AN INVESTIGATION OF THE EQUIVALENT CIRCUIT OF A CONDUCTIVITY CELL

A Thesis submitted in fulfilment of the
requirements of Rhodes University
for the degree of Master of Science

By

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Rhodes University,
Grahamstown,
1953.

ACKNOWLEDGEMENTS.

Thanks are due to Professor W. F. Barker, B.Sc., Ph.D., F.R.I.C. for a grant from the Chemistry Department's Research Fund, without which this work would not have been possible, and for his encouragement and interest.

Also to Dr. J. A. Gledhill for his constant interest and help.

Also to Professor E. Newbery for his kindness in lending a copy of the manuscript of his paper on "Residual Currents".

And to many others for help in many ways.

SUMMARY.

(i) A linear circuit is shown not to explain the behaviour of a conductivity cell towards a long rectangular pulse of amplitude less than the decomposition potential of the solution in the cell.

(ii) It is shown that the flow of current through the cell is governed by diffusion to the electrode. The diffusion current expression is the familiar one used in the case of diffusion up to a plane micro-electrode, except that in this case the concentration in the layer next to the electrode is not zero, but only somewhat less than the bulk concentration.

(iii) Except during a short initial period (less than 10 seconds), the resistance of the electrolytic cell varies directly with the square root of the time for which an e.m.f. (less than the decomposition potential) is applied to the cell, and inversely with the concentration difference between the electrode surface and the bulk of the solution.

CONTENTS.

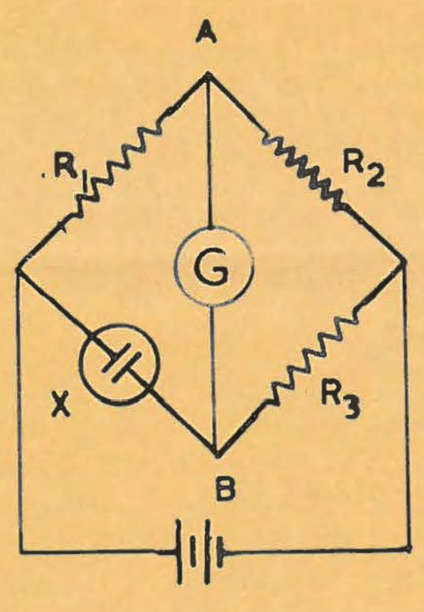

FIG. 1

I. INTRODUCTION.

In the measurement of conductivities of electrolytic solutions it is customary to measure the resistance of the solution with a Wheatstone bridge (Fig. 1). The electrolyte, contained in a cell with two platinum electrodes, forms one arm of the bridge. If direct current (d.c.) is used, the condition for balance (i.e. no current flowing between A and B) is

$$\frac{R_1}{R_2} = \frac{X}{R_3}$$

The use of d.c., however, causes electrolytic action resulting in the formation of gas films at the electrodes and concentration changes due to transport phenomena. This method is therefore not suited for the measurement of small resistances. Even in the case of large resistances, or if a high degree of precision is required, elaborate precautions must be taken to minimise polarisation and thus obtain satisfactory results (1).

Kohlrausch, Wien and others investigated the use of alternating current (a.c.) to overcome these polarisation effects at the electrodes. They obtained such an improvement in accuracy that a.c. has since been used almost exclusively in electrolytic conductivity measurements. The circuit is the same as that used when measuring with d.c., except that earphones replace the galvanometer as null point indicator and an oscillator is substituted for the battery. According to the theory of a.c. networks, the equation for balance is

$$\frac{Z_1}{Z_2} = \frac{Z_3}{Z_4},$$

the Z's representing impedances containing resistive and reactive components. In order to obtain an expression for the resistance of the solution in the cell it is necessary to examine the electrical characteristics of the cell and other arms of the bridge.

It is found that the measured resistance of the cell is greater than the actual resistance of the electrolyte between the electrodes by an amount depending on the frequency of the a.c. used (2,3). Within limits, the higher the frequency the more nearly does the measured resistance approach the actual value. This is explained by considering the electrolyte in the layers adjacent to the electrodes separately from the remaining bulk of the solution. In the layers the concentration changes throughout the current cycle, and the longer the duration of the cycle (i.e. the lower the frequency) the greater will be the change. Now the measured resistance depends on the change of concentration which has occurred. With increasing frequency this change will decrease and the measured resistance will approach the true value. Jones and Christian (3), working empirically, found a relation between the apparent series resistance R_4 of the cell and the true resistance r_t of the electrolyte

$$\begin{aligned} R_4 &= r_t + Kp^{-\frac{1}{2}} \\ &= r_t + \Delta r \ , \end{aligned}$$

where $p = 2\pi$ x frequency and K is a constant. A condenser effect is shown at the electrodes of a conductance cell and for the purpose of a.c. bridge measurements the cell may therefore, as a first approximation, be considered to consist of a resistance and capacity in series (4). The usual technique in conductivity measurements is to measure the resistance at several frequencies and plot these values against $p^{-\frac{1}{2}}$. Linear extrapolation to infinite frequency gives a value ~~for~~

for the true resistance r_t of the electrolyte (3).

Considering the cell to behave like a simple series resistance and capacitance, an expression may be derived for R_4 which is actually less than r_t. This is contrary to the experimentally observed behaviour. Jones and Christian found that the introduction of the "polarisation resistance" term Δr produces an equivalent circuit in which the capacity is shunted by a leak of high resistance. A second approximation to the equivalent circuit of the cell is therefore a resistance and a leaky capacity in series. Factors affecting the value of the capacity are the size and condition of the electrode surface, the nature of the electrolyte being measured and the reactions which may occur at the electrodes.

Measurements over a wide range of frequencies are required to determine the additional elements which make the simulating network more precise. Simulating networks were originally derived from steady state a.c. measurements. In order to test whether these would apply for the transient currents which flow immediately after switching the source of a.c. to the cell, Acree and his co-workers (2) made various oscillograph tests. They took oscillograms to show the waveforms of the potential across the cells and the current through them for a number of cycles after switching on the source of a.c. This was carried out at different points on the potential wave-form. These oscillograms show that the simulating network obtained from steady state relations serves equally well for the transient state. The precision was, however, only of the order of 5 per cent. They also suggested as a close approximation a high resistance leak in parallel with a capacity, which is in series with a resistance. They found that the equivalent capacity was independent of frequency provided that the e.m.f. was less than the decomposition potential. At higher e.m.f.'s a shift occurred in the current peaks and the current through the cell no longer had a sinusoidal form, indicating that the cell ceased to have the properties of a leaky condenser in series with a resistance.

In the present work the response of the cell to square pulses is investigated. As has been pointed out, the accurate representation of the simulating network requires measurements over a large range of a.c. frequencies. Applying a square pulse to the electrolytic cell is equivalent to applying all frequencies from zero upwards, since by Fourier's theorem the pulse may be analysed into an infinite number of sine waves of all frequencies from 0 to ∞. An advantage of the pulse method is that the responses of equivalent series and parallel R-C combinations to transients differ, whereas to a given a.c. frequency equivalent series and parallel R-C combinations respond in an identical manner (5).

Since experimental observation indicated that, on application of an e.m.f. of the order of 1 volt, the current through a conductance cell fell to $\frac{1}{e}$ of it's initial value in a length of time of the order of 3 seconds, most information of the cell characteristics will be obtained by using pulses of length about 10 seconds. The best way to observe the effect of such a pulse would appear to be by using an oscilloscope with a slow sweep. This apparatus is however highly specialised and unobtainable in this department. The next best procedure appeared to be to measure the current response with a short period galvanometer. Since the periods of the galvanometers used were less than 2 seconds, it was expected that useful information about the cell characteristics could be obtained in this manner.

In this work it is attempted to fit linear circuits, containing a resistance in series with one, two and three capacities with leaks, to the experimental data. A circuit containing two capacities - one with leak and one without leak - is also tried. The Laplace transformation (6) is used to calculate the current responses of these circuits to a square pulse. In each case the expression for the current is found to be the sum of a number of exponential terms. This is fitted to the experimental data as described in Appendix I. It is shown that no linear circuit adequately explains the behaviour of the cell.

It is then assumed that the current which flows is due to diffusion of ions to the electrodes. Fick's laws of diffusion are used to derive an equation relating current to time. This equation fits the experimental curves well, which is taken to indicate that the current flow is indeed controlled by diffusion. Using this expression an equivalent circuit containing a constant resistance and a variable resistance in series, is derived. This circuit, in which the total resistance varies directly with the square root of the time and with the voltage, explains the experimental curves adequately.

Scale : 1" = 2"

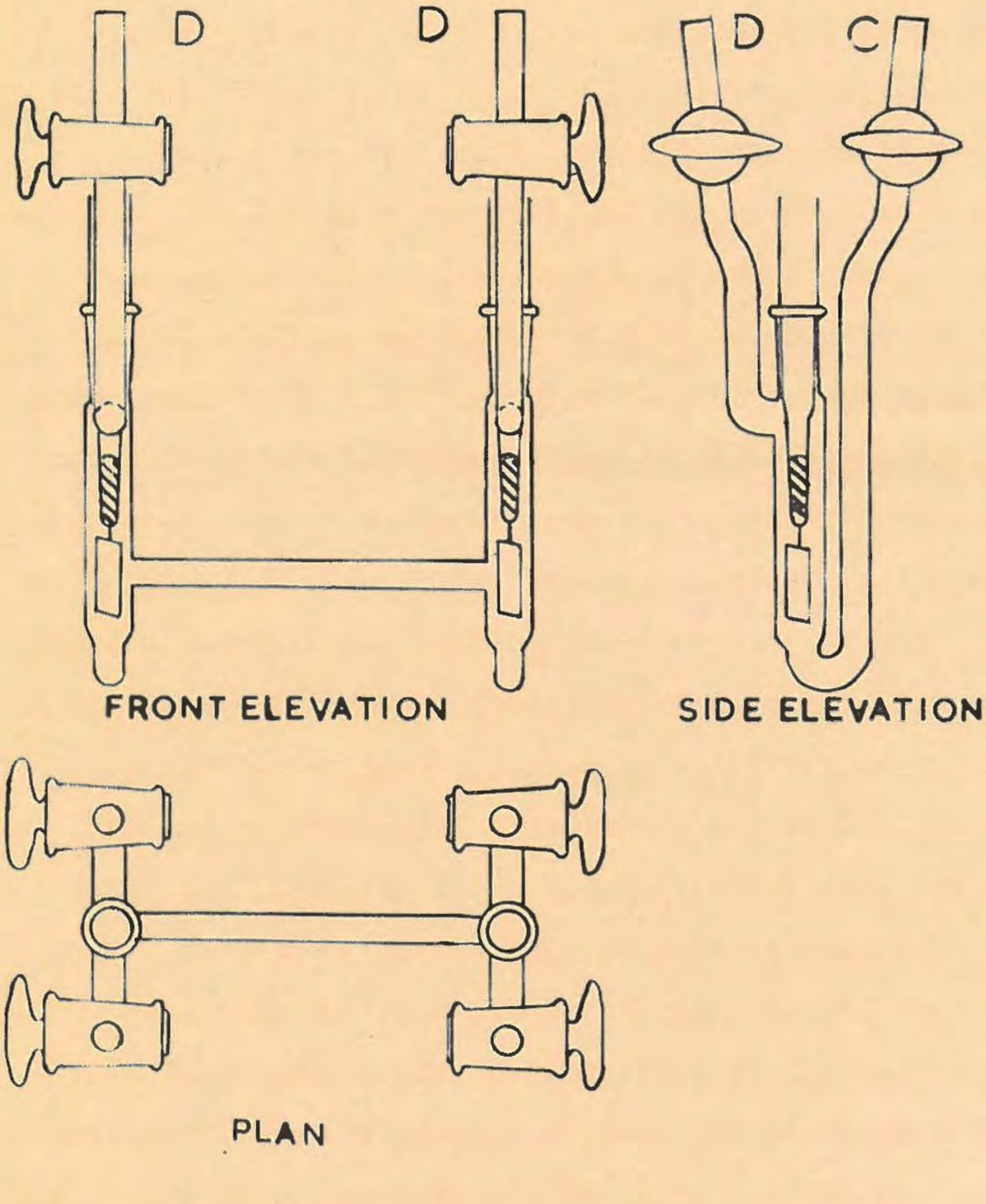

FIG. 2a

II. Apparatus and Technique.

(i) The Cell and Electrodes.

The cell (Fig. 2a) is made of Pyrex glass and is so designed that the electrodes may be removed for cleaning purposes. The electrodes are strips of polished platinum, 2cm x ½cm and 0.4mm thick, sealed into the ends of glass tubes by means of a blue glass seal. The tubes fit into the cell through standard taper ground glass joints. The solution is introduced into the cell through either of the capillary tubes C. Air displaced by the solution entering the cell escapes through the tubes D. Taps are provided at the ends of these tubes so that the solution in the cell may be kept out or contact with the air. Electrical contact to the electrodes is made by means of amalgamated copper wires dipping into mercury contained in the tubes to which the electrodes are sealed.

The cell is so designed that the distance between the electrodes is large (10cm), thus diminishing the effect of diffusion of solution from one electrode to the other. On application of a pulse of 2 volts to the cell containing 0.01N KCl solution, the effect of diffusion is observed only after 50 minutes, which is much longer than the duration of the pulse used. By making the distance between the electrodes large, the electrostatic capacity between the electrodes is made negligible, being of the order of 0.5pFd.

Since the condition of the electrode surface is probably the most important single factor influencing the reproducibility of results, much attention was paid to the initial polishing of electrodes and subsequent cleaning between runs. Before use the electrodes were polished successively with fine emery paper, Brasso

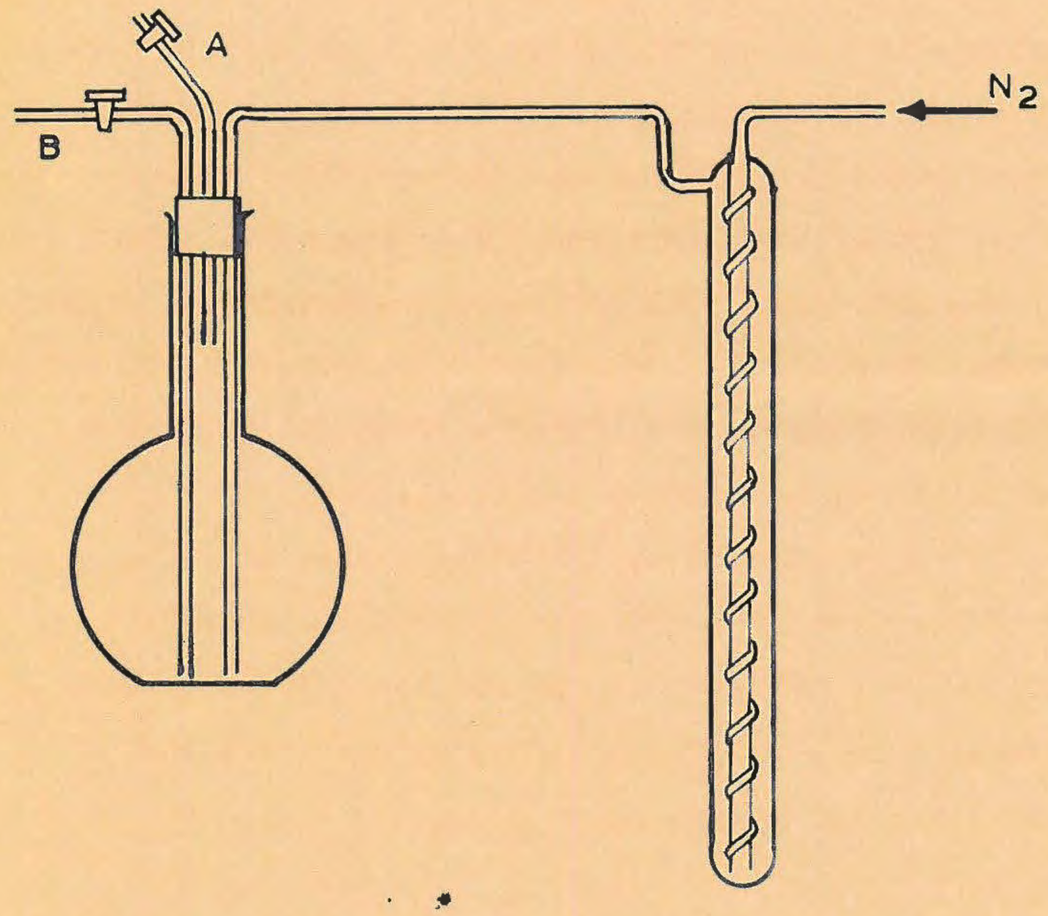

FIG. 2b

and rouge (red ferric oxide). This produced a highly polished surface on which no scratches could be observed with the naked eye. The electrodes were also cleaned after every run. At first it was attempted to restore the electrodes to their original condition by heating to redness in a Bunsen flame. This, however altered the condition of the surface of the platinum, as shown by the formation of etched markings. It was later found that equally reproducible results were obtainable merely by boiling the electrodes in distilled water for 15 to 30 minutes. This treatment did not alter visibly the surface of the electrodes. The most satisfactory reproducibility was obtained by re-polishing with rouge after every run. With this procedure, results with a reproducibility of 15 to 20 per cent were obtained. Great care was taken in handling the electrodes. They were never allowed to stand in the electrolytic solution for longer than necessary and when not in use were kept immersed in distilled water. Two pairs of electrodes were used and yielded results which were the same within the experimental error.

(ii) The Saturator and Storage Flask.

Since the presence of air in the solution produced results which differed appreciably from those obtained using de-aerated solutions, it was necessary to bubble nitrogen through to remove oxygen and carbon dioxide. This was effected by passing dry nitrogen from a gas cylinder through a saturator and thence through the solution (contained in a flat-bottomed 1½ l. flask) for approximately 3 hours (Fig. 2b). It is necessary to saturate the gas since the passage of dry nitrogen through the solution would remove water and

and hence concentrate the solution. In order to saturate the nitrogen at the vapour pressure of the solution, the same solution was used in the saturator as in the flask. The flask was fitted with two outlet tubes A and B, of which B reached to the bottom of the flask. A constant slow stream of nitrogen was allowed to bubble through the solution.

Since it was not intended to make absolute conductivity measurements, the use of A.R. quality KCl was adequate in preparing the solutions of concentrations 0.1 and 0.01N which were used in the cell. Before transferring the solution to the cell, a current of nitrogen was blown through the latter in order to remove the air present. The cell was filled with solution by connecting tube B of the flask to one of the inlet tubes C of the cell, closing the tap on A and allowing the nitrogen pressure which built up in the flask to force the solution up through B into the cell. The flask, saturator and cell were immersed in the thermostat.

(iii) The Thermostat.

A thermostat of capacity about 30 gallons was used. With a 250 watt heater and toluene thermoregulator a constant temperature of 25°C was maintained to within 0.05°. All current readings in this work were taken at this temperature.

(iv) The Galvanometers.

Two instruments were used. The first was a Baird and Tatlock galvanometer (catalogue no. G1026/372) of resistance 608 ohms, period 1.1 seconds and sensitivity 20mm per μAmp at 1 metre. The zero shift in this instrument was appreciable, having a magnitude of up to 10mm after full scale deflection. It was found to be dependent on a number of factors: (a) the size of the deflection, (b) the length of time for which the coil was deflected and (c) the direction in which the deflection occurred. The effect of the first two factors was minimised by passing a current through the galvanometer before the run, sufficient to produce a deflection of about 300mm for 15 minutes, and then re-adjusting the zero. The effect of the third factor was eliminated by deflecting always in the same direction.

