0%
k at 10°C	.00140	.00160	.0065	.0125
k at 18°	.00171	$.00194_1$	$.0079_4$	$.0152_7$
k at 20°	.00180	.00203	.0083	.0159
k at 30°	.00222	.00248	$.0102_5$	.0195
k at 40°	.00265	.00295	.0123	.0233
k at 50°	.00309	.00344	.0144	.0272
k at 60°	.00355	.00396	$.0165_5$	.0312
k at 70°	.00401	.00450	$.0187_5$	.0352
k at 80°	.00447	.00506	.0209	.0393
k at 90°	.00493	.00562	.0230	.0434
k at 100°	.	.00617	.0250	.0474
k at 110°	$(.0058_5)$	.00670	.0270	.0513
k at 120°		.00722	.0289	.0551
k at 130°	$(.0067_5)$	.00772	.0308	.0587
k at 140°		.00819	.0326	.0622
k at 150°	(.0076)	.00864	.0344	.0655
k at 160°		.00906	.0361	.0686
k at 170°	$(.0083_5)$	.00946	$.0377_5$	.0715
k at 180°		.00984	$.0393_5$	.0741
k at 190°	(.0090)	.0102	.0408	.0763
k at 200°		$.0105_5$	.0421	.0780
k at 210°	$(.0095_5)$	$.0108_5$	.0432	.0793
k at 220°		$.0111_5$	.0441	.0803
k at 230°	(.0100)	.0114	.0448	.0811

the manner shown in Fig.11 approximate values of the specific conductivity of any intermediate solution may be read off for any temperature up to 230°C, indeed the values given in brackets in Table No.6 for the 0.1 per cent solution were obtained in this way.

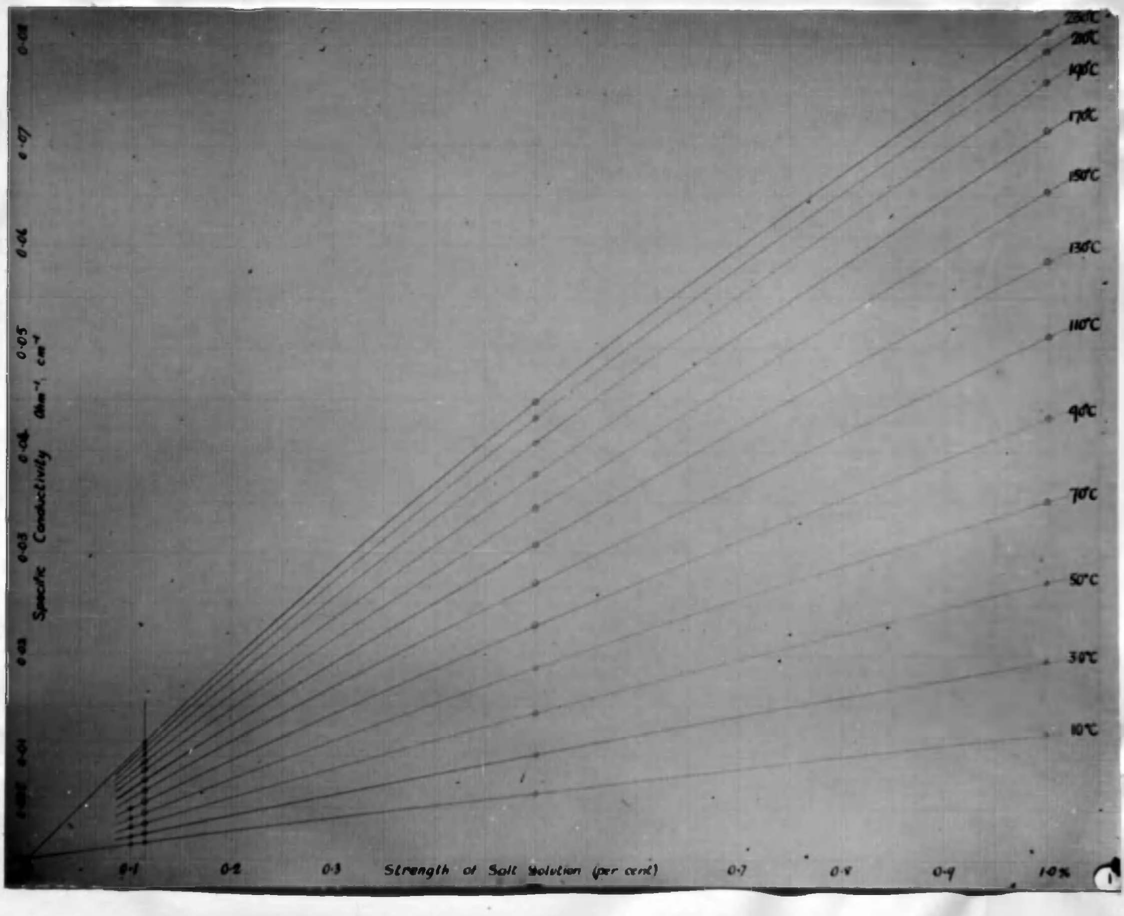


Fig. 11.

Combined Graph from which the Specific Conductivity of Sodium Chlorine solutions of any strength up to one per cent at any temperature up to 230°C may be read off directly. (Reduced).

Possible Sources of Error.

Three possible sources of error at the high temperatures were considered.

(i) Change in insulating property of pyrex-glass. Bousfield and Lowry (8) had shown that the conductance of a glass test-tube when heated from 95°C to 225°C increased to be 1754 times its value at 95°C, so a test was made to see whether pyrex retained its insulating property any better. The pyrex test-tube was filled with mercury and supported inside a wider test-tube containing mercury, and the resistance between amalgamated copper leads dipping into the mercury inside and outside the tube was measured. This proved to be about a megohm at room temperature and more than 100,000 ohms when the temperature was raised to 230°C. This resistance acting in parallel with the solution tends to make the measured resistance slightly lower than it ought to be, but since the measured resistances of the cell at this high temperature were of the order of 36 ohms, 65 ohms, and 250 ohms, respectively, for the 1 per cent, 0.5 per cent, 0.114 per cent solutions, this introduced an error of only 1 in 3000, 2 in 3000, and 1 in 400 in the three cases.

(ii) Change in the value of the cell-constant. Due to the expansion of the different parts of the conductivity-cell when the temperature is increased, the value of the

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(8) Bousfield and Lowry: Proc. Roy. Soc. 71, 1902, P.42.

cell-constant might be expected to alter. Readings taken for different conductivity cells show that an approximate value for the cell-constant is obtained by dividing the distance between the electrodes by the area of cross-section of the liquid column between and <u>not</u> the area of an electrode. In the present case, a rough sketch of which appears alongside, the distance between the electrodes (X and Y) was 7 cm, the area of the cross-section of the liquid column was 2.27 sq.cm., and the area of an electrode was .75 sq.cm. The cell constant was found to be 2.9_0 which is much nearer to $\frac{7}{2.27}$ i.e. 3.0_8, than to $\frac{7}{.75}$ i.e. 9.3. Approximately, therefore, the change produced in the cell constant may be calculated from the change in the distance between the electrodes (l) and in the area of section of the pyrex tube (A).

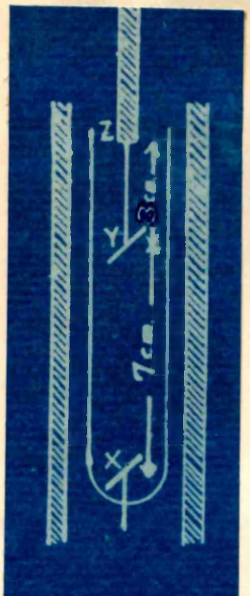

Fig. 12.

The upper electrode was supported by 3 cm. of platinum wire (Y Z) from the central pin of the sparking plug. The length X Z would increase according to the linear coefficient of expansion of steel (i.e. .000011 per Centigrade degree) and Z Y would increase according to the coefficient for platinum (i.e. .0000088 per degree). Thus the length X Y between the electrodes would increase for a rise of one Centigrade degree by (10 x .000011 - 3 x .000009) cm i.e. by .000083 cm., which means an increase of .000012 cm. per cm.

of gap for a rise of one Centigrade degree.

The area of section of the vessel would increase according to the superficial coefficient of expansion of pyrex, i.e. 2 x .0000032 or .0000064 per Centigrade degree. Thus if $\frac{\ell'}{A'}$ represents the cell-constant at the highest temperature, say 200°C above room temperature, $\ell' \doteqdot \ell \times (1 + 200 \times .000012) \doteqdot \ell \times 1.0024$, and, $A' \doteqdot A\ (1 + 200 \times .0000064) \doteqdot A \times 1.0013$, so that $\frac{\ell^1}{A^1} \Big/ \frac{\ell}{A} \doteqdot \frac{1.0024}{1.0013} \doteqdot 1.001$, showing that the cell constant may be expected to increase by only about 1 in 1000 when the vessel is heated through 200°C.

(iii) Change in concentration of solution.

The density of saturated steam increases with rise in temperature so that the weight of steam contained inside the cell increases due to evaporation of some of the water from the solution and from the jacket water. The volumes of solution and of jacket-water used were 20 c.c. and 40 c.c. respectively and the volume of the remaining space inside the cell was estimated at about 13 c.c. From the specific volume of saturated steam at 218°C - namely 90.1 c.c. per gm. the mass of steam produced in the space was found to be $\frac{13}{90.1}$ i.e. .144 gm, and assuming it to come partly $(\frac{2}{3})$ from the jacket-water, and partly $(\frac{1}{3})$ from the solution, it was estimated that the concentration of the solution would thereby increase by about $\frac{.048}{20}$ i.e. by about 1 in 400.

This would decrease the measured resistance, as would also the fall in insulating power of the pyrex, but the change in cell-constant would increase it, so that even at the highest temperature the resultant effect would be of a low order, of the nature of 1 in 400. Since the readings of resistance, particularly at the higher temperatures, were not accurate to more than about 1 in 200, (and for the .114 per cent solution to about one per cent), the error arising from these sources was counted negligible. It was naturally much smaller for lower temperatures.

Comparison with results of previous experiments.