Since the sensitivity of the galvanometer was found to increase by 0.1 per cent for every 1°C rise in temperature, it was kept at a constant temperature in a Celotex box (50 x 40 x 30 cm). A 75 watt heater and a Sunvic bi-metallic spiral regulator were used to maintain a temperature of 25°C constant to within 1°C.

For the second part of this work a Tinsley galvanometer of sensitivity 167mm per μAmp at 1 metre, became available. It had a stable zero and low resistance (10.1 ohms). These factors together its greater sensitivity made it far more suitable. Nevertheless the same precautions were observed as with the Baird and Tatlock galvanometer.

The galvanometers were calibrated by passing measured currents through the coils. A shunt of total resistance 10,000 ohms was used with the galvanometer and the calibration made for each shunt range. The current passed was calculated by measuring, with a Leeds Northrup potentiometer, the potential drop caused across a 5,000 or 10,000 ohm resistance. Since plotting deflection against current required a cumbersome graph if the required accuracy was to be obtained, the calibration

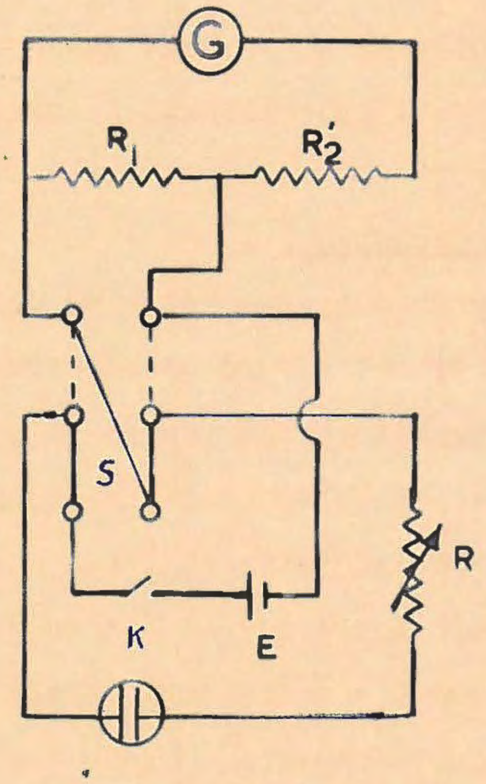

FIG. 2c

graphs were drawn in the following manner : deviations from the linear relation $i = \frac{\delta}{n}$ were plotted against the deflection δ, where n is an integer chosen to give the best fit. For example, a current of 23.58 μAmps produced a deflection of 497.6mm. Dividing the deflection by 20 gives an approximate value of 24.58 μAmps for the current. The difference, 1.30 μAmps, between the true and the approximate current and the deflection 497.6mm are used to plot one of the points on the calibration curve. The same value of n, 20, was naturally used for all other points on this calibration curve.

(v) The Pulse Circuit and Technique.

A square pulse is produced by switching an e.m.f. E on to the electrodes at time t = 0 and short-circuiting the cell at time $t = \tau$, where τ is the length of pulse required. A 2 volt lead accumulator used in conjunction with a potential divider of total resistance 30 ohms provides pulses of amplitudes E from 0.1 to 2 volts (Fig. 2c). After time $t = \tau$ the cell is allowed to discharge through the galvanometer.* Since the direction in which the current now flows is opposite to that in which it flowed on charging, a switch is arranged to pass the current through the galvanometer in the same direction. $\frac{R_1}{R_1 + R_2}$ is the nominal value of the shunt ratio used having values 1, 1/3, 1/10, 1/30, 1/100, 1/300, 1/1000. But since the resistance R_G

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* The terms "charge" and "discharge" are used to describe the current response of the cell. This assumes the cell to behave like a condenser or system of condensers which on applying a certain e.m.f. becomes charged and on short-circuiting a discharge takes place.

of the galvanometer is in series with R_2' The true value of the shunt ratio is $\frac{R_1}{R_1 + R_2}$, where $R_2 = R_2' + R_G$.

Since a different resistance is brought into the circuit each time the shunt ratio is changed, it is necessary to alter R by a corresponding amount, so that the total resistance or the circuit is kept constant at 10,000 ohms, excluding the resistance of the cell.

While the electrodes were left to stand in the KCl solution in the cell for 15 minutes in order to attain temperature equilibrium, precautions were taken to minimise the zero shift of the galvanometer and the lead accumulator was allowed to discharge through the potential divider. This second precaution was necessary since it usually took 5 to 10 minutes before the e.m.f. of the accumulator became steady to within 0.01 volt. The potential divider was then adjusted to yield the desired e.m.f., as measured on a Leeds-Northrup potentiometer.

At time t = 0 switch K was closed and the stop watch started. Current readings were then taken, the first at 3 seconds. Since the decay was approximately exponential it was necessary to take readings at short intervals at the beginning of the run, becoming less frequent as the current decreased. The input voltage was checked after about 900 seconds. At the end of the pulse the switch S was thrown over and current readings taken on discharge in the same way as for charge. At the conclusion of the run the electrodes were removed, rinsed and placed in distilled water. Since two pairs of electrodes were used, one pair could be cleaned while the other was in use.

The response of the cell was measured with input voltages over the range 0.1 to 2 volts for the 0.01N

KCl solution (using the Baird and Tatlock galvanometer) and over the range 0.1 to 0.75 volts for the 0.1N KCl solution (using the Tinsley galvanometer).

(vi) The Conductivity Bridge.

A Pye Wheatstone bridge with variable ratio arms was used to measure the resistance of the cell. A 1000 c.p.s. oscillator was used as the source of e.m.f. and earphones used as the null point indicator. The resistance of the cell containing 0.01N KCl was found to be 27,000 ohms, and 3000 ohms when containing 0.1N KCl at 25°C.

III. Results.

A specimen plot (Graph 1) of current (i_t) against time (t) for a 1000 second pulse shows the following general characteristics:

(i) The current falls very rapidly for the first few seconds after the pulse is applied. The first recorded current after 3 or 5 seconds generally has a value of between 1/2 and 1/10 of the value (i_0), calculated for the current at t = 0. i_0 is calculated from the relation $i_0 = \frac{E}{R}$, where E is the applied voltage and R is the resistance of the solution when measured with a.c. (henceforth referred to as the a.c. measured resistance). Since there is no deposited layer of atoms at the electrode surface until after the pulse is applied, it is unlikely that the resistance at t = 0 will differ from the a.c. measured value.

(ii) The i-t curve flattens out very much at larger t, so that the plot at first sight appears to be exponential. This is, however, not the case since the plot of log i against t (Graph 2) is not linear. The current decay after 500 seconds is approximately exponential, but the rate of drop before 500 seconds is too fast.

(iii) After 1000 seconds, when the e.m.f. becomes zero at the end of the pulse, a discharge of current in the opposite direction occurs. At 3 or 5 seconds after the discharge is commenced, the current is slightly less than its corresponding value on charging.

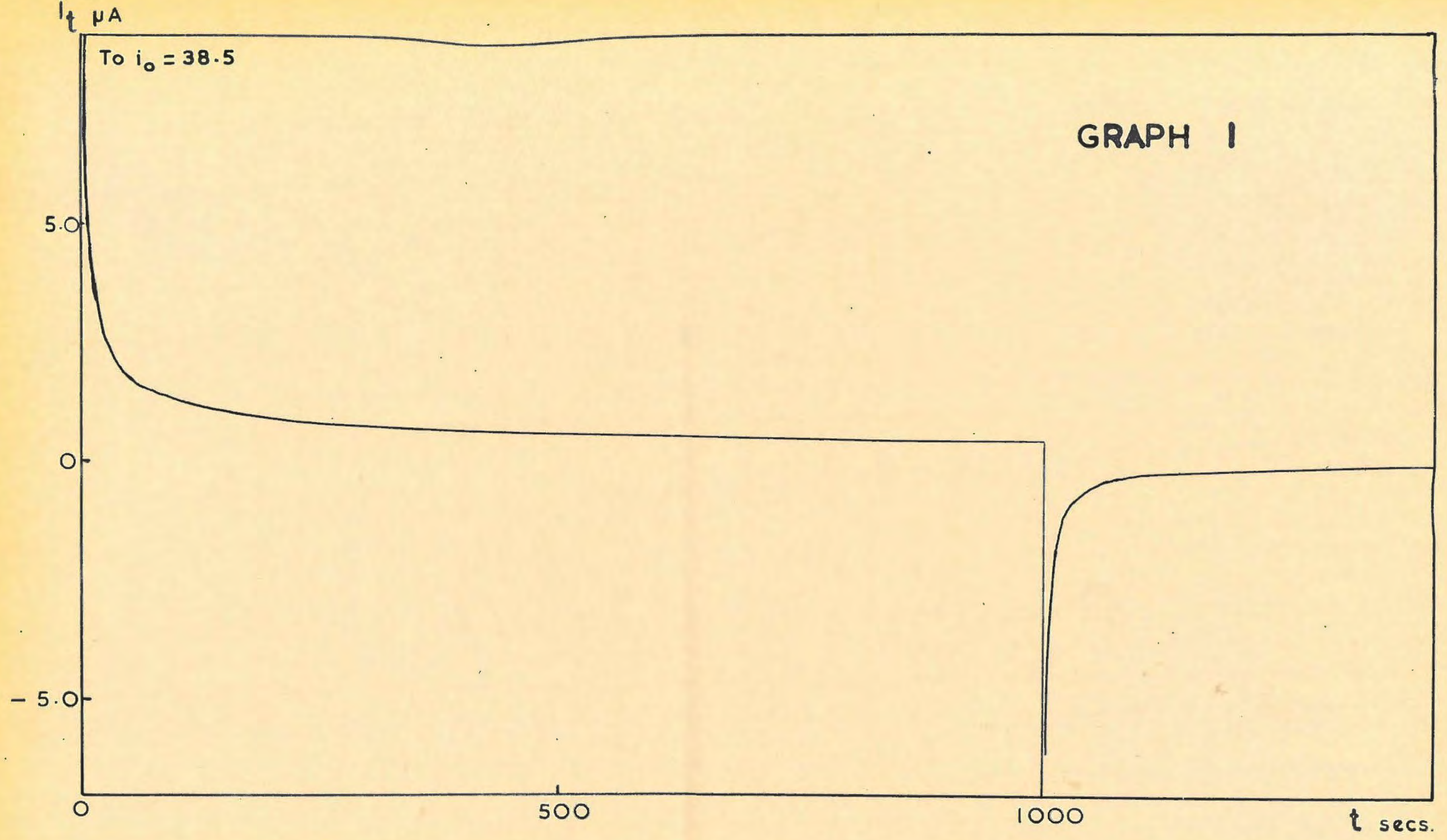
(iv) The discharging current is always numerically less than the charging current at the corresponding time. The area under the curve above the time axis is always less than that below, indicating that a large part of the charge passed into the cell is apparently lost, i.e. does not flow out again during the discharge.

This is in accordance with ovservations made by Newbery (7) in his investigation of residual currents.

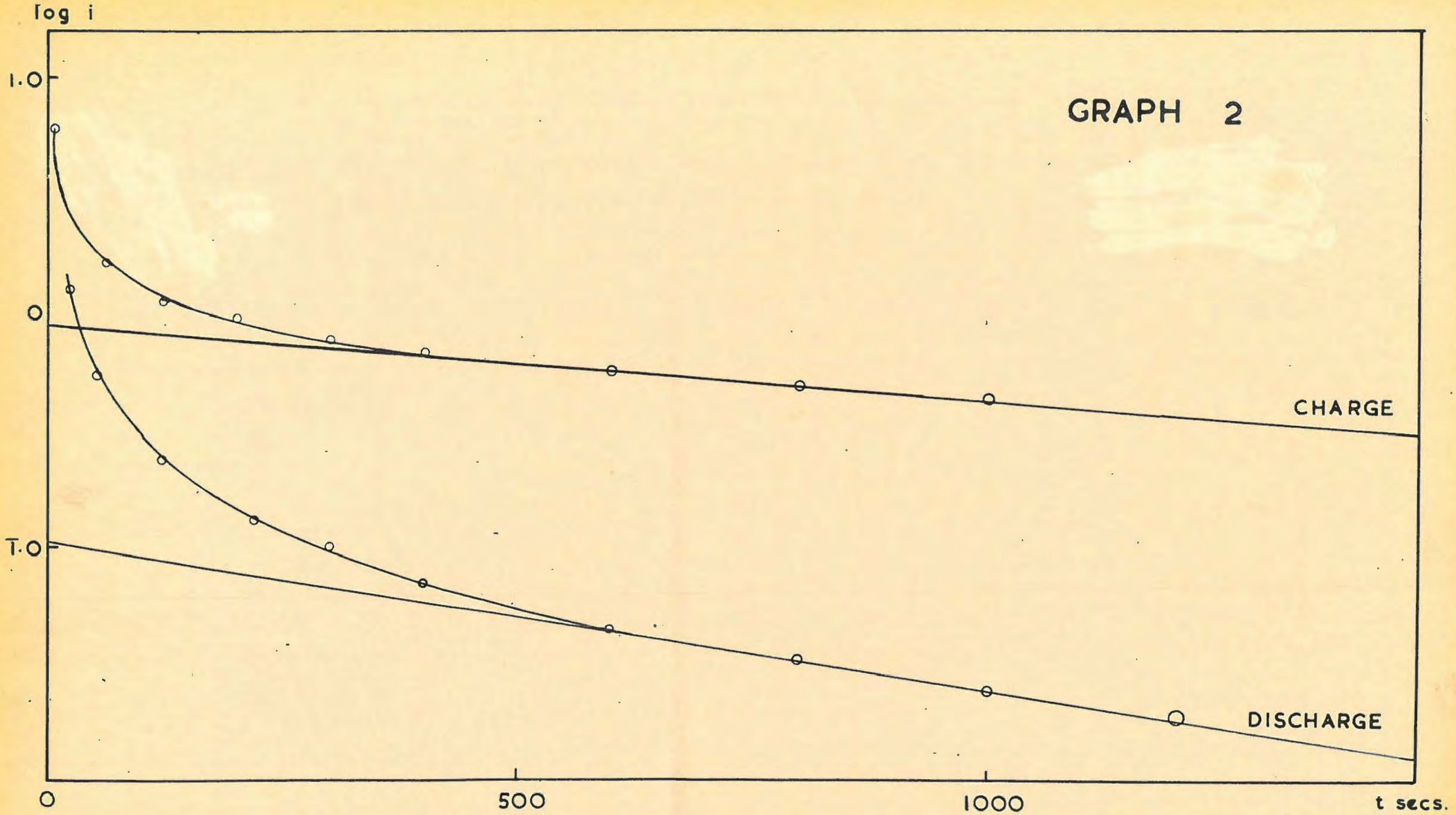
(v) The general shape of the curve is the same as the current response curve to a square pulse of a series resistance and capacity, if the pulse length is of the same order as the time constant of the circuit (5).

The usual convention of plotting points as circles, the size of which indicate the probable error involved, is used throughout this work. This is however inconvenient in the case of large errors. The error is then indicated by a straight line.

From the large number of i-t curves available at each value of E the three curves which appeared to be nearest the mean were chosen, and the mean current at each time calculated from these. In this way a fictitious i-t curve was obtained which was taken to represent the mean behaviour of the cell at a particular value of E. For future reference the data for discharge at different values of E are included (Appendix V).



GRAPH I



GRAPH 2

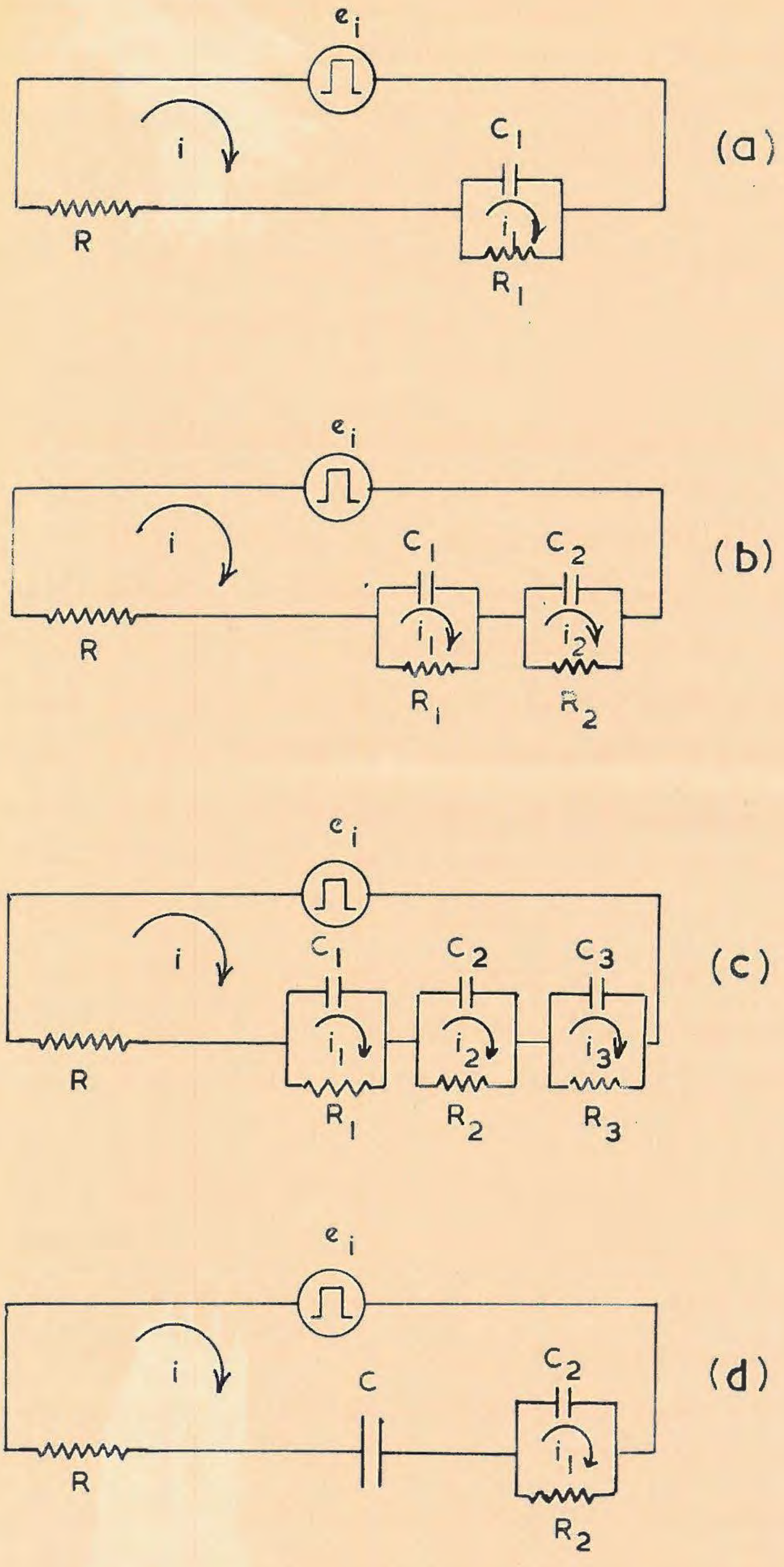


FIG. 3

Note: In order to conform to the Kirchhoff equations given in Appendix I the small loops in this figure should be inverted so that R_1, R_2 and R_3 are above and C_1, C_2 and C_3 below.