A comparison of the results with those obtained by Noyes and Coolidge was made as follows. The strength of a half per cent solution in terms of Normal at 218°C, 140°, and 100° was first calculated on the assumption that the solution expanded with rise in temperature at the same rate as pure water. (Thus, using 0.9986 and 0.840 gm. per c.c. as the density of water at 18° and 218°C respectively the half per cent solution .0858 Normal at 18°C becomes $.0858 \times \frac{.840}{.9986}$ Normal at 218°C.) For each temperature a graph was then drawn, from the results of Noyes and Coolidge, of equivalent conductivity against strength in terms of normal <u>at that temperature</u>, and from these graphs the equivalent conductivity of the half per cent solution was read off.

In this way the following table of comparison was obtained for the half per cent solution:

	k_{218}	k_{140}	k_{100}
From Expts. by Writer	.0439	.0326	.0250
From results of N. & C.	.0430	.0327	.0247

For the one per cent solution the highest value that could be checked was that for 100°C. The results of Noyes and Coolidge yielded .0476 for k_{100} as compared with .0474 obtained by the writer.

Thus the results obtained in this paper are seen to compare favourably with those obtained previously and they are thought to be correct to about one in a hundred.

Theory.

The general shape of the conductivity-curves is worthy of some consideration. Taking, for example, the curve for the one per cent solution, the 'slope' of the curve is seen to be fairly constant at first, so that the 'temperature-coefficient' $\left\{ \frac{1}{k} \times \frac{dk}{dt} \right\}$ near 18°C may be used to obtain the value of the specific conductivity at temperatures 40° or 50° above normal without much error. But after about 80°C the temperature-coefficient is seen to decrease gradually with rise in temperature, for the curve becomes distinctly convex upwards, indicating that there is likely to be a maximum value of conductivity at some temperature in the neighbourhood of 300°C, after which the temperature-coefficient would be negative and the conductivity would tend to a minimum or zero value.

With aqueous solutions a maximum value in the conductivity-temperature curve has seldom been obtained because of the difficulty in experimenting at the high temperatures involved. Hagenbach (9), however, succeeded once in obtaining a maximum of conductivity in the case of a solution of potassium

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(9) A. Hagenbach Ann. d. Physik 5, 2, 1901, P.276.

chloride in water at a temperature of 310°C before his apparatus exploded, but with solutions of different halides in liquid sulphur dioxide, he obtained maximum turning-points in the curves at much lower temperatures. Thus, in the case of a solution of potassium iodide in liquid sulphur dioxide, heated up from 18°C, the conductivity was a maximum at 87°C, and thereafter decreased smoothly until the critical temperature of the solution was almost reached. Just before the critical temperature, however, the change became rapid, but above it the change was again slow, the conductivity falling to zero, a few degrees higher than the critical temperature. Walden and Centnerszwer (10), also using liquid sulphur dioxide as solvent, obtained similar results, and it is to be expected that the general form of a conductivity-temperature curve, drawn for the full range, will show a rise from a zero value to a maximum and thence a fall to zero in the region of the critical temperature of the solution. An argument in support of this is given in what follows.

According to the theory of Arrhenius, the process of the conduction of electricity through a solution is carried on by the migration of the positive and negative ions into which molcules of the solute are split up, and this hypothesis is generally accepted today. But, whereas varied allied

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(10) Walden and Centnerszwer: Zeits.Phys.Chem. Vol.39, 1902, P. 549.

phenomena were originally explained in terms of the 'partial dissociation' of the electrolyte, nowadays the theory has gained ground that all the molecules of the dissolved substance are dissociated when solution takes place. This theory of 'complete dissociation' was put forward by Sutherland (11) in 1907, and since then support has been given to it by many workers, notably Debye and Huckel (12) who have developed the theory mathematically.

According to the modern theory, then, there are two influences retarding the motion of an ion when an electric field is applied between two electrodes placed in the solution. Firstly, it seems that an ion is 'hydrated' (13), i.e. it gains an 'atmosphere' of water molecules which move with it and the viscosity forces between them and neighbouring molecules produce a resistance to the motion of the ion which increases with its speed. If the ion were alone in the solution - the state of infinite dilution - this viscous resistance would be the only controlling factor in addition to the applied field and the ion would attain to a steady speed dependent on the coefficient of

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(11) Sutherland: Phil. Mag., Vol.14, 1907, Page 1.

(12) Debye and Huckel: Phys. Zeits. 24, 1923, Pages 185, 305.

(13) Bredig: Zeits. Phys. Chem., 13, 1894, P.277.

viscosity of the solvent.

But the ions cannot be considered as 'isolated' in ordinary solutions. Each positive ion is attracted by neighbouring negative ions and repelled by neighbouring positive ions, so that the applied force has to drag an ion away from the attraction of unlike ions going the opposite way, and against the repulsion of like ions going in the same direction. These 'Coulomb' forces, obeying the law: Force $= \frac{q_1 . q_2}{K . d^2}$, are greater the smaller the value of K, the specific inductive capacity of the solvent, and greater, too, when the solution is concentrated. (So much so, that their effect used to be explained by saying that in concentrated solutions some of the molecules were not split up into ions, i.e. in terms of partial dissociation.)

Under the combined influence of the viscosity of the solvent and the inter-ionic forces, the ions settle down to steady speeds, for a given applied force, and a definite quantity of electricity is carried over per second. In a given strength of solution, therefore, the conductivity is determined by the viscosity and the specific inductive capacity of the solvent, and the effect produced on the conductivity by a change of temperature depends on the change which takes place in these two properties.

For the lowest temperatures attainable by a given solution the viscosity is very great, and if the temperature can be determined at which the viscosity becomes infinite, that should give also the temperature at which the speeds of the ions are reduced to zero and the solution ceases to become conducting. Starting from this point a rise in temperature decreases both the viscosity and the specific inductivity capacity of most solvents. The effect of the former change alone would be to increase the conductivity, and of the latter alone would be to decrease it.

If the viscosity-temperature curve for water is drawn from the values given in tables (14), it is seen to fall very rapidly at first and more slowly afterwards, e.g. the temperature-coefficient at 10° is numerically double that of 150°C. On the other hand, the graph of 1930 values (15) of dielectric constant of water between 0°C and 80°C is a very flat curve, showing an almost regular decrease in dielectrive constant between 20°C and 80°C. As a result, at lower temperatures the effect of the decrease in viscosity predominates, and the combined effect is that the conductivity increases as the temperature rises. At higher temperatures, where the change of viscosity becomes much slower, the effect of the change in specific inductive capacity predominates, and in spite of the lowered viscosity the interionic forces become so strong that the conductivity decreases, and the general shape of the conductivity-temperature curve is as already described.

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(14) Int. Crit. Tables, Vol.5, P.10. (temp. 0°C to 160°C)

(15) Cuthberton & Maass, Jour.Amer.Chem.Soc., Vol.52, 1930,P.483.

Section (b). Concentrated Solutions of Sulphuric Acid.

Introduction.

In the manufacture of sulphuric acid, a test of the concentration of the product is generally made by determining its specific gravity by means of a hydrometer, or a specific gravity bottle. But even the latter and more accurate method does not provide a sure test, unless the specific gravity is known to be less than 97 per cent, for although the specific gravity increases with the concentration up to about 97 per cent, it thereafter decreases. Thus, according to the results of Lunge and Isler for the specific gravity of sulphuric acid at 15°C (1), the value of 1.840 for the specific gravity at 15°C would mean a concentration of either 95.60 per cent or 99.20 per cent.

The results of Kohlrausch (2), however, show that as the concentration of sulphuric acid is increased from 93 per cent to 99.75 per cent its electrical conductivity persistently decreases, the change becoming more rapid at higher concentrations, so that when the concentration reaches 99.75 per cent, the specific conductivity has fallen to less than one tenth of its value at 93 per cent. It seemed feasible,

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(1) 'The Chemists' Year Book' 1915, Vol.2, P.451.

(2) Landolt-Bornstein Tabellen, Vol.II, 1923, P.1077.

therefore, thet an instrument of the 'electrical salinometer' type could be designed to provide a sensitive means of testing the concentration of sulphuric acid in the process of manufacture, and tables were consulted for the necessary data. The table of the results of Kohlrausch, just referred to, gives the specific conductivity at 18°C for the whole range of concentration, and also this mean temperature-coefficient for the interval 18°C to 25°C. But, in manufacture, the finished product may come out at higher temperatures, and as no data seemed to be available for these higher temperatures, the writer was asked to determine experimentally the conductivity, at different temperatures up to 50°C, of a number of strengths of acid above 90 per cent.

Apparatus and Materials.

Experiments were first carried out with three samples of pure acid as follows.

(1) The acid sold as 'pure for analysis', found to be of concentration about 94 per cent.

(2) A sample of the 'middle third' of the condensate of a still in a local manufacturer's - about 98 per cent.

(3) A sample of concentration about 99 per cent, prepared by adding a calculated amount of water to 'acid 20 per cent fuming' (that is 80 parts of sulphuric acid containing 20 parts of sulphur trioxide in solution).

The strengths of these three samples were kindly found by titration by Mr. H.G.A.Anderson, B.Sc., of the Chemistry Department of the College.

After an interval of several months four samples of 'commercial oil of vitriol' (C.O.V.) were obtained and experimented with. These were of a brownish tint, due to some impurity. They had been titrated at the source and were labelled as follows -

(4) 'C.O.V. 93.71 per cent',

(5) 'C.O.V. 94.90 per cent',

(6) 'C.O.V. 97.18 per cent',

(7) 'C.O.V. 99.04 per cent'.

The standard conductivity cell when filled with some of the first sample, 'acid pure for analysis', had a very low resistance, about two ohms, so that a special cell had to be prepared which would give a resistance of some hundreds of ohms.

This special cell was made in the form of a 'U' of pyrex glass tubing approximately 0.86 cm. bore. The electrodes were platinum discs, of diameter about 0.65 cm., with short platinum wire leads from them fused into the bottom of narrow pyrex tubes. These narrow tubes were suspended one in each limb of the U tube and kept in their proper positions by means of vulcanite collars fitted to them. The electrodes were thus about 4 inches above the bend of the U-tube when in position, and before their insertion the solution used was always poured in to depth of 4½ inches above the bend. Connection was made to the electrodes by means of thick copper wires dipping into mercury at the foot of the narrow pyrex tubes. A large copper can containing water proved to be a suitable heating bath since the maximum temperature desired was only 50°C.