IV. Attempts to fit various linear circuits to the data.

A linear circuit is one in which all the elements (in this case resistances and capacities) behave in a manner which can be described by a first degree equation.

The mathematical treatment of the responses of the following four circuits is given in Appendix I.

(i) Series resistance and capacity with leak (Fig. 3a).

When a potential difference less than the decomposition potential is applied to an aqueous solution of an electrolyte, hydrogen, presumably as a monomolecular film, will be deposited on the surface of the cathode. This film effectively insulates the electrode from the electrolyte, forming a condenser of capacity about 6 μFd per sq. cm. (7). Some H atoms diffuse out of this film either into the solution or into the platinum of the electrode. In order to replace these, some H ions must diffuse from the bulk of the solution up to the film and lose their charge. Consequently the condenser will behave as if it has a high resistance leak across it.

The first circuit investigated was therefore a simple series resistance and "leaky" capacity. The series resistance R is the a.c. measured resistance of the solution plus the circuit resistance. This is also the circuit suggested as a first approximation by Acree and his co-workers(2).

In order to test this circuit on the available data it is necessary to assume that the current through the cell falls to a definite value (i_∞)after infinite time, and choose a value for this current. That the current does fall to a definite value has been shown by Scarpa and Denina in their paper on the electrical resistance of the electrode-electrolyte double layer (8). In measuring the resistance of an H_2SO_4 solution they found that the current became steady after 50 days, although with small current densities periods of pseudo-stability were observed.

If a linear circuit fits the conductivity cell, Ohm's law will be obeyed and i_∞ will be given by $\frac{E}{R + R'}$ where R' represents the sum of all the resistance leaks across condensers present. In practice it was found that only with small E (0.1 volt)is the current nearly steady at t = 1000 seconds. From these figures for $i_\infty (=i_{1000})$ at 0.1 volts, i_∞ can be found for other values of E. These values of i_∞ are henceforth referred to as the experimental values, and are included in the following four tables for comparison with the calculated figures.

From Table 1 it is seen that for 0.01N KCl solution R_1 varies between 900 and 23,000 ohms and C_1 is approximately constant at 0.1 - 0.3 Fd. over the e.m.f. range 0.1 to 0.75 volts. For 0.1N solution R_1 is much smaller and increases from 52 to 390 ohms, whereas C_1 has very large values decreasing from 18.6 to 3.1 Fd. Even with the largest values of R_1, $\frac{E}{R + R_1}$ is never sufficiently small to account for the magnitude of i_∞, being approximately 60 times too large in the case of 0.01N KCl and 750 times too large for 0.1N solution. The value 0.3 Fd. is much larger than would be expected for a monomolecular film of hydrogen at the surface

of the cathode. This is therefore not a good equivalent circuit for the cell.

Table 1. Ref. Fig. 3a.

Table 9.

E	R_1 ohms	C_1 Fd.	i_∞ calcd. μAmp.	i_∞ exptl. μAmp.
(a) 0.01N KCl.				
0.10	905	0.300	2.59	0.04
0.20	1,130	0.267	5.15	0.08
0.30	1,360	0.267	7.68	0.12
0.40	1,890	0.224	10.10	0.16
0.50	2,980	0.131	12.30	0.20
0.75	3,020	0.218	18.41	0.30
1.00	3,390	0.388	24.3	0.40
1.25	6,340	0.500	28.4	0.50
1.50	10,100	0.390	31.4	0.60
1.80	14,100	0.141	34.8	0.72
2.00	23,100	0.608	32.9	0.80
(b) 0.1N KCl.				
0.10	52	18.6	7.66	0.010
0.20	65	19.7	15.30	0.020
0.30	130	10.5	22.8	0.030
0.40	208	7.3	30.2	0.040
0.50	260	5.2	37.7	0.050
0.75	390	3.1	56.0	0.075

(ii) Series resistance and two capacities with leaks (Fig. 3b).

It was thought that since the previous circuit takes into account the condenser effect at only one electrode, this may be a source of error. Possibly a similar gas film is formed at the anode, which acts as a high capacity condenser. Newbery (7) investigated residual currents by a series of experiments in which the current passing between a pair of unattackable electrodes was measured when the applied e.m.f. was changed by regular small steps. As a result of these he came to the conclusion that current passed is used reversibly (a) in generating gas at one or both electrodes at low pressure thus forming metal:gas film:electrolyte condensers; (b) in charging these condensers and (c) to generate more gas to replace that lost by diffusion into the electrolyte and into the electrodes.

A second and, perhaps, more probable circuit is therefore that shown in Fig. 3b. The introduction of a second resistance and capacity into the equivalent circuit is an improvement since this circuit fits the data above 100 seconds. Table 2 gives the results of the mathematical treatment (Appendix I) of this circuit and shows that the second capacity is smaller than the first. For 0.01N KCl R_2 is of the order of 3,000 ohms and C_2 is about 0.03 Fd. For 0.1N KCl R_2 is slightly greater than R_1 and C_2 is about one tenth of C_1 being of the order of 0.5 Fd. This circuit however still does not adequately represent the behaviour of the cell during the first 100 seconds of the application of the pulse and the calculated figures for i_∞ are still much too great.

Table 2. Ref. Fig. 3b.

Table 10.

E	R_1 ohms	R_2 ohms	C_1 Fd.	C_2 Fd.	i_∞ calcd. μ Amp.	i_∞ exptl. μ Amp.
(a) 0.01N KCl.						
0.10	710	2,200	0.38	0.007	2.46	0.04
0.20	1,400	1,500	0.22	0.034	4.92	0.08
0.30	1,500	1,700	0.25	0.041	7.35	0.12
0.40	2,600	1,550	0.27	0.021	9.55	0.16
0.50	3,250	3,400	0.11	0.021	11.40	0.20
0.75	3,600	6,100	0.18	0.014	15.82	0.30
1.00	4,550	7,900	0.29	0.011	19.92	0.40
1.25	8,740	13,300	0.36	0.048	21.0	0.50
1.50	11,300	3,600	0.35	0.044	28.5	0.60
1.80	16,200	5,000	0.12	0.034	30.6	0.72
2.00	24,600	2,600	0.37	0.059	30.8	0.80
(b) 0.01N KCl.						
0.10	51	210	19	0.55	7.55	0.010
0.20	104	286	12	0.42	14.95	0.020
0.30	198	243	6.9	0.52	22.3	0.030
0.40	261	259	5.8	0.45	29.6	0.040
0.50	312	445	4.3	0.29	36.4	0.050
0.75	433	559	2.9	0.25	54.5	0.075

(iii) Series resistance and three capacities with leaks (Fig. 3c).

At the electrode at which the monatomic layer of hydrogen is formed, there is in addition the Stern-Gouy double layer. These both may behave like condensers with leaks. In the equivalent circuit containing two condensers, the capacity due to the diffuse layer was, in effect, regarded as negligible compared to the capacity of the atomic layer. Alternatively the concept of two capacities due to atomic layers of hydrogen and chlorine at the electrodes may be incorrect. There is a possibility that there is only a diffuse layer at the anode, since each Cl^- ion which reaches the surface of the electrode may lose an electron leaving an activated chlorine atom, which may remove a platinum ion from the electrode and diffuse back into the solution. There is, therefore, some possible justification for assuming that the equivalent circuit contains three condensers with leaks (Fig. 3c).

From Table 3 it is seen that for both 0.01N and 0.1N KCl solutions C_3 is approximately one tenth of C_2, being of the order 0.005 Fd. for the 0.01N solution and 0.05 Fd. for the 0.1N solution. The value of R_3 is of the same order of magnitude as R_2. Since the extra capacity and resistance introduce two more constants into the current expression this expression fits the data better than previously. Only for the first 50 seconds of the charging period is i greater than the predicted value. Nevertheless, from the magnitude of i_∞ it is seen that in spite of the introduction of a third resistance and capacity into the equivalent circuit a considerable portion of the resistance of the solution remains unaccounted for.

Table 3. Ref. Fig. 3c.

Table 11.

E	R_1 ohms	R_2 ohms	R_3 ohms	C_1 Fd.	C_2 Fd.	C_3 Fd.	i_ω calc. μAmp.	i_ω expt. μAmp.
(a) 0.01N KCl.								
0.10	1,016	2,210	3,410	0.27	0.007	0.0010	2.26	0.04
0.20	1,390	1,560	2,680	0.22	0.033	0.0026	4.61	0.08
0.30	1,578	1,792	2,740	0.23	0.032	0.0041	6.85	0.12
0.40	2,360	2,580	2,990	0.18	0.024	0.0043	8.75	0.16
0.50	3,640	3,760	3,700	0.11	0.019	0.0046	10.25	0.20
0.75	3,770	6,520	3,620	0.17	0.020	0.0071	14.51	0.30
1.00	4,770	9,350	4,390	0.28	0.012	0.0060	17.48	0.40
1.25	10,800	15,850	7,500	0.29	0.009	0.0026	17.18	0.50
1.50	14,300	5,600	10,910	0.28	0.031	0.0033	21.9	0.60
1.80	20,600	7,300	10,360	0.10	0.030	0.0030	23.5	0.72
2.00	32,000	3,770	12,500	0.37	0.041	0.0031	23.2	0.80
(b) 0.1N KCl.								
0.10	33	113	322	29.5	1.02	0.058	7.34	0.010
0.20	72	190	392	18.0	0.64	0.046	14.66	0.020
0.30	127	229	480	11.0	0.55	0.050	21.6	0.030
0.40	202	227	440	7.5	0.51	0.057	28.8	0.040
0.50	364	370	888	3.8	0.35	0.033	34.2	0.050
0.75	555	686	910	2.3	0.21	0.037	49.5	0.075

(iv) Series resistance, capacity and capacity with leak (Fig. 3d).

A possibility that also arises is that the current through the cell would fall to zero if left for a long enough time. This implies that the resistance across one of the condensers (probably that due to the monatomic layer of hydrogen atoms) in the equivalent circuit, is infinite.

The simple case of one condenser and resistance in parallel and a second condenser in series, is considered. Note that this circuit is a special case of circuit 3b in which $R_1 = \infty$ (Fig. 3d). This circuit does not explain the behaviour of the cell adequately since the calculated values of R are about 10 to 100 times greater than the measured ones. In Table 4, R_2 is calculated using equation (I.5.22) (Appendix I(v)) where R is the calculated value (not the measured resistance). The values of C_1 and C_2 are smaller than before, being of the order of magnitude of 0.001 Fd. for both solutions. The initial steep drop in current below 150 seconds is also not explained by this circuit.

Table 4. Ref. Fig. 3d.

Table 12.

E	R ohms	R_2 ohms	C_1 Fd.	C_2 Fd.
(a) 0.01N KCl.				
0.10	860,000	615,000	0.00132	0.00039
0.20	728,000	494,000	0.00131	0.00053
0.30	575,000	405,000	0.00139	0.00069
0.40	426,000	323,000	0.00162	0.00093
0.50	303,000	246,000	0.00172	0.00136
0.75	182,000	217,000	0.00279	0.00192
1.00	160,000	190,000	0.00463	0.00140
1.25	101,000	113,000	0.0133	0.00231
1.50	114,000	48,100	0.0228	0.00531
1.80	92,900	32,800	0.0134	0.00930
2.00	80,300	26,800	0.0944	0.00538
(b) 0.1N KCl.				
0.10	1,100,000	910,000	0.00072	0.00031
0.20	743,000	819,000	0.00085	0.00038
0.30	427,000	472,000	0.00169	0.00063
0.40	354,000	320,000	0.00239	0.00072
0.50	237,000	220,000	0.00288	0.00127
0.75	169,000	168,000	0.00362	0.00180

(V). The Diffusion Aspect.

One of the processes occurring in the neighbourhood of an electrode (which is at a potential different to that in the bulk of the solution) is diffusion. If transport to the electrode is governed by diffusion alone i.e. in the absence of other factors such as stirring, convection, chemical action at the electrodes etc., Fick's laws of diffusion are operative (9,10,11,12).

Diffusion Currents and Linear Diffusion Coefficients.

The direction of diffusion is from regions of higher to regions of lower concentration and its rate is governed by Fick's laws. If dN is the number of moles of substance diffusing in the the x-direction in time dt across a plane of cross-sectional area A, at which the the concentration gradient is $\frac{\partial C}{\partial x}$, then

$$dN = D\,A\,\frac{\partial C}{\partial x}\,dt \qquad \ldots\ldots\ldots\ldots(5.1)$$

$$\frac{\partial C}{\partial t} = D\,\frac{\partial^2 C}{\partial x^2} \qquad \ldots\ldots\ldots\ldots(5.2)$$

where D is called the diffusion coefficient.

The diffusion current (i.e. the current which flows due to the loss or gain of charge by an electro-reducible or electro-oxidisable ion diffusing to the electrode) must not be confused with the polarographic residual current. Ions which undergo oxidation or reduction at an electrode are, in general, supplied by two forces: (a) a diffusive force proportional to the concentration gradient at the electrode surface and (b) an electrical force, proportional to the electric potential difference between the surface and the solution. Ions are therefore supplied partly by diffusion and partly by electrical migration, so that the limiting current set up in the polarographic case, due to the extreme state of concentration polarisation, may be regarded as the sum of a "diffusion current" and a "migration current". In the presence of an excess of "indifferent" electrolyte (i.e. one which does not possess ions which undergo reaction at the electrode), practically all the current through the solution will be carried by the indifferent ions. The transference number of the ions undergoing reaction is reduced practically to zero and the migration component of the limiting current is nullified, so that the limiting current becomes solely a diffusion current. The residual current is the small current (small relative to the diffusion current) which flows before the decomposition potential of the electrolyte is reached (11).

The case of diffusion up to a plane electrode is considered. Consider the electrode to be at position $x = 0$ and a diffusion field to be established by application of a voltage sufficient to produce the diffusion current. Then if C is the bulk concentration and C_0 the concentration of the diffusing substance at the electrode surface, the following are the boundary conditions:

At $t = 0$, $C_0 = C$ and at $t > 0$, $C_0 = 0$ (or $C \gg C_0$) for the polarographic case since, if deposition of the diffusing substance occurs at the electrode, the layer of electrolyte adjacent to the electrode will become so depleted of diffusing ions that the concentration there is virtually zero.

The solution of (5.2) under the above boundary conditions is given by Kontecky and Pliva as

$$C_{x,t} = C\ 2\ (\pi)^{-\frac{1}{2}} \int_0^z e^{-y^2}\ dy \qquad \text{............(5.3)}$$

$$= C\ x\ \mathrm{erf}\ z \qquad \text{............(5.4)}$$

where erf z is termed the "error function", and where

$$z = \frac{x}{2}\ (Dt)^{-\frac{1}{2}} \qquad \text{............(5.5)}$$

The error function has been calculated for various values of z, and is given in Table II-1 of Kolthoff and Lingane (11). The value of the error function rapidly approaches unity as a limit for the boundary conditions stated above, and hence the integral itself approaches $(\frac{\pi}{2})^{\frac{1}{2}}$ with increasing z. The plot of $\frac{C_{x,t}}{C}$ against x is a curve (11, p.24), the slope of which is the concentration gradient at the corresponding value of x. It is seen that the concentration gradient is greatest at x = 0.

The solution (5.3) however only holds under the given boundary conditions. If $C_0 > 0$ at $t > 0$ (which is a likely possibility in the application of the theory to the present work) it is necessary to derive an expression for $C_{x,t}$ corresponding to (5.3). Following the treatment of Harned (10) we introduce the variable $y = \frac{x}{t^{\frac{1}{2}}}$ into equation (5.2):

$$\frac{y}{2}\frac{dC}{dy} = -\ D\ \frac{d^2C}{dy^2} \qquad \text{............(5.6)}$$

Therefore $\qquad \frac{d^2C}{dy^2}\Big/\frac{dC}{dy} = -\ \frac{y}{2D}$

and $\qquad \frac{d}{dy}\ \ln \frac{dC}{dy} = -\ \frac{y}{2D}$

Integrating: $\quad \int d\ \ln \frac{dC}{dy} = -\ \frac{1}{2D}\int y\ dy$

or $$\ln \frac{dC}{dy} = -\frac{y^2}{4D} + \text{constant} \qquad \ldots\ldots(5.7)$$

Let $$\text{constant} = -\ln I$$

then $$\ln I \frac{dC}{dy} = -\frac{y^2}{4D}$$

and $$I \frac{dC}{dy} = e^{-y^2/4D} \qquad \ldots\ldots\ldots\ldots(5.8)$$

Now $$\frac{dC}{dx} = \frac{dC}{dy} \cdot \frac{dy}{dx}$$

$$= \frac{1}{I} e^{-y^2/4D} \, t^{-\frac{1}{2}}$$

$$= \frac{1}{It^{\frac{1}{2}}} e^{-x^2/4Dt} \qquad \ldots\ldots\ldots\ldots(5.9)$$

In order to find the value of the constant I integrate (5.9) from 0 to ∞ with respect to x.

$$\int \frac{dC}{dx} dx = \frac{1}{It^{\frac{1}{2}}} \int_0^{\infty} e^{-x^2/4Dt} \, dx$$

$$= \frac{1}{It^{\frac{1}{2}}} (\pi Dt)^{\frac{1}{2}}$$

$$= C - C_0$$

Therefore $$I = \frac{(D\pi)^{\frac{1}{2}}}{C - C_0} \qquad \ldots\ldots\ldots\ldots(5.10)$$

and substituting back into (5.9)

$$\frac{dC}{dx} = (C - C_0)\,(\pi Dt)^{-\frac{1}{2}} \, e^{-x^2/4Dt}$$

Integrating: $$\int_{C_0}^{C_{x,t}} dC = (C - C_0)\,(\ Dt)^{-\frac{1}{2}} \int_0^{x} e^{-x^2/4Dt} \, dx$$
$$\ldots\ldots\ldots\ldots(5.11)$$

and introducing the variable

$$z = \frac{x}{2} (Dt)^{-\frac{1}{2}}$$

into 5.11 gives

$$C_{x,t} - C_0 = (C - C_0) (\pi D)^{-\frac{1}{2}} \int_0^z e^{-z^2} 2D^{\frac{1}{2}} dz$$

$$= 2(C - C_0)\pi^{-\frac{1}{2}} \int_0^z e^{-z^2} dz \quad \text{........(5.12)}$$

i.e. $C_{x,t} = C_0 + (C - C_0) \text{ erf } z$ ....(5.13)

and the same error function is obtained as in (5.3). The expression (5.12) holds for the case where some of the ions diffusing to the electrode surface are not discharged immediately, so that there is a finite concentration of these ions at the electrode surface.

The diffusion current i_t is governed by the flux of electro-reducible or electro-oxidisable substance at the electrode surface, according to:

$$i_t = n F A f_{x=0,t} \quad \text{............(5.14)}$$

$$= n F A D \left(\frac{\partial C}{\partial x}\right)_{x=0,t} \quad \text{........(5.15)}$$

where $f_{x=0,t}$ is the flux at the electrode of surface area A, n is the number of Faradays required per mole and F is the Faraday.