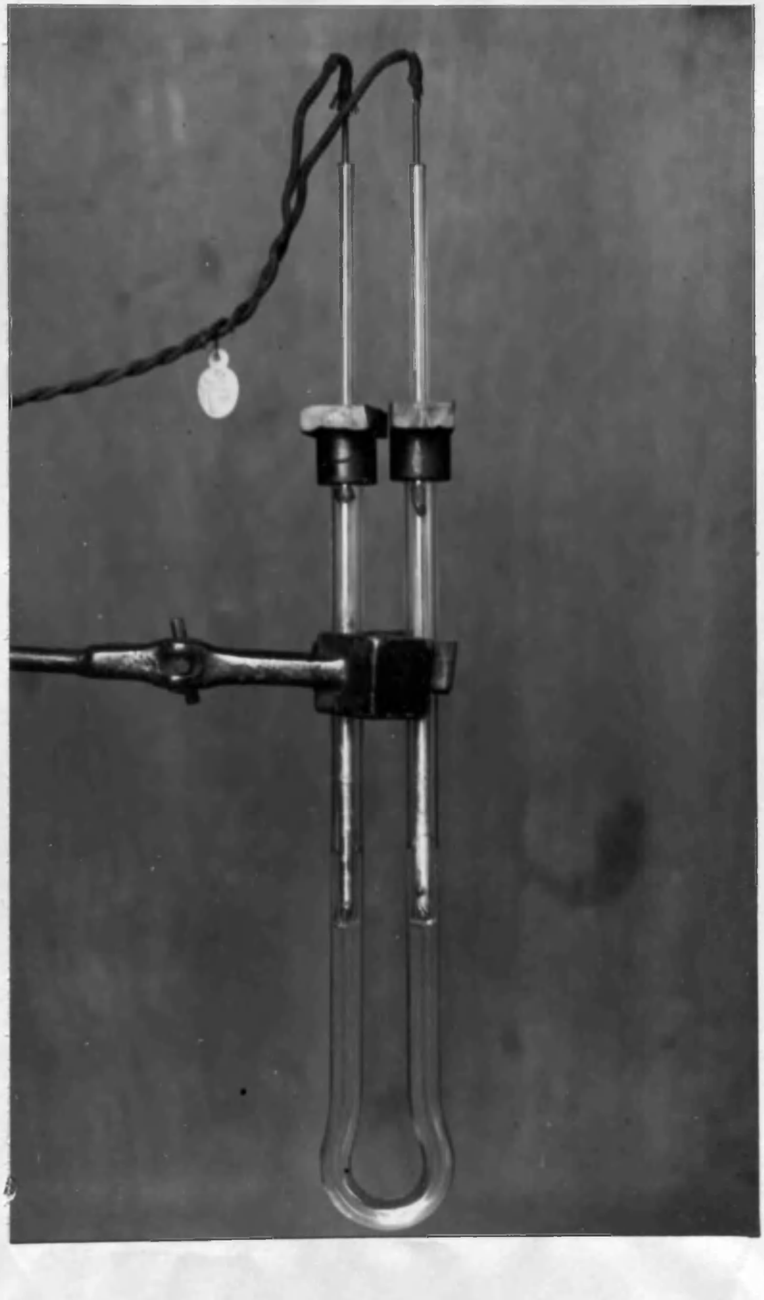


Fig. 13.

Special Conductivity Cell for H_2SO_4 Solutions.