By differentiating (5.3)

$$\left(\frac{\partial C}{\partial x}\right)_{x=0,t} = C (\pi Dt)^{-\frac{1}{2}} \quad \text{...........(5.16)}$$

Hence $i_t = n F C A \left(\frac{D}{\pi t}\right)^{\frac{1}{2}}$ ....(5.17)

or in the case where $C_0 > 0$ at $t > 0$

$$i_t = n\,F\,(C - C_0)\,A\,\left(\frac{D}{\pi t}\right)^{\frac{1}{2}} \quad ....(5.18)$$

The limitations of equations (5.17) and (5.18) are the following:

(1) It is assumed that the current flowing is only that due to diffusion of the ions in question and not to their migration to the electrode surface i.e. there is an excess of an indifferent electrolyte present. In this work it seems plausible to assume at first that the current is that due to the diffusion of hydrogen ions and the potassium chloride acts as the excess of indifferent electrolyte necessary to prevent the migration of diffusing ions. If some migration of the diffusing ions (of transport number n_+) occurs, then the total flux to surface area A of the electrode becomes

$$A\,f_{x=0,t} = D\,A\,\left(\frac{\partial C}{\partial x}\right)_{x=o,t} + \frac{n_+\,i_t\,A}{nF}$$

$$= D\,A\,C\,(\pi Dt)^{-\frac{1}{2}} + \frac{n_+\,i_t\,A}{nF} \quad ......(5.19)$$

From equation (5.14)

$$A\,f_{x=0,t} = \frac{i_t}{nF}$$

Therefore $\dfrac{i_t}{nF} = DAC(\pi Dt)^{-\frac{1}{2}} + \dfrac{n_+ i_t A}{nF}$

$$i_t(1 - n_+) = nFCA\left(\frac{D}{\pi t}\right)^{\frac{1}{2}} \quad ....(5.20)$$

Now $(1 - n_+)$ is the sum of the transport numbers of all the other non-diffusing ions in the solution. If $(1 - n_+) = n_s$ then

$$i_t = \frac{nFCA}{n_s}\left(\frac{D}{\pi t}\right)^{\frac{1}{2}} \qquad \ldots\ldots\ldots\ldots(5.21)$$

This equation applies for the case where $C_0 \ll C$. If C_0 is appreciable, equation (5.21) becomes

$$i_t = \frac{nF(C - C_0)}{n_s}\left(\frac{D}{\pi t}\right)^{\frac{1}{2}} \qquad \ldots\ldots\ldots\ldots(5.22)$$

Although i_t is greater than before it still varies inversely with the square root of t.

(2) The diffusion current equations are strictly applicable only to linear diffusion to the electrodes. In the experiments of Laitinen and Kolthoff (11) on diffusion currents, they ensured that diffusion was only linear by having a glass mantle with an open end extending perpendicularly to the electrode surface. Since some non-linear diffusion occurs in the present work, these equations would be expected to predict low current values.

(3) The setting up of concentration gradient $\frac{C}{\delta}$ (or $\frac{C - C_0}{\delta}$) (where δ = thickness of the diffusion layer) may not be instantaneous.

All the diffusion current equations (5.17), (5.18), (5.21) and (5.22) are of the form

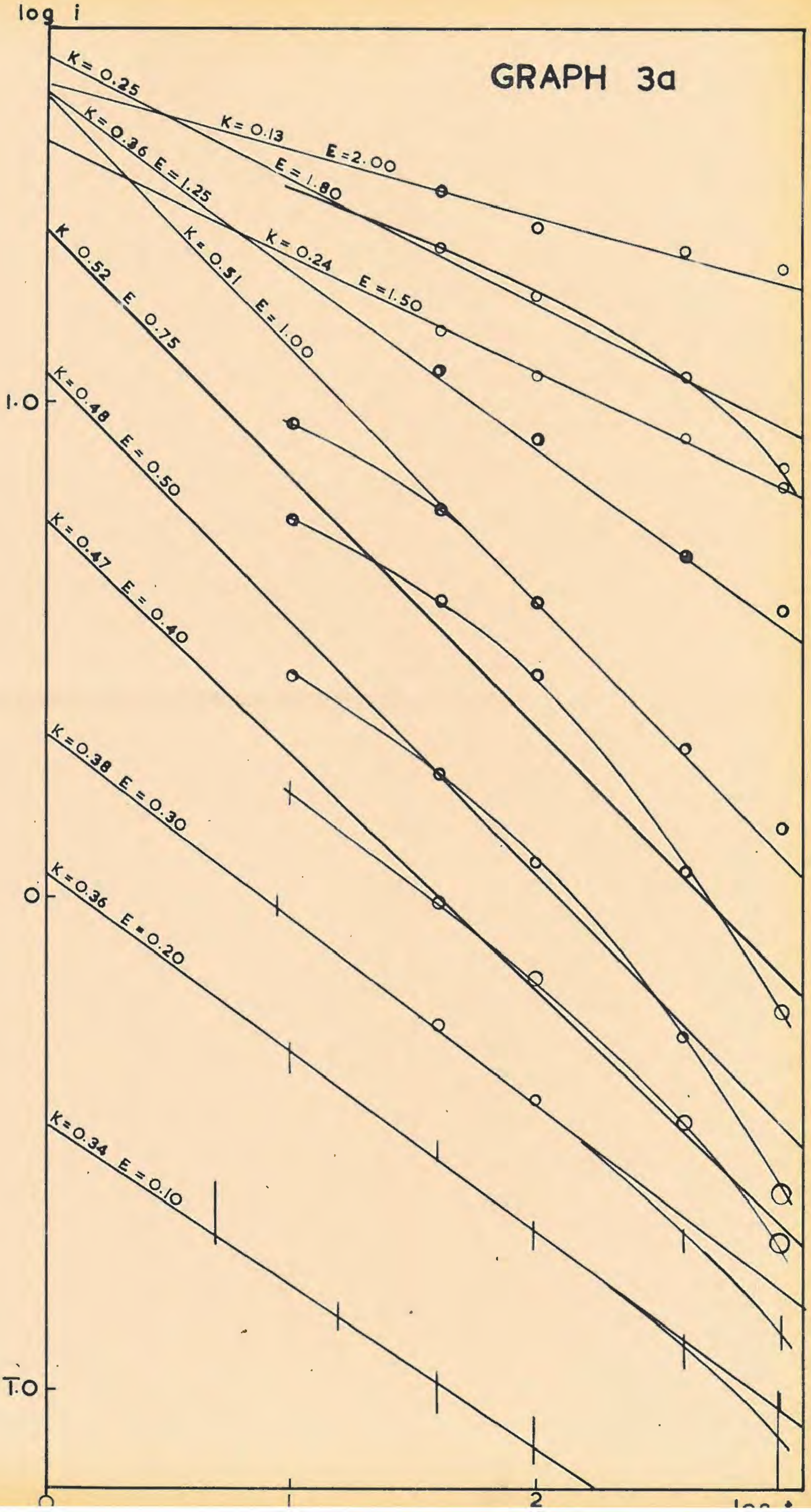
$$i_t = K\, t^{-\frac{1}{2}} \qquad \ldots\ldots\ldots\ldots(5.23)$$

and

$$\log i_t = \log K - \tfrac{1}{2}\log t \qquad \ldots\ldots\ldots\ldots(5.24)$$

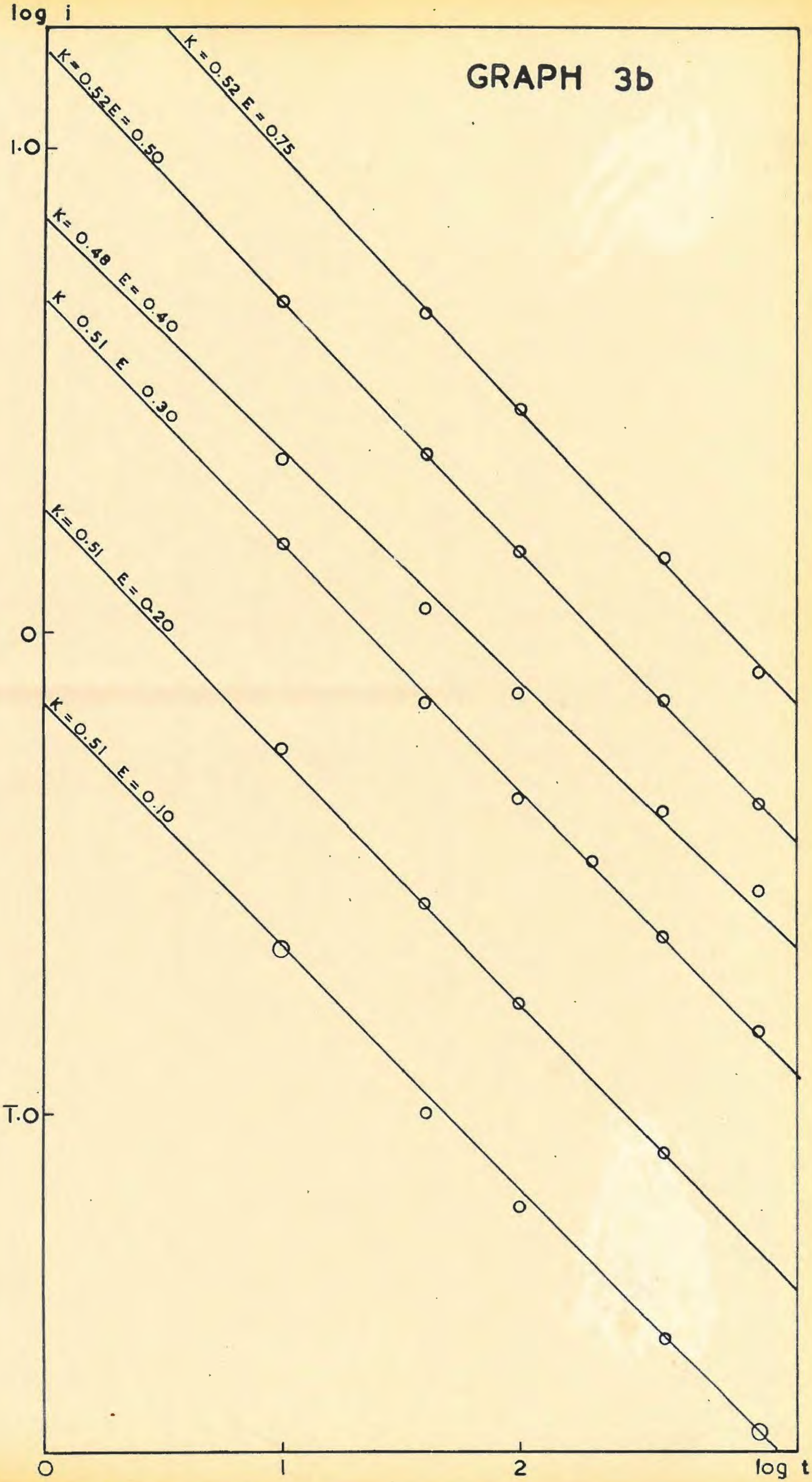
The plot of log i against log t should therefore be a straight line of slope $-\frac{1}{2}$. Good such straight lines were obtained for the 0.1N KCl solution but in the case of 0.01N solution, straight lines of slope greater than $-\frac{1}{2}$, or curves, were obtained (Graphs 3).

The fact that Fick's laws, as represented by equations (5.17), (5.18), (5.21) and (5.22), are obeyed reasonably well, suggests that the form of the equivalent circuit will be governed by diffusion to the electrode.



GRAPH 3a

log i
1.0
0
$\bar{1}.0$
0
1
2
K = 0.25
K = 0.13 E = 2.00
E = 1.80
K = 0.36 E = 1.25
K = 0.24 E = 1.50
K = 0.51 E = 1.00
K 0.52 E 0.75
K = 0.48 E = 0.50
K = 0.47 E = 0.40
K = 0.38 E = 0.30
K = 0.36 E = 0.20
K = 0.34 E = 0.10


GRAPH 3b

log i
1·0
0
$\bar{1}$·0
0
1
2
log t
K = 0.52 E = 0.75
K = 0.52E = 0.50
K = 0.48 E = 0.40
K 0.51 E 0.30
K = 0.51 E = 0.20
K = 0.51 E = 0.10

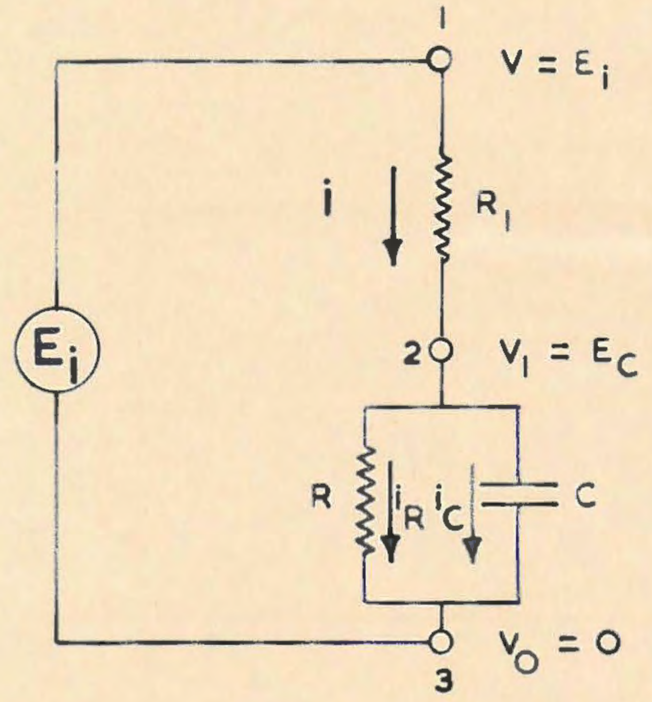


FIG. 4a

VI. Non-linear Circuits.

In all the linear circuits considered thus far the current as a function of time may be written

$$i_t = \frac{E}{R} f(t)$$

i.e. $$\frac{i_t}{E} = \frac{1}{R} f(t) \qquad \ldots\ldots\ldots\ldots(6.1)$$

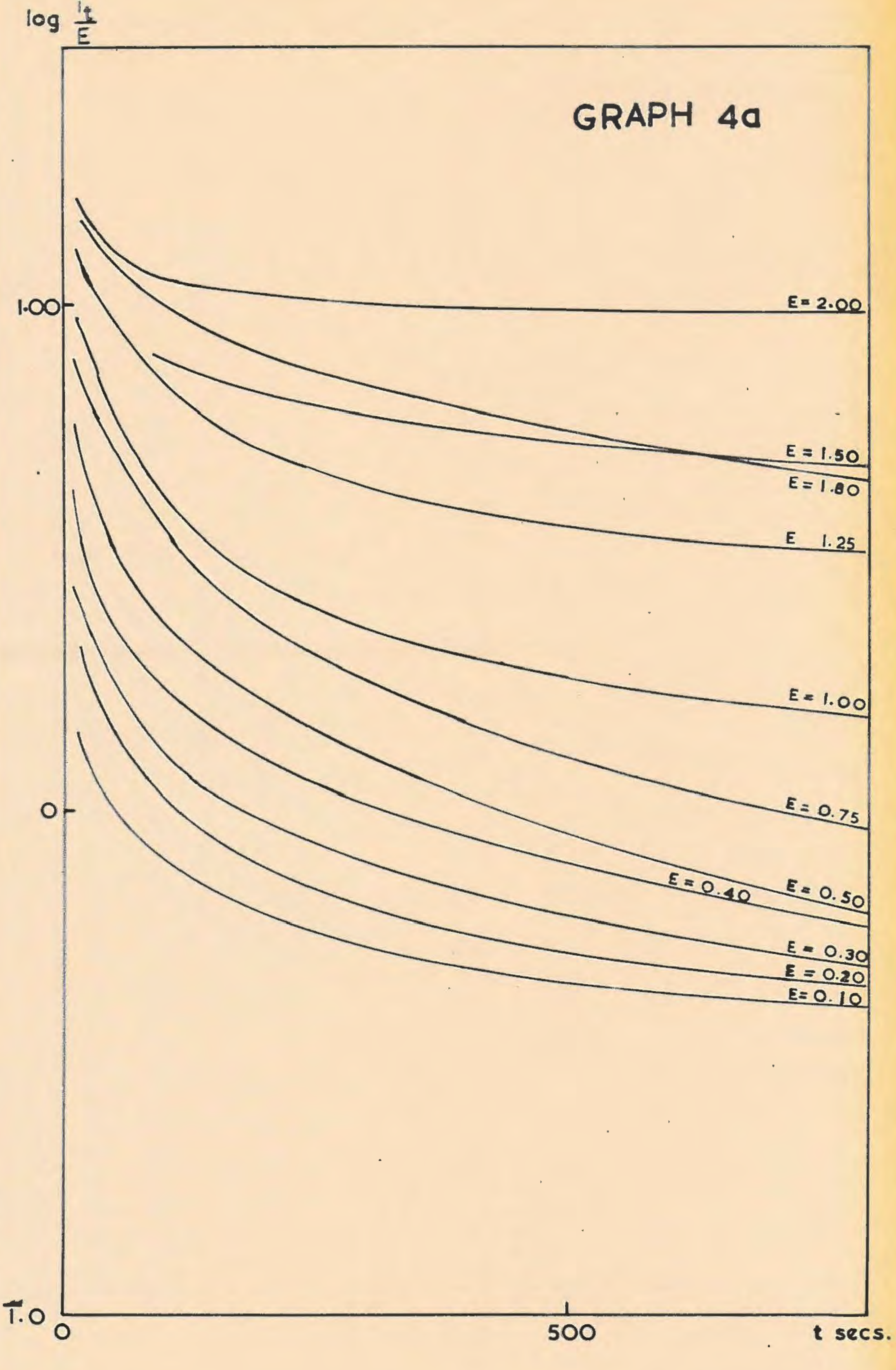
where f(t) is a function of time containing R's and C's as constants. It follows that at any particular value of t, i_t/E should be constant. A plot of i_t/E (or log i_t/E) against t should therefore yield the same curve for different values of E. Curves were obtained (Graphs 4) in which the values of i_t/E were dependent upon E; they increased with increasing E. Evidently then, one or more of the elements in the equivalent circuit depends upon E and we cannot expect to find a circuit with constant elements which will fit the observed currents for all E's.

(i) Series resistance and capacity with variable leak (Fig. 4a).

In the equivalent circuit (Fig. 4a) the resistance leak across the condenser is considered to be variable, depending on the potential E_C across the condenser, which varies with time.

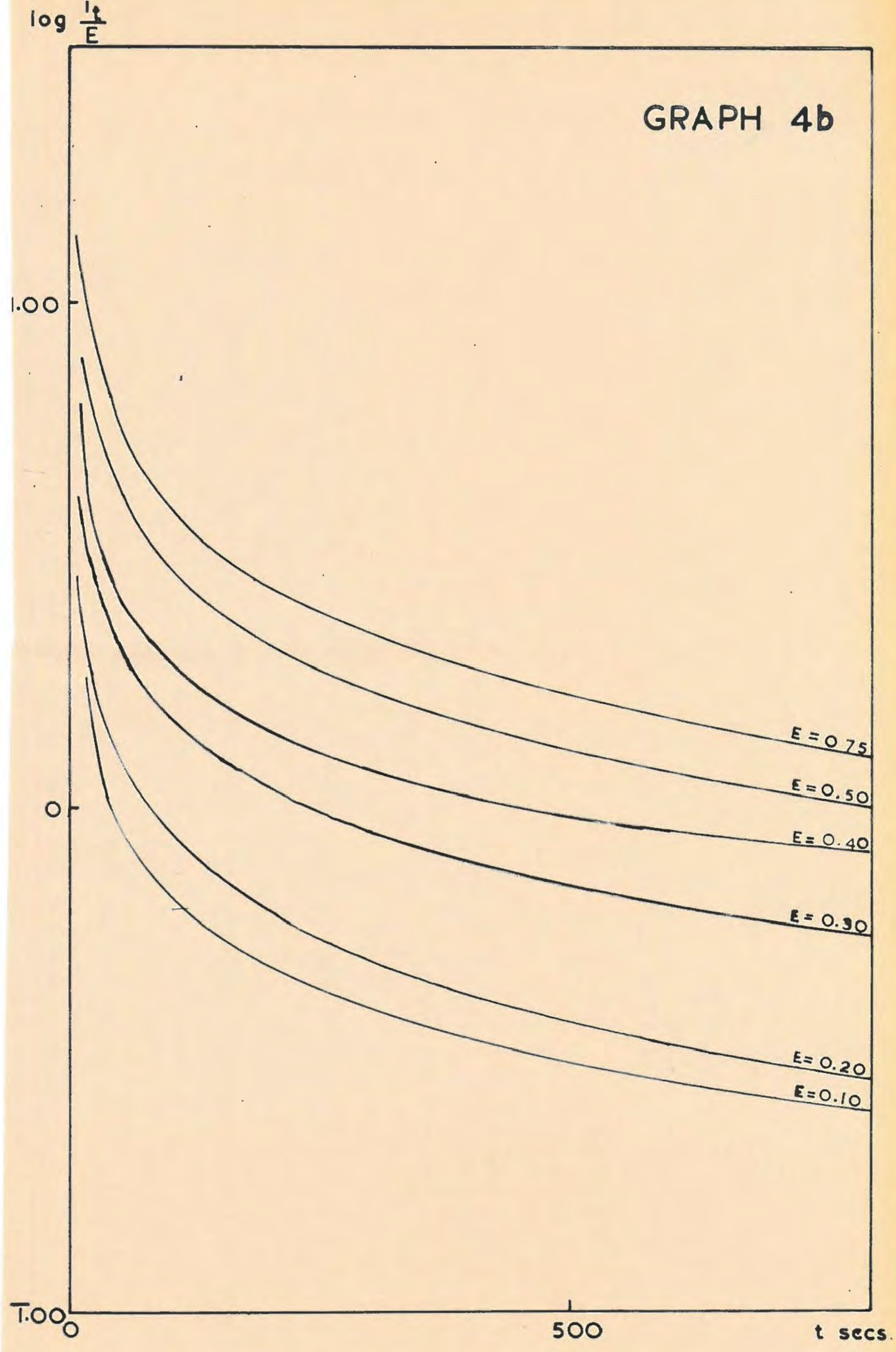
Let $R = R(E_C) = R_t$ and let the potentials at the nodes 1 and 2 be E_i and E_C with respect to the potential at node 3 as zero. Current i through the main branch of the circuit divides at node 2 into i_R and i_C through the R and C branches respectively. R_1 is the measured resistance of the solution.

The variation of R with time may be found approximately



GRAPH 4a

log $\frac{i_t}{E}$
1.00
0
$\bar{1}.0$
0
500
t secs.
E= 2.00
E = 1.50
E= 1.80
E 1.25
E= 1.00
E= 0.75
E= 0.40
E= 0.50
E = 0.30
E = 0.20
E= 0.10



GRAPH 4b

$\log \frac{i_t}{E}$
1.00
0
$\bar{1}.00$
0
500
t secs.
E = 0.75
E = 0.50
E = 0.40
E = 0.30
E = 0.20
E = 0.10

by assuming that after 1000 seconds i_t has reached its constant value so that the condenser is fully charged. Then R', the apparent resistance of the solution after 1000 seconds may be written as

$$R' = R_t + R_1 \qquad \text{.............(6.1.1)}$$

$$= R_t \quad \text{since } R_t \gg R_1 \text{ as is shown by the values of } i_\infty.$$

Now $$R' = \frac{E}{i_R} = \frac{E}{i_{1000}}, \text{ since the condenser is fully charged} \quad \text{....(6.1.2)}$$

R' was calculated (Table 5) and plotted against E to give a rectangular hyperbola. On plotting log R' against log E an approximate straight line of slope unity was obtained over the range E = 0.1 to 0.75 volts (Graphs 5). Therefore

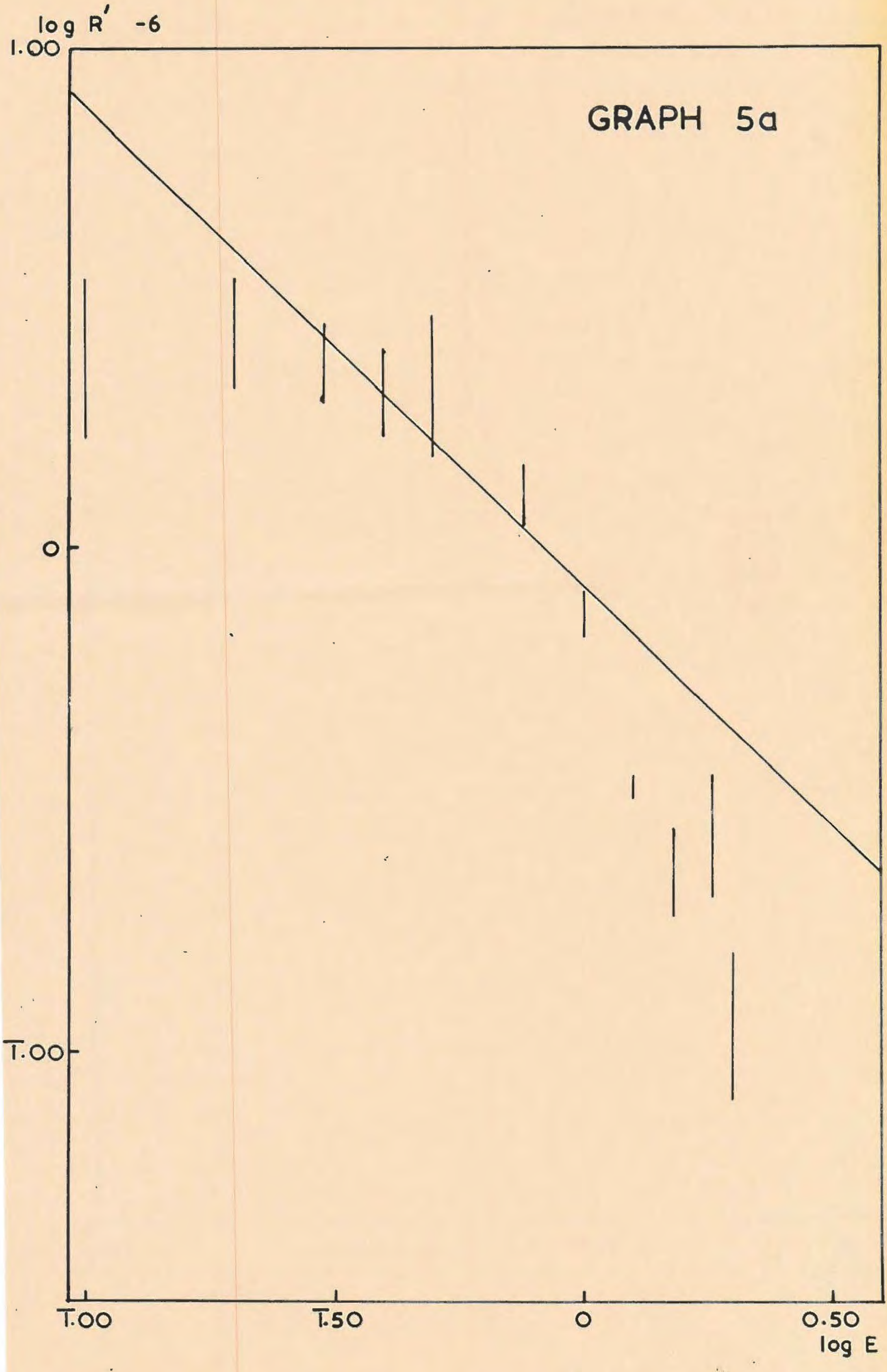
$$R' = \frac{K}{E} \qquad \text{............(6.1.3)}$$

and $$\log R' = \log K - \log E \qquad \text{............(6.1.4)}$$

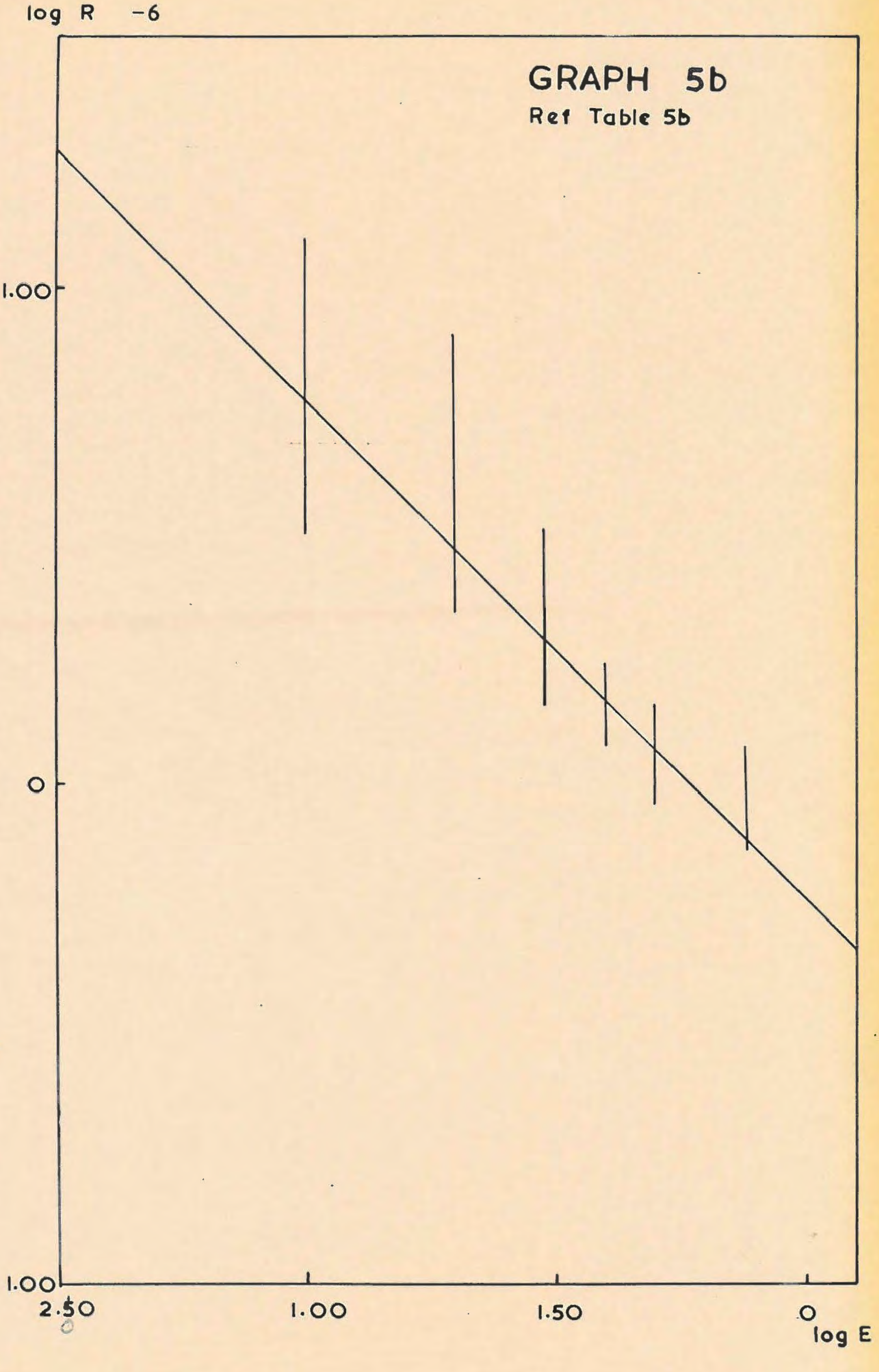
(Partial electrolysis occurs above 0.75 volts and the current flowing is greater than if electrolysis had not occurred. Consequently above 0.75 volts the value of R' as calculated from equation (6.1.2) will be smaller than that predicted by equation (6.1.4).

If R' varies with E in this manner then it is reasonable to assume that before the condenser is fully charged, R varies with E_C in the same way;

i.e. $$R_t = \frac{K}{E_C} \qquad \text{............(6.1.5)}$$



GRAPH 5a



GRAPH 5b

Ref Table 5b

Table 5. Ref. Fig. 4a.

E volts	log E	i_{1000} Amp.	R' ohms $\times 10^{-6}$	log R'
(a) 0.01N KCl. Ref. Graph 5a.				
0.10	$\bar{1}.00$	0.04	2.50	0.40
0.20	$\bar{1}.30$	0.08	2.50	0.40
0.30	$\bar{1}.48$	0.13	2.31	0.37
0.40	$\bar{1}.60$	0.20	2.00	0.30
0.50	$\bar{1}.70$	0.25	2.00	0.30
0.75	$\bar{1}.88$	0.59	1.26	0.10
1.00	0.00	1.38	0.72	$\bar{1}.86$
1.25	0.10	3.79	0.33	$\bar{1}.52$
1.50	0.18	6.74	0.22	$\bar{1}.35$
1.80	0.26	7.2	0.25	$\bar{1}.40$
2.00	0.30	18.6	0.11	$\bar{1}.04$
(b) 0.1N KCl. Ref. Graph 5b.				
0.10	$\bar{1}.00$	0.022	4.57	0.66
0.20	$\bar{1}.30$	0.052	3.86	0.59
0.30	$\bar{1}.48$	0.149	2.01	0.30
0.40	$\bar{1}.60$	0.286	1.40	0.15
0.50	$\bar{1}.70$	0.445	1.12	0.05
0.75	$\bar{1}.88$	0.83	0.91	$\bar{1}.96$

Using the equation (6.1.5) for expressing R_t in terms of E, the circuit may be analysed (Appendix II). The solution is

$$\log_{10} \frac{V}{B + V} + \log_{10} \left(\frac{B + 2V}{iR_1} - 1\right) = \frac{0.868K'D}{C} t$$

where B, V and D are constants defined in Appendix II.

A graphical method of finding C from this equation is by plotting log $(\frac{B + 2V}{iR_1} - 1)$ against t when a straight line of slope $\frac{0.868K'D}{C}$ and intercept log $\frac{V}{B + V}$ should be obtained. It was found that $\frac{B + 2V}{iR_1}$ was much greater than 1 and therefore this plot is virtually that of log $\frac{B + 2V}{iR_1}$ against t (Graphs 6), which was found to be non-linear over the first 500 seconds. This circuit is thus unsatisfactory since it fails to explain the behaviour of the conductance cell for the first 500 seconds after applying an e.m.f.

A fact that emerges, if C is calculated from the slope of the linear portion of the curves, is that the the cell behaves after 500 seconds as if it contains a condenser of approximately constant capacity. The value of this capacity is 0.03 Fd. in the case of the 0.01N solution and 0.1 Fd. for the 0.1N KCl solution (Table 6). In this table the two values of K' used are those obtained from graphs 5.

(a) 0.01N KCl: $K' = 1.201 \times 10^{-6}$ and $R_1 = 37{,}700$ ohms.

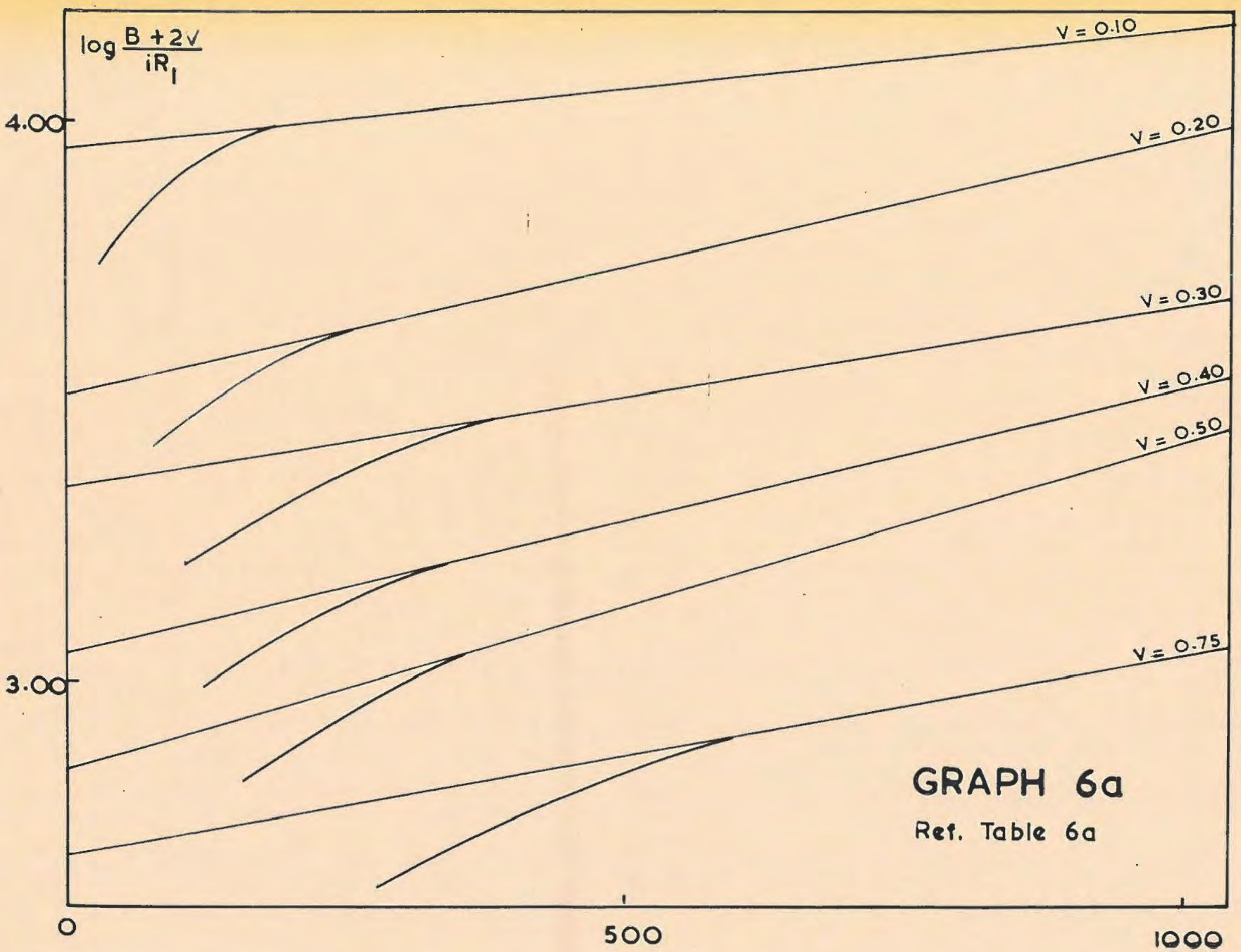
Now $B = \frac{1}{K'R_1}$ (Appendix II; equation II.9)

$= 22.1$

(b) 0.1N KCl: $K' = 1.700 \times 10^{-6}$ and $R_1 = 13{,}000$ ohms.