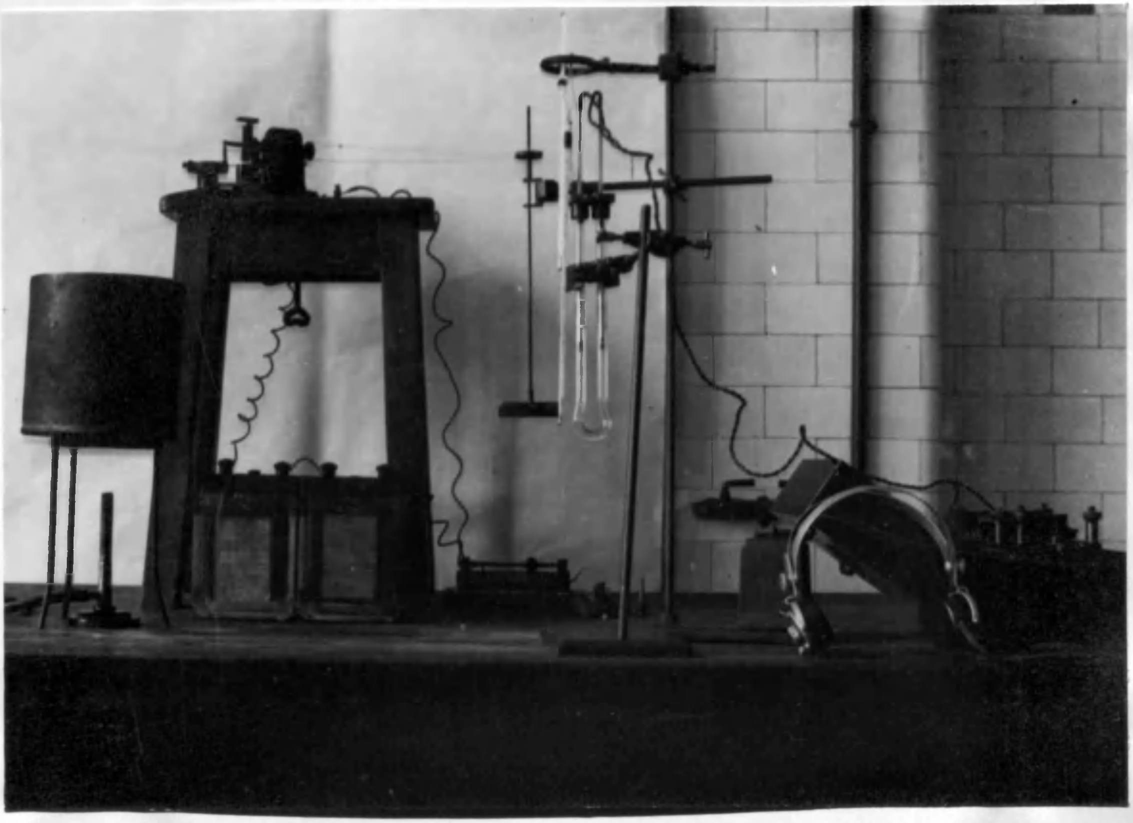


Fig. 14.

Complete Apparatus for Experiments with H_2SO_4 Solutions.

Procedure.

The cell-constant was measured by using a five per cent solution of sodium chloride, whose specific conductivity at 18°C, .0672 ohm $^{-1}$. cm^{-1}, is intermediate between those of the extremes of acid dealt with. A number of readings of resistance of the cell when filled with this solution were taken for temperatures in the neighbourhood of 18°C, and from a large scale graph of the reciprocal of resistance against temperature the mean value of 544 ohms was obtained for the resistance of the solution at 18°C. Thus the value obtained for the cell-constant was 36.5_6 cm^{-1}. At the end of the tests with the pure acid the cell was washed out and its constant redetermined, and the value obtained differed from the above by less than one in five hundred.

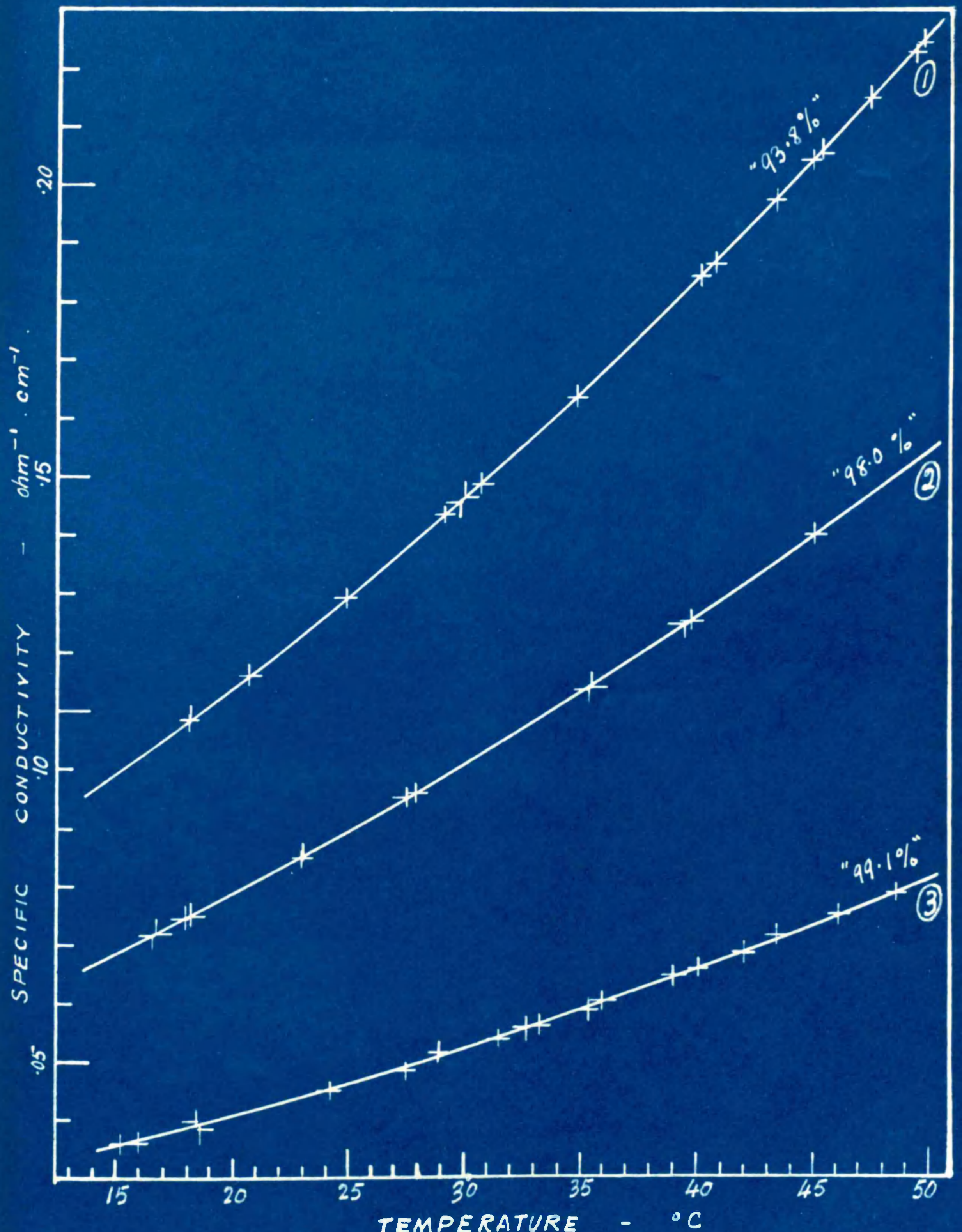
The experiments with the impure acid were carried out after an interval of several months, and in case the cell had altered by lying about for that time, the determination of the cell-constant was repeated. The value obtained was 36.1_5 cm^{-1}, and when it was again measured at the end of the tests it was still 36.1_5, and this was taken as the cell-constant for the experiments with the impure acid.