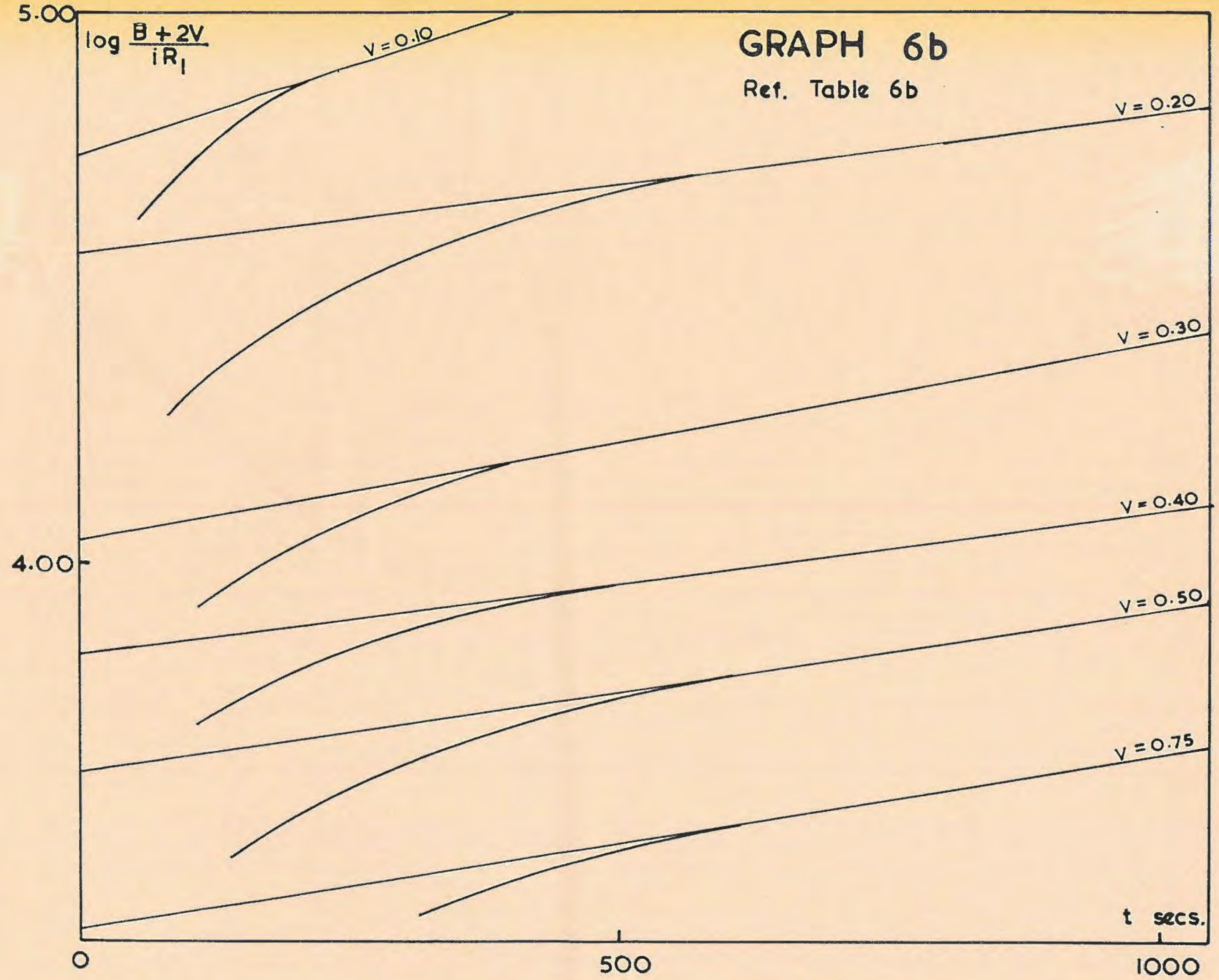
Therefore $B = 45.3$

D is calculated from B using equation (II.14).



GRAPH 6a

Ref. Table 6a



GRAPH 6b

Ref. Table 6b

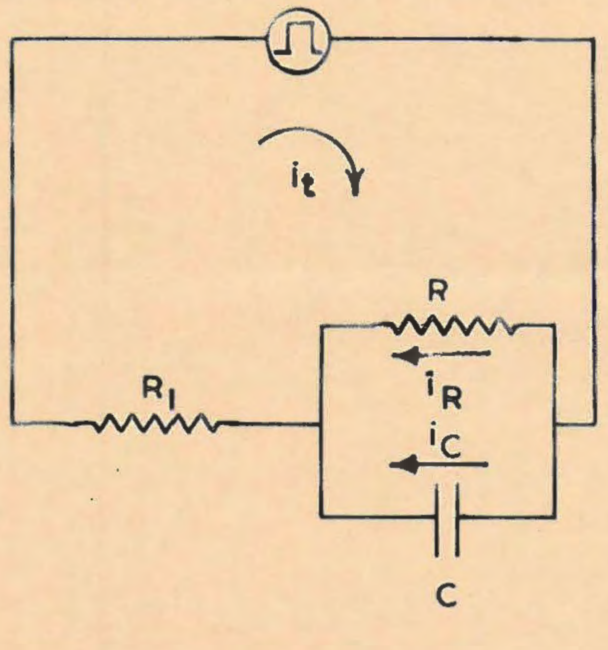


FIG. 4b

Table 6. Ref. 4a.

E	0.868K'D $\times 10^6$	$\frac{0.868K'D}{C} \times 10^3$	C Fd.
(a) 0.01N KCl. Ref. Graph 6a.			
0.10	11.62	0.22	0.053
0.20	11.73	0.46	0.026
0.30	11.83	0.32	0.037
0.40	11.94	0.47	0.025
0.50	12.04	0.57	0.021
0.75	12.31	0.35	0.035
(b) 0.1N KCl. Ref. Graph 6b.			
0.10	33.6	0.64	0.053
0.20	33.7	0.25	0.135
0.30	33.8	0.36	0.097
0.40	34.0	0.26	0.130
0.50	34.1	0.30	0.113
0.75	34.5	0.31	0.109

(ii) <u>Series resistance and capacity with variable leak (Fig. 4b)</u> (the variation in leak being found empirically assuming that C is known).

If the circuit (Fig. 4b) containing a variable leak resistance R fits the conductivity cell the variation in R may be found empirically provided R_1 and C are known . R_1 is assumed to be the measured resistance of the cell. Upper and lower limits o C may easily be established.

(a) Considering the lower limit of capacity to be that due to a layer of hydrogen atoms at the surface of the electrode, this capacity may be calculated to be approximately 20 μFd (7). Newbery in his investigation of the response of a cell to regular small e.m.f. steps, found that a 20 μFd condenser responded to the voltage steps he used in the same manner as the cell.

(b) Assuming that the cell behaves like a perfect condenser (i.e. without leak) the capacity of the cell is given by $C = \frac{Q}{E}$, where Q is the number of coulombs required to charge the condenser to potential E. Q is obtained by integration below the charge curves (Table 7). These are maximum values of C since by integration to find C, it is assumed that the condenser is perfect and no charge is lost through a resistance leak. These maximum values of C increase with increasing E. Assuming that the amount of charge lost through the condenser leak is higher the greater the charging potential, the maximum value of C may be taken as that found for a charging potential of 0.1 volts. The limits decided upon in this manner were 20 and 400 μFd.

In the circuit (Fig.4b) i_t is the current through the main branch of the circuit and i_R and i_C the currents through R and C respectively, have the directions indicated. Then

$$i_t = i_R + i_C \qquad \text{............(6.2.1)}$$

Now

$$E_C = \text{potential across C}$$

$$= E - iR_1 \qquad \text{............(6.2.2)}$$

$$= \frac{Q}{C}.$$

Therefore

$$i_C = \frac{dQ}{dt} = C\frac{dE_C}{dt} \qquad \text{............(6.2.3)}$$

But

$$\frac{dE_C}{dt} = \frac{dE}{dt} - R_1\frac{di}{dt} \quad \text{by (6.2.2).}$$

$$= - R_1\frac{di}{dt} \quad \text{at constant E} \quad \text{.......(6.2.4)}$$

Therefore $i_C = - C\, R_1 \frac{di}{dt}$ by (6.2.3) ....(6.2.5)

and by Ohm's law $i_R = \frac{E_C}{R}$ ....(6.2.6)

i_C may be found at any value of t by measuring the slope $\frac{di}{dt}$ of the i against t plot at that value of t and using equation (6.2.5); hence i_R from equation (6.2.1), E_C from equation (6.2.2) and R from equation (6.2.6).

This derivation is included for theoretical interest only. It will be shown in the next section that the introduction of a capacity into the equivalent circuit is unnecessary to explain the portion of the charge curve studied in this work i.e. from 3 seconds onwards.

Table 7.

E	Q μcoul.	C μFd.
(a) 0.01N KCl		
0.10	56.0	560
0.20	134.5	672
0.30	242	807
0.40	406	1,015
0.50	636	1,272
0.75	1,388	1,850
1.00	2,360	2,360
1.25	5,850	4,680
1.50	8,630	5,750
1.80	10,390	5,760
2.00	20,500	10,250
(b) 0.1N KCl.		
0.10	48.9	489
0.20	118.5	592
0.30	309	1,030
0.40	518	1,295
0.50	962	1,924
0.75	1,850	2,465

(iii) Equivalent circuit governed by diffusion.

The diffusion current expression

$$i_t = K\ t^{-\frac{1}{2}} \qquad \text{............(5.23)}$$

may be used in conjunction with the derivation in the previous section to establish values of R at different times.

From (5.23)

$$\frac{di_t}{dt} = -\tfrac{1}{2} K t^{-3/2} \qquad \ldots\ldots\ldots\ldots(6.3.1)$$

and by (6.2.1) and (6.2.3)

$$i_t = i_R + i_C$$

Therefore $i_R = i_t - i_C = Kt^{-\frac{1}{2}} - \tfrac{1}{2}CR_1 t^{-3/2}$.

$$= Kt^{-\frac{1}{2}}(1 - \tfrac{1}{2}CR_1 t^{-1}) \qquad \ldots\ldots(6.3.2)$$

According to (6.2.6) and (6.3.2)

$$R = \frac{E_C}{i_R} = \frac{E - Kt^{-\frac{1}{2}}R_1}{Kt^{-\frac{1}{2}}(1 - \tfrac{1}{2}CR_1 t^{-1})} \qquad \ldots\ldots\ldots\ldots(6.3.3)$$

In this expression it is seen that unless t is small the term $\tfrac{1}{2}CR_1 t^{-1}$ in the denominator may be considered negligible.

(To illustrate this substitute the maximum value of C of 400 μFd and the measured value of R_1 in the case of the 0.01N KCl solution:

$$\tfrac{1}{2}CR_1 = \tfrac{1}{2} \times 400 \times 10^{-6} \times 0.037 \times 10^{6} = 7.4$$

and for the 0.1N solution

$$\tfrac{1}{2}CR_1 = \tfrac{1}{2} \times 400 \times 10^{-6} \times 0.013 \times 10^{6} = 2.6 \qquad).$$

Since the term containing C in (6.3.3) is negligible (except for t less than 10 seconds) the equation simplifies to

$$R = \frac{E - Kt^{-\frac{1}{2}}R_1}{Kt^{-\frac{1}{2}}} = \frac{E}{K}t^{\frac{1}{2}} - R_1 \qquad \ldots\ldots\ldots\ldots(6.3.4)$$

or $$R = \frac{E - i_tR_1}{i_t} \qquad \ldots\ldots\ldots\ldots(6.3.5)$$

and the plot of R (as calculated from 6.3.5) against $t^{\frac{1}{2}}$ should be a straight line of slope $\frac{E}{K}$ and intercept $-R_1$. Good such straight lines (Graphs 7) were obtained in the case of 0.1N KCl solutions right down to the smallest measured values of t. In the case of the 0.01N solution the expected positive deviation in R was obtained for small t. (These graphs are, of course, those of Graphs 3 in other form).

Assuming that H^+ ions diffusing up to the electrodes are responsible for the diffusion current, it is necessary to know the diffusion coefficient of HCl in computing the theoretical value of K. The method of estimating the diffusion coefficient of HCl is shown in Appendix III. It is found to be 3.2×10^{-5} cm^2/sec.

Therefore if the current is due to H^+ ions diffusing up to the electrode, K should have the value given by equation (5.17):

$$K = n\ F\ C\ A\ (\frac{D}{\pi})^{\frac{1}{2}}$$

where $n = 1$

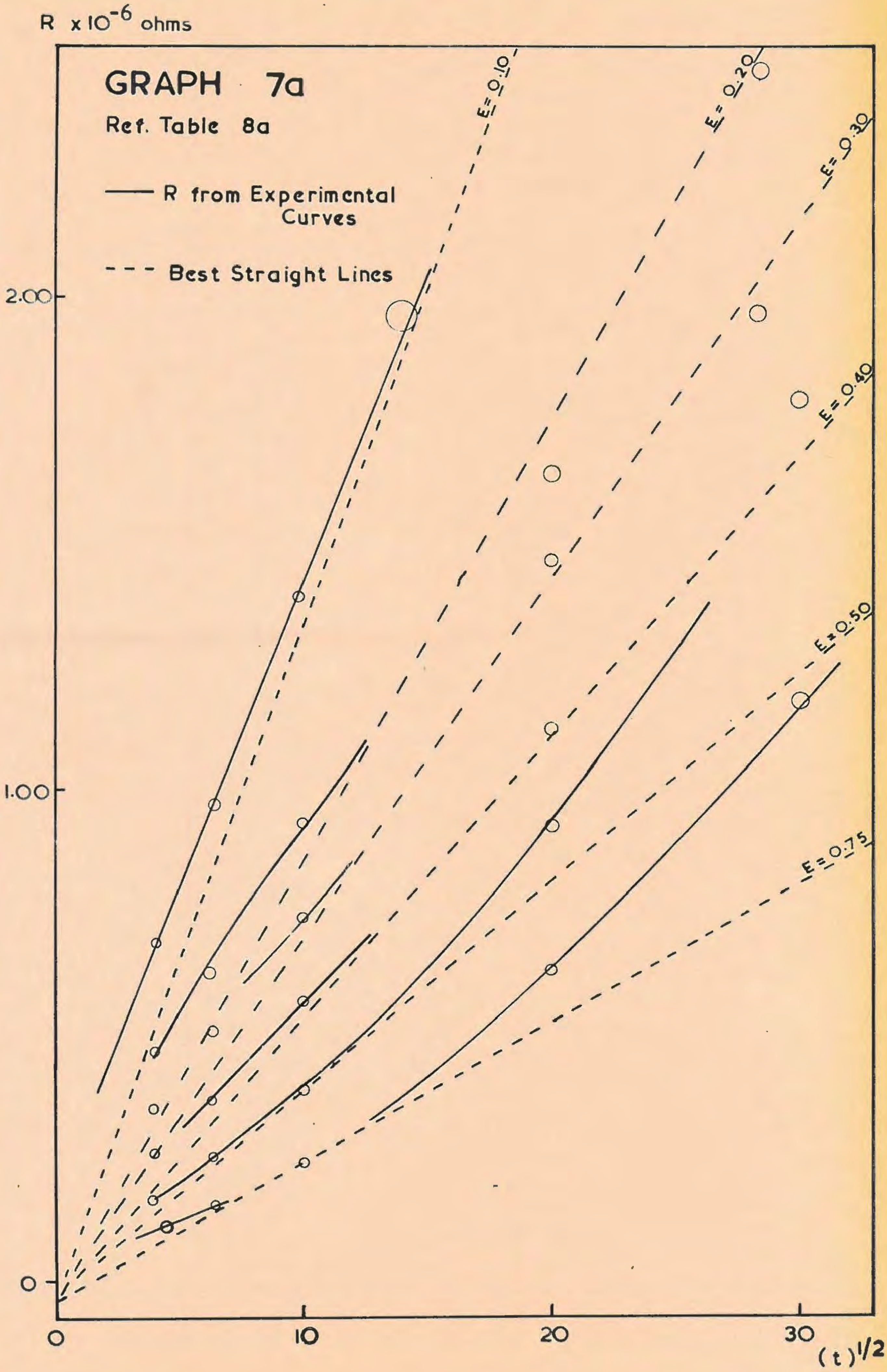
$F = 96{,}500$ coulombs

$C = 10^{-10}$ gm ions / ml since the removal of CO_2 renders the solution neutral.

$A = 2$ cm^2

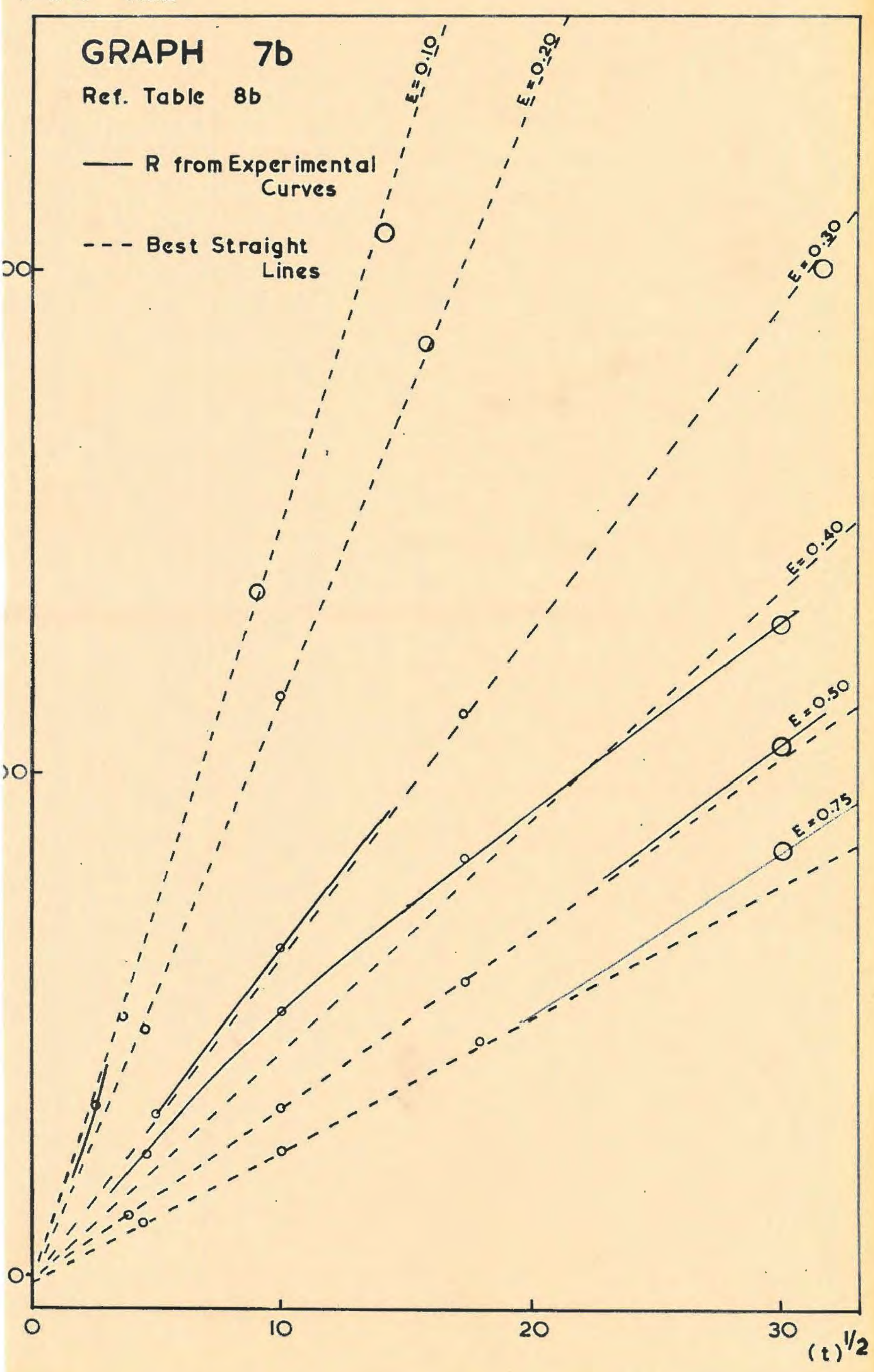
$D = 3.2$ cm^2/sec.

This gives a value for K of 6.14×10^{-8} Amps sec$^{\frac{1}{2}}$,



GRAPH 7a

Ref. Table 8a



GRAPH 7b

Ref. Table 8b

which is seen to be much smaller than any of the experimental values in Table 8. This presumably indicates that the concentration of H^+ ions in the solution is insufficient to account for the observed current in terms of diffusion.

It seems more probable that K^+ ions (with a diffusion coefficient of 1.9×10^{-5} $cm^2/sec.$) are responsible for the diffusion current. Substituting this value of D in equation (5.17) and values for C of 10^{-5} 10^{-4} gm ions/ml for the two concentrations of KCl used, the following values of K are obtained:

$$\text{(a) } 0.01N \text{ KCl: } K = 1 \times 96{,}500 \times 2 \times \left(\frac{1.9 \times 10^{-5}}{3.14}\right)^{\frac{1}{2}} \times 10^{-5}$$
$$= 4.75 \times 10^{-3}$$

$$\text{(b) } 0.1N \text{ KCl: } K = 1 \times 96{,}500 \times 10^{-4} \times \left(\frac{1.9 \times 10^{-5}}{3.14}\right)^{\frac{1}{2}} \times 2$$
$$= 4.75 \times 10^{-2}$$

It is seen that these values of K are much larger than the observed ones. It is suggested that this is due to the fact that when a steady state has been set up, the concentration of diffusing ions at the electrode surface is not zero. Furthermore, since there is no excess of indifferent electrolyte (the concentration of H^+ being negligible compared to the K^+ ion concentration) some K^+ ions will migrate to the electrode surface. In this case equation (5.22) is applicable. The expression for K is then (according to equation 5.22):

$$K = \frac{n\ F\ (C - C_0)\ A}{n_s} \left(\frac{D}{\pi}\right)^{\frac{1}{2}}$$

which reduces K since $(C - C_0)$ is smaller than C.

n_s is very nearly 0.5 in the case of KCl in water. $(C - C_0)$ was calculated for the various values of E at the two concentrations (Table 8)and it was found that C_0 was only a little smaller than the bulk concentration and depended on E. When the polarographic diffusion current flows, the layer adjacent to the electrode is completely depleted of ions since the applied voltage is greater than the decomposition potential of the electrolyte. In this work however potentials much below the decomposition potential are used and probably only very little deposition occurs.

In table 8: since the graphical value of K (obtained from the plot of R against $t^{\frac{1}{2}}$) is given by

$$K_{graph.} = \frac{n\,F\,(C - C_0)\,A}{n_s}\left(\frac{D}{\pi}\right)^{\frac{1}{2}}$$

and the calculated value of K is given by

$$K_{calcd.} = n\,F\,C\,A\left(\frac{D}{\pi}\right)^{\frac{1}{2}}$$

therefore $$\frac{K_{graph}}{K_{calcd}} = \frac{C - C_0}{n_s C}$$

and $$C - C_0 = n_s\,C\,\frac{K_{graph}}{K_{calcd}} \quad \ldots\ldots\ldots\ldots.(6.3.6)$$

This circuit in which the resistance varies proportionately to the square root of the time and the e.m.f. applied (as in equation 6.3.4), is the most satisfactory deduced for a conductivity cell. The fitting of this equation to the a.c. response of cells will form the subject of future work in this department. It is also intended to test this diffusion theory on solutions of other electrolytes containing H^+ ions (such as HCl), and on concentrations of KCl other than the two concentrations used in this work.

Table 8.

E	$\frac{E}{K}$ x 10^{-6}	K_{graph} x 10^6	$\frac{K_{graph}}{K_{calc.}}$ x 10^5	$C - C_0$ gm eq./l x 10^5	C_0 gm eq./l
(a) 0.01N KCl. Ref. Fig. 7a.					
0.10	0.137	0.73	15.4	0.077	0.009999
0.20	0.089	2.25	47.2	0.236	0.009998
0.30	0.073	4.11	86,2	0.431	0.009996
0.40	0.056	7.15	150.0	0.75	0.009993
0.50	0.043	11.62	244	1.22	0.009988
0.75	0.028	26.8	562	2.86	0.009971
(b) 0.1N KCl. Ref. Fig. 7b.					
0.10	0.151	0.662	1.39	0.069	0.099999
0.20	0.116	1.725	3.63	0.181	0.099998
0.30	0.064	4.69	9.89	0.494	0.099995
0.40	0.045	8.90	18.7	0.935	0.099991
0.50	0.034	14.7	30.9	1.54	0.099985
0.75	0.025	30.0	63.1	3.15	0.099969

Appendix I.

Calculation of the Responses of Linear Circuits to Square Pulses by the Laplace Transformation.

(i) Introduction.

The behaviour of linear circuits, when subjected to discontinuous voltage inputs may be calculated by solving Kirchhoff's voltage or current relationships for the branches of the circuit. A most elegant mathematical technique for accomplishing this solution is by means of the Laplace transformation (6). By means of this transformation, functions of a real variable (say t) are transformed into functions of a complex variable (s), where

$$s = \sigma + j\omega, \qquad \ldots\ldots\ldots\ldots(I.1.1)$$

and σ and ω are real variables and $j = (-1)^{\frac{1}{2}}$, by multiplication by e^{-st} and integration over t from 0 to ∞. The function of t transforms to a much simpler function of s, which is more amenable to mathematical treatment. The direct ($\mathcal{L}$) transformation is written

$$\mathcal{L}[f(t)] = F(s) = \int_0^\infty f(t)\, e^{-st}\, dt \quad \ldots\ldots\ldots(I.1.2)$$

Consider as an example the discontinuous function

$f(t) = 0$ for $t < 0$

$\quad = E$ for $t \geqslant 0$.

This transforms into

$$F(s) = \int_0^\infty f(t)\, e^{-st}\, dt$$

$$= \int_0^\infty E\, e^{-st}\, dt \qquad \text{for } t \geqslant 0$$

$$F(s) = -\frac{E}{s} e^{-st}\Big|_0^\infty$$

$$= \frac{E}{s}$$

The rather complicated function, f(t), transforms to the simple function, $\frac{E}{s}$.

After the solution of the transformed Kirchhoff's relationships, the inverse ($\mathcal{L}^{-1}$) Laplace transformation is used to find the solution in terms of t. Tables of function-transform (f-t) pairs have been constructed (6), which are used to pass from a function, f(t), to its transform, F(s), and vice-versa.

A rectangular pulse of unit amplitude starting at t = 0 and ending at t = τ, may be considered as the sum of a positive unit step at t = 0 and an equal negative step at t = τ. (A unit step at t = a has the form f(t) = 0 when t $<$ a and f(t) = 1 when t $\geqslant$ a.) The Laplace transform is thus

$$\mathcal{L}(\text{unit pulse}) = e^{-0s}.\frac{1}{s} - e^{-\tau s}.\frac{1}{s}$$

$$= \frac{1}{s} - \frac{e^{-\tau s}}{s} \qquad \ldots\ldots\ldots\ldots(I.1.3)$$

The effect of multiplying a transform by $e^{-\tau s}$ is merely to move the time function through an interval τ (6: operation-transform 10). Since the inverse transform $\mathcal{L}^{-1}(\frac{1}{s})$ is the unit step, u(t) at t = 0 (6: f-t 1.101), the response to a pulse of unit amplitude may be found by solving the equations for a unit step at the origin and then subtracting an identical function from it at time t = τ (as the second term in I.1.3). The response to a pulse of amplitude E is obtained by multiplying the whole function by E. It is therefore only necessary to solve the Kirchhoff's relationships for a step at the origin.

(ii) Series resistance and capacity with leak (Fig. 3a).

The mathematical treatment of this circuit (and each of the three circuits to follow) is conveniently considered in three stages:

(a) To obtain the current expression.

The currents i and i_1 in the branches of this circuit have, by convention, the directions indicated. e_i is the input voltage [*]. Kirchhoff's current relationships for the branches are

$$R_1(i - i_1) + Ri = e_i \quad \ldots\ldots\ldots\ldots\text{(I.2.1)}$$

$$R_1(i - i_1) - \frac{1}{C_1}\int_0^t i_1\,dt = 0 \quad \ldots\ldots\ldots\ldots\text{(I.2.2)}$$

which, re-written with terms in i and i_1 collected, become

$$(R + R_1)i - R_1 i_1 = e_i \quad \ldots\text{(I.2.3)}$$

$$R_1 i - R_1 i_1 - \frac{1}{C_1}\int_0^t i_1\,dt = 0 \quad \ldots\text{(I.2.4)}$$

By means of the Laplace transformation each of the functions of time in these expressions may be transformed into functions of a new variable s. Considering each term in turn:

---

[*] e_i, i, i_1 etc. are functions of t and should be written $e_i(t)$, $i(t)$, $i_1(t)$ etc., but for the sake of convenience the variable t is omitted. Similarly s is omitted in writing the transforms E, I, I_1 etc.

i becomes I where $I = \int_0^\infty i\, e^{-st}\, dt$ ....(I.2.5)

and

i_1 becomes I_1 where $I_1 = \int_0^\infty i_1 e^{-st}\, dt$ ....(I.2.6)

The function, $f(t) = \frac{1}{C_1}\int_0^t i_1\, dt$, becomes

$$F(s) = \int_0^\infty \left[\frac{1}{C_1}\int_0^t i_1\, dt\right] e^{-st}\, dt$$

Integrating by parts:

$$F(s) = \frac{1}{C_1}\left[-\frac{1}{s}\, e^{-st}\int_0^t i_1\, dt\,\Big|_0^\infty - \int_0^\infty -\frac{1}{s}\, e^{-st} i_1\, dt\right].$$

Since $e^{-st} = 0$ when $t = \infty$ and $\int_0^t i_1\, dt = 0$ when $t = 0$, the first term in the integrated expression above is 0, so that

$$F(s) = \frac{1}{C_1}\left[-\int_0^\infty -\frac{1}{s}\, e^{-st}\, i_1\, dt\right]$$

$$= \frac{1}{C_1}\left[I_1\right] \text{ by (I.2.6)} \qquad \text{............(I.2.7)}$$

e_i, being a step of amplitude E at the origin, transforms to $\frac{E}{s}$, so that

$$\mathcal{L}\, e_i = \frac{E}{s} \qquad \text{............(I.2.8)}$$

The transformed forms of equations (I.2.3) and (I.2.4) therefore are

$$(R + R_1)I \quad - \quad R_1 I_1 \quad = \quad \frac{E}{s} \qquad \text{............(I.2.9)}$$

$$R_1 I \quad - \quad (R_1 + \frac{1}{C_1 s})I_1 \quad = \quad 0 \qquad \text{............(I.2.10)}$$

Solving for I from (I.2.9) and (I.2.10) by determinants:

$$I = \frac{E}{s}\begin{vmatrix} 1 & -R_1 \\ 0 & -(R_1 + \frac{1}{C_1 s}) \end{vmatrix} - \begin{vmatrix} R + R_1 & -R_1 \\ R_1 & -(R_1 + \frac{1}{C_1 s}) \end{vmatrix}$$

$$= \frac{E}{s}\,\frac{(R_1 + \frac{1}{C_1 s})}{(R + R_1)(R_1 + \frac{1}{C_1 s}) - R_1{}^2}$$

Multiplying numerator and denominator by $\frac{s}{R_1}$, gives

$$I = \frac{E}{s}\,\frac{(s + \frac{1}{C_1 R_1})}{Rs + \frac{1}{C_1} + \frac{R}{C_1 R_1}}$$

$$= \frac{E}{R}\,\frac{(s + \alpha_1)}{s(s + \beta)} \qquad \text{............(I.2.11)}$$

where $\alpha_1 = \frac{1}{C_1 R_1}$ ....(I.2.12)

$$\beta = \alpha_1(1 + \frac{R_1}{R}) \qquad \text{............(I.2.13)}$$

From f-t pair no. 1.107 (6), the function of which (I.2.11) is the transform is

$$i = \frac{E}{R}(\frac{\alpha_1}{\beta} - \frac{\alpha_1 - \beta}{\beta}\,e^{-\beta t})$$

$$= \frac{E}{R}\,(\frac{R}{R + R_1} + \frac{R_1}{\alpha_1(R + R_1)}\,e^{at})$$

$$= \frac{E}{R}\,(\frac{R}{R + R_1} + \frac{a + \alpha_1}{a}\,e^{at})$$

$$= \frac{E}{R + R_1} + \frac{E}{R}\,\frac{a + \alpha_1}{a}\,e^{at} \qquad \text{...........(I.2.14)}$$

where $a = -\beta = -\alpha_1\ (1 + \frac{R_1}{R})$ ....(I.2.15)

(b) To fit the current expression (I.2.14) to the data.

The first term in equation (I.2.14) is seen to be a constant and is the limiting value of i at large t, since a is negative. Designating the quantity $\frac{E}{R + R_1}$ as i_∞, equation (I.2.14) has the form

$$i = i_\infty + i'$$

or $$i - i_\infty = i' = A\ e^{-Bt} \qquad \text{............(I.2.16)}$$

and $$\ln i' = \ln A - Bt$$

or $$\log_{10} i' = \log_{10} A - \frac{Bt}{2.303} \qquad \text{............(I.2.17)}$$

A plot of $\log_{10} i'$ against t should thus be a straight line of slope $- \frac{B}{2.303}$ and intercept $\log_{10} A$ on the log i' -axis. i' (= $i - i_\infty$) was calculated (AppendixIV) and $\log_{10} i'$ plotted against t. A plot was obtained which was only linear from about 500 seconds onwards (Graphs 8). The constants A and B were found from the straight line portions of the plots, log A and $- \frac{B}{2.303}$ being the intercept and slope respectively.

(c) Evaluation of α_1, R_1 and C_1 from A and B.

From equations (I.2.14) and (I.2.16)

$$A = \frac{E}{R} \frac{a + \alpha_1}{a} \qquad \text{............(I.2.18)}$$

and $$B = - a = \alpha_1 \left(1 + \frac{R_1}{R}\right) \qquad \text{............(I.2.19)}$$

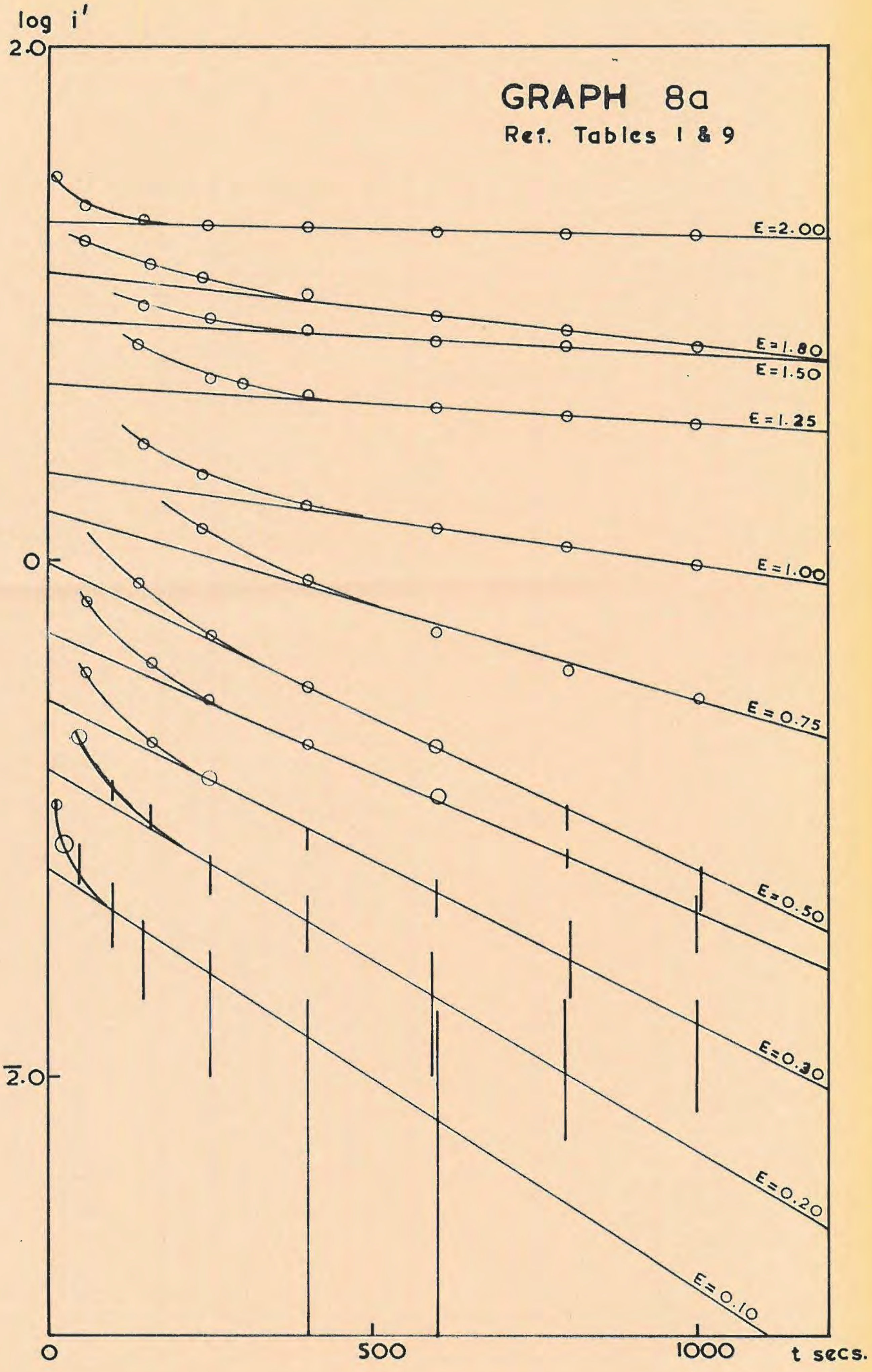
From (I.2.18) and (1.2.19)