Since the thermometer used was not immersed in the solution under test but in the bath water, the heat was applied slowly, and several times between room temperature and 50°C, the temperature was steadied till the resistance obtained remained constant for several minutes. Again, by syphoning off some of the water and replacing it with cold water, the bath temperature was steadied and noted and the resistance of the cell measured at intervals on the way down.

In the case of the most concentrated solutions, e.g. samples (3) and (7), it was found at the end of a set of readings that the values of the conductivity at lower temperatures were slightly higher on the way down than on the way up. This was probably due to the hygroscopic nature of strong sulphuric acid causing it to absorb some moisture from the air and thus make the solution weaker and, in consequence, more conducting. Accordingly, when the results were plotted, the graphs in such cases was drawn between the two sets of points, and the final tabulated values of specific conductivity were read off from the mean graph.

This helps to explain why in these cases the strength of the acid as derived from the graph of Kohlrausch's values of specific conductivity at 18°C is rather less than the value obtained by titration. This applies specially to samples (6) and (7) as the titrations of the impure acids were done a considerable time before the conductivity experiments.

The conductivity-temperature curves are now given (reduced), and the tables of results derived from them giving the specific conductivity at temperatures 15, 20, ----- 50°C. In the case of the impure acids the 'Kohlrausch' values of



Reduced Reproduction of Graphs of SPECIFIC CONDUCTIVITY against TEMPERATURE for H_2SO_4 Solutions (pure).

Fig. 15.

FINAL TABLE OF RESULTS
for
PURE SULPHURIC ACID SOLUTIONS.

No. of Sample	1	2	3
Concentration (by titration) : %	$93{\cdot}8_0$	$97{\cdot}9_5$	$99{\cdot}1_0$
Specific Conductivity at 18°C (k_{18}) : $ohm^{-1}\cdot cm^{-1}$	0·1078	0·0744	0·0383
Concentration from Kohlrausch's Graph.	$93{\cdot}8_0$	$97{\cdot}6_5$	$99{\cdot}0_5$
k at 15°C	0·0991	0·0685	0·0353
k at 20°C	0·1138	0·0784	0·0405
k at 25°C	0·1295	0·0891	0·0462
k at 30°C	0·1463	0·1006	0·0522
k at 35°C	0·1644	0·1129	0·0587
k at 40°C	0·1837	0·1259	0·0656
k at 45°C	0·2042	0·1396	0·0730
k at 50°C	0·2254	0·1539	0·0807
Ratio $k_{30} : k_{18}$	1·36	1·35	$1{\cdot}36_5$
Ratio $k_{45} : k_{18}$	1·90	1·88	1·91

Reduced Reproduction of Graphs of Specific Conductivity agt. Temperature for H_2SO_4 (impure).

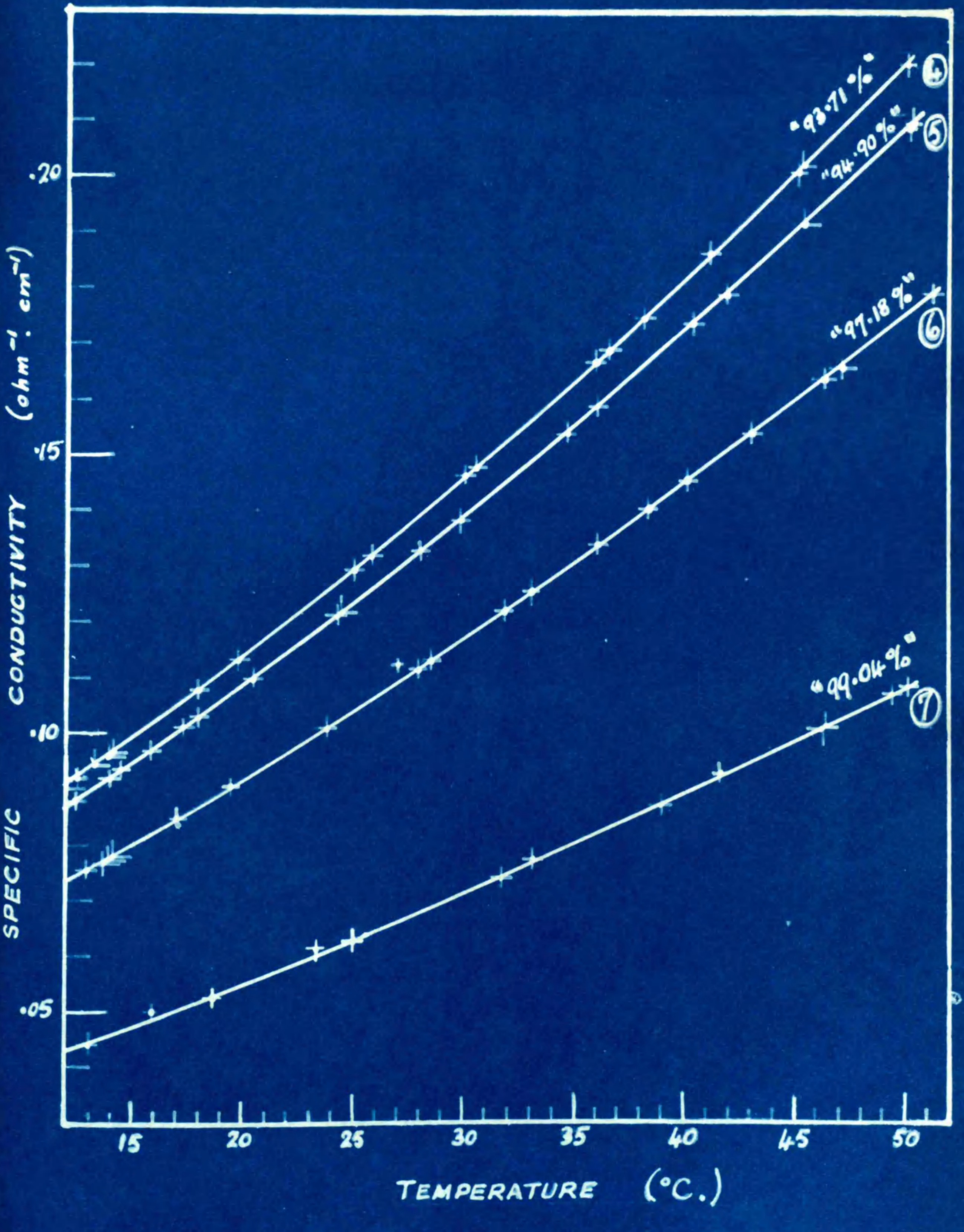


Fig. 16.

FINAL TABLE OF RESULTS

for

COMMERCIAL OIL OF VITRIOL SOLUTIONS. (IMPURE).

No. of Sample	4	5	6	7
Concentration (by titration) : %	93·71	94·90	97·18	99·04
Specific Conductivity at 18°C (k_{18}) : ohm^{-1} cm^{-1}	0·1076	0·1027	0·0866	0·0521
Concentration from Kohlrausch's Graph	($93{\cdot}8_5$)	($94{\cdot}9_5$)	(96·7)	(98·65)
k at 15°C	0·0989	0·0947	0·0798	0·0477
k at 20°C	0·1135	0·1083	0·0915	0·0550
k at 25°C	0·1291	0·1229	0·1038	0·0628
k at 30°C	0·1457	0·1385	0·1168	0·0711
k at 35°C	0·1633	0·1551	0·1305	0·0798
k at 40°C	0·1817	0·1725	0·1449	0·0889
k at 45°C	0·2008	0·1904	0·1598	0·0983
k at 50°C	0·2205	0·2087	0·1751	0·1079
Ratio $k_{30} : k_{18}$	$1{\cdot}35_5$	1·35	1·35	$1{\cdot}36_5$
Ratio $k_{45} : k_{18}$	1·87	1·86	1·85	1·89

concentration are given in brackets, as these really apply to pure acids having the same specific conductivity at 18°C.

Comment on the Final Table of Results.

When the conductivity-temperature graphs are examined, it is seen that they all consist of flat curves, concave upwards, indicating that the range of temperature dealt with is well below the maximum conductivity point. The curves are not flat enough for the temperature-coefficient at 18°C to give an accurate value of the specific conductivity at a temperature much higher, say at 45°C, but the tables show that the mean temperature-coefficient for the range 18°C to 45°C is almost the same in each case. Thus the conductivity at 18°C multiplied by 1.875 gives the conductivity at 45° with an error of less than two per cent, and for 30°C the corresponding factor is 1.355 with an error of less than one per cent.

From the point of view of the temperature-compensator of a 'salinometer', this is fortunate, as that part of the mechanism has to provide the same compensation for the same change in temperature no matter what strength of solution is present and an accuracy of 1 in 50 is as much as can be hoped for.

Acknowledgments.

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It should be noted that much of the above paper has already been published in the Journal of The Royal Technical College, Glasgow, January 1931, P.395.