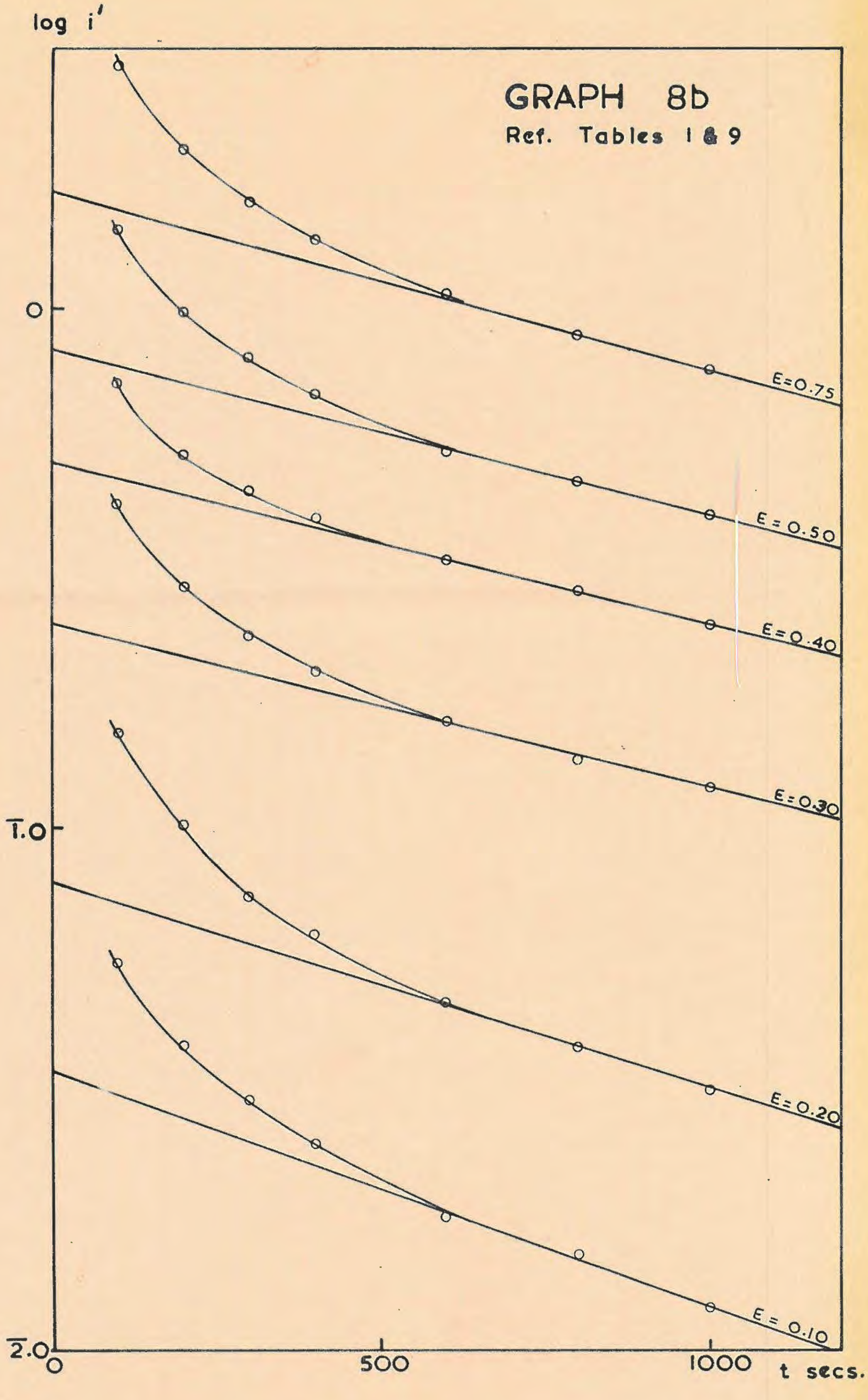
$$\alpha_1 = a \left(A \frac{R}{E} - 1\right) = B \left(1 - A \frac{R}{E}\right) \qquad \text{......(I.2.20)}$$

$$R_1 = R \left(\frac{B}{\alpha_1} - 1\right) \qquad \text{............(I.2.20)}$$

GRAPH 8a

Ref. Tables 1 & 9





GRAPH 8b

Ref. Tables 1 & 9

From (I.2.12) $C_1 = \frac{1}{\alpha_1 R_1}$ ....(I.2.21)

The values of log A, $-\frac{B}{2.303}$, A, B and α_1 are given in Table 9, and the corresponding values of R_1 and C_1 in Table 1.

<u>Table 9.</u> Ref. Fig. 3a.

Table 1.

E	log A + 6	$\frac{B}{2.303}$ x 10^3	A x 10^6	B x 10^3	α_1 x 10^3
(a) 0.01N KCl.		Ref. Graph 8a.			
0.10	$\bar{2}.80$	1.64	0.063	3.78	3.69
0.20	$\bar{1}.18$	1.48	0.151	3.42	3.32
0.30	$\bar{1}.45$	1.24	0.282	2.86	2.76
0.40	$\bar{1}.71$	1.08	0.513	2.49	2.37
0.50	$\bar{1}.99$	1.20	0.977	2.76	2.56
0.75	0.16	0.71	1.445	1.640	1.520
1.00	0.33	0.36	2.14	0.830	0.762
1.25	0.68	0.16	4.79	0.369	0.316
1.50	0.93	0.14	8.51	0.322	0.254
1.80	1.11	0.30	12.88	0.691	0.503
2.00	1.30	0.05	20.0	0.115	0.0713
(b) 0.1N KCl.		Ref. Graph 8b.			
0.10	$\bar{2}.53$	0.45	0.0339	1.038	1.033
0.20	$\bar{2}.86$	0.34	0.0724	0.785	0.781
0.30	$\bar{1}.39$	0.32	0.245	0.738	0.730
0.40	$\bar{1}.68$	0.29	0.479	0.670	0.660
0.50	$\bar{1}.92$	0.33	0.832	0.761	0.745
0.75	0.22	0.35	1.66	0.807	0.783

(iii) Series resistance and two capacities with leaks (Fig. 3b).

(a) To obtain the current expression.

The currents i_1, i_2 and i in the branches of this circuit have the directions indicated. e_i is the input voltage. Kirchhoff's current relationships for the branches are

$$R_1(i - i_1) + R_2(i - i_2) + Ri = e_i \quad (I.3.1)$$

$$R_1(i - i_1) - \frac{1}{C_1}\int_0^t i_1 \, dt = 0 \quad (I.3.2)$$

$$R_2(i - i_2) - \frac{1}{C_2}\int_0^t i_2 \, dt = 0 \quad (I.3.3)$$

which re-written with terms in i, i_1 and i_2 collected, become

$$(R + R_1 + R_2)i - R_1 i_1 - R_2 I_2 = e_i \ldots (I.3.4)$$

$$R_1 i - R_1 i_1 - \frac{1}{C_1}\int_0^t i_1 \, dt = 0 \ldots (I.3.5)$$

$$R_2 i - R_2 i_2 - \frac{1}{C_2}\int_0^t i_2 \, dt = 0 \ldots (I.3.6)$$

which by direct Laplace transformation become

$$(R + R_1 + R_2) - R_1 I_1 - R_2 I_2 = e_i \ldots\ldots\ldots (I.3.7)$$

$$R_1 I - (R_1 + \frac{1}{C_1 s}) I_1 = 0 \ldots\ldots\ldots (I.3.8)$$

$$R_2 I - (R_2 + \frac{1}{C_2 s}) I_2 = 0 \ldots\ldots\ldots (I.3.9)$$

Solving for I from (I.3.7), (I.3.8) and (I.3.9) gives

$$I = \frac{E}{s}\,\frac{\begin{vmatrix} 1 & -R_1 & -R_2 \\ 0 & -(R_1 + \frac{1}{C_1 s}) & 0 \\ 0 & 0 & -(R_2 + \frac{1}{C_2 s}) \end{vmatrix}}{\begin{vmatrix} R + R_1 + R_2 & -R_1 & -R_2 \\ R_1 & -(R_1 + \frac{1}{C_1 s}) & 0 \\ R_2 & 0 & -(R_2 + \frac{1}{C_2 s}) \end{vmatrix}}$$

$$= \frac{E}{s}\,\frac{(R_1 + \frac{1}{C_1 s})(R_2 + \frac{1}{C_2 s})}{(R + R_1 + R_2)(R_1 + \frac{1}{C_1 s})(R_2 + \frac{1}{C_2 s}) - R_2^2(R_1 + \frac{1}{C_1 s}) - R_1^2(R_2 + \frac{1}{C_2 s})}$$

Multiplying numerator and denominator by $\frac{s^2}{R_1 R_2}$:

$$I = \frac{E}{s}\,\frac{(s + \frac{1}{C_1 R_1})(s + \frac{1}{C_2 R_2})}{(R + R_1 + R_2)(s + \frac{1}{C_1 R_1})(s + \frac{1}{C_2 R_2}) - R_2 s(s + \frac{1}{C_1 R_1}) - R_1 s(s + \frac{1}{C_2 R_2})}$$

$$= \frac{E}{s}\,\frac{(s + \alpha_1)(s + \alpha_2)}{(R + R_1 + R_2)(s + \alpha_1)(s + \alpha_2) - R_2 s(s + \alpha_1) - R_1 s(s + \alpha_2)}$$

where, by analogy with (I.2.12)

$$\alpha_1 = \frac{1}{C_1 R_1} \qquad \text{............(I.3.10)}$$

$$\alpha_2 = \frac{1}{C_2 R_2} \qquad \text{............(I.3.11)}$$

$$I = \frac{E}{s} \frac{(s + \alpha_1)(s + \alpha_2)}{s^2 R + s(R\alpha_1 + R\alpha_2 + R_1\alpha_1 + R_2\alpha_2) + (R + R_1 + R_2)\alpha_1\alpha_2}$$

$$= \frac{E}{R} \frac{(s + \alpha_1)(s + \alpha_2)}{s\left[s^2 + s(\alpha_1 + \alpha_2 + \frac{R_1}{R}\alpha_1 + \frac{R_2}{R}\alpha_2) + (1 + \frac{R_1}{R} + \frac{R_2}{R})\alpha_1\alpha_2\right]}$$

$$= \frac{E}{R} \frac{(s + \alpha_1)(s + \alpha_2)}{s(s^2 + \beta s + \gamma)} \qquad \ldots\ldots\ldots\ldots(I.3.12)$$

where $\beta = \alpha_1(1 + \frac{R_1}{R}) + \alpha_2(1 + \frac{R_2}{R})$ ....(i.3.13)

$\gamma = \alpha_1\alpha_2(1 + \frac{R_1}{R} + \frac{R_2}{R})$ ....(I.3.14)

If the polynomial in s in the denominator of (I.3.12) has as its roots s = a and s = b, then (I.3.12) may be written

$$I = \frac{E}{R} \frac{(s + \alpha_1)(s + \alpha_2)}{s(s - a)(s - b)} \qquad \ldots\ldots\ldots\ldots(I.3.15)$$

Since $(s - a)(s - b) = s^2 + s\beta + \gamma$

therefore by (I.3.13) and (I.3.14)

$$\beta = -(a + b) = \alpha_1(1 + \frac{R_1}{R}) + \alpha_2(1 + \frac{R_2}{R}) \qquad \ldots\ldots(I.3.16)$$

$$\gamma = ab = \alpha_1\alpha_2(1 + \frac{R_1}{R} + \frac{R_2}{R}) \qquad \ldots\ldots\ldots\ldots(I.3.17)$$

Equation (I.3.15) transforms (f-t pair no. 1.111) back to

$$i = \frac{E}{R}\left[\frac{\alpha_1\alpha_2}{ab} + \frac{a^2 + a(\alpha_1 + \alpha_2) + \alpha_1\alpha_2}{a(a - b)}\,e^{at} + \frac{b^2 + b(\alpha_1 + \alpha_2) + \alpha_1\alpha_2}{b(b - a)}\,e^{bt}\right]$$

$$= \frac{E}{R}\left[\frac{1}{1 + \frac{R_1}{R} + \frac{R_2}{R}} + \frac{(a + \alpha_1)(a + \alpha_2)}{a(a - b)}\,e^{at} + \frac{(b + \alpha_1)(b + \alpha_2)}{b(b - a)}\,e^{bt}\right]$$

$$= \frac{E}{R + R_1 + R_2} + \frac{E}{R}\left[\frac{(a + \alpha_1)(a + \alpha_2)}{a(a - b)}\,e^{at} + \frac{(b + \alpha_1)(b + \alpha_2)}{b(b - a)}\,e^{bt}\right] \quad ..(I.3.18)$$

(b) To fit the current expression (I.3.18) to the data.

The first term $\frac{E}{R + R_1 + R_2}$ is the value of i_∞ and equation (I.3.18) has the form

$$i = i_\infty + i_1 + i_2 \quad ....(I.3.19)$$

or $$i - i_\infty = i' = A\,e^{-Bt} + C\,e^{-Dt} \quad ....(I.3.20)$$

i_∞ is assumed to have the same value as that chosen in analysing the previous circuit.

An attempt was made to fit the equation (I.3.18) to the available data by the method of least squares, but this was abandoned because of the extremely laborious arithmetic involved. The following method was used:

Plot log i' against t.

Case I: If $D \gg B$, then for large t

$$i' = A\,e^{-Bt} \text{ since } C\,e^{-Dt} \text{ is nearly zero} \quad (I.3.21)$$

and $\ln i' = \ln A - Bt$

or $\log_{10} i' = \log_{10} A - \frac{B}{2.303}\,t \quad \ldots(I.3.22)$

and therefore the latter part of the plot will be a straight line of slope $-\frac{B}{2.303}$ and intercept $\log_{10} A$ on the log i'-axis.

Case II: If $B \gg D$, then for large t

$$i' = C\,e^{-Dt} \text{ since } A\,e^{-Bt} \text{ is nearly } 0 \quad ..(I.3.23)$$

and $\ln i' = \ln C - Dt$

or $\log_{10} i' = \log_{10} C - \frac{D}{2.303}\,t \quad \ldots.(I.3.24)$

and similarly to Case I, the latter part of the plot will be a straight line of slope $-\frac{D}{2.303}$ and intercept $\log_{10} C$.

Case III: If $B \approx D$ and $D > B$, equation (I.3.20) may be written

$$i' = A\,e^{-Bt}\left(1 + \frac{C}{A}\,e^{-(D - B)t}\right) \quad \ldots\ldots(I.3.25)$$

Since $(D - B)$ is a small positive quantity, $e^{-(D - B)t}$ will be nearly 1 for small t. Therefore

$$i' = A\,e^{-Bt}\left(1 + \frac{C}{A}\right)$$

$$= (A + C)\,e^{-Bt} \qquad \ldots\ldots\ldots\ldots\ldots(I.3.26)$$

and $\ln i' = \ln (A + C) - Bt$

or $\log_{10} i' = \log_{10}(A + C) - \frac{B}{2.303}\,t$ (I.3.27)

and therefore the first part of the plot will be a straight line of slope $-\frac{B}{2.303}$ and intercept $\log_{10}(A + C)$.

In each of these three cases we have an expression for i_1 (or i_2). Hence i_2 (or i_1) may be found:

$$i_2 = i' - i_1 = C\,e^{-Dt} \qquad \ldots\ldots\ldots\ldots\ldots(I.3.28)$$

and $\log_{10}i_2 = \log_{10}C - \frac{D}{2.303}\,t$ ....(I.3.29)

A plot of log i_2 against t will be a straight line of slope $-\frac{D}{2.303}$ and intercept log C if the circuit fits (Graphs 9).

(c) <u>Evaluation of α_1, α_2, R_1, R_2, C_1 and C_2 from A, B, C, D.</u>

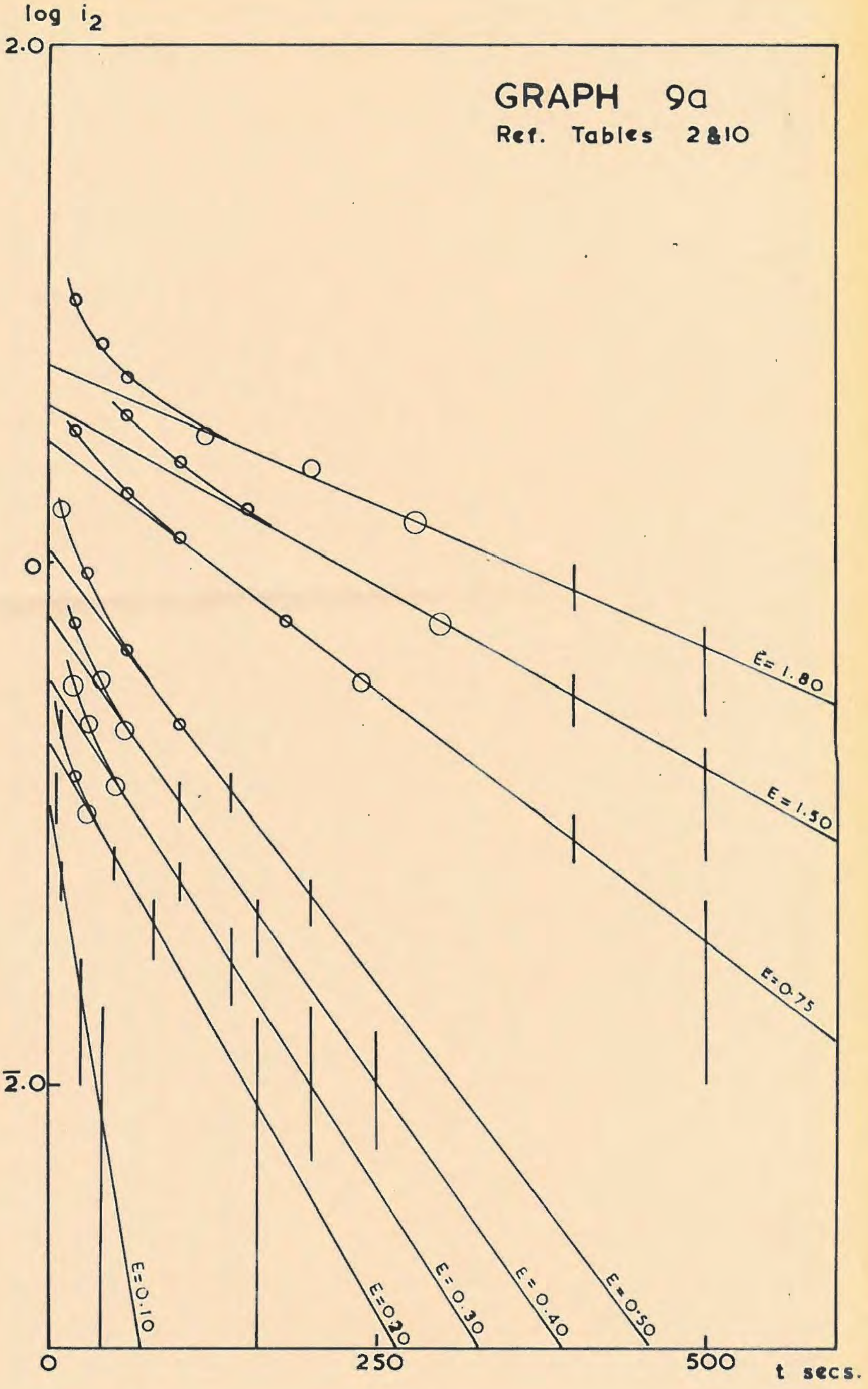
From equations (I.3.18) and (I.3.20)

$$A = \frac{E}{R}\,\frac{(a + \alpha_1)(a + \alpha_2)}{a(a - b)} \qquad \ldots\ldots\ldots\ldots(I.3.30)$$

$$B = -\,a \qquad \ldots\ldots\ldots\ldots(I.3.31)$$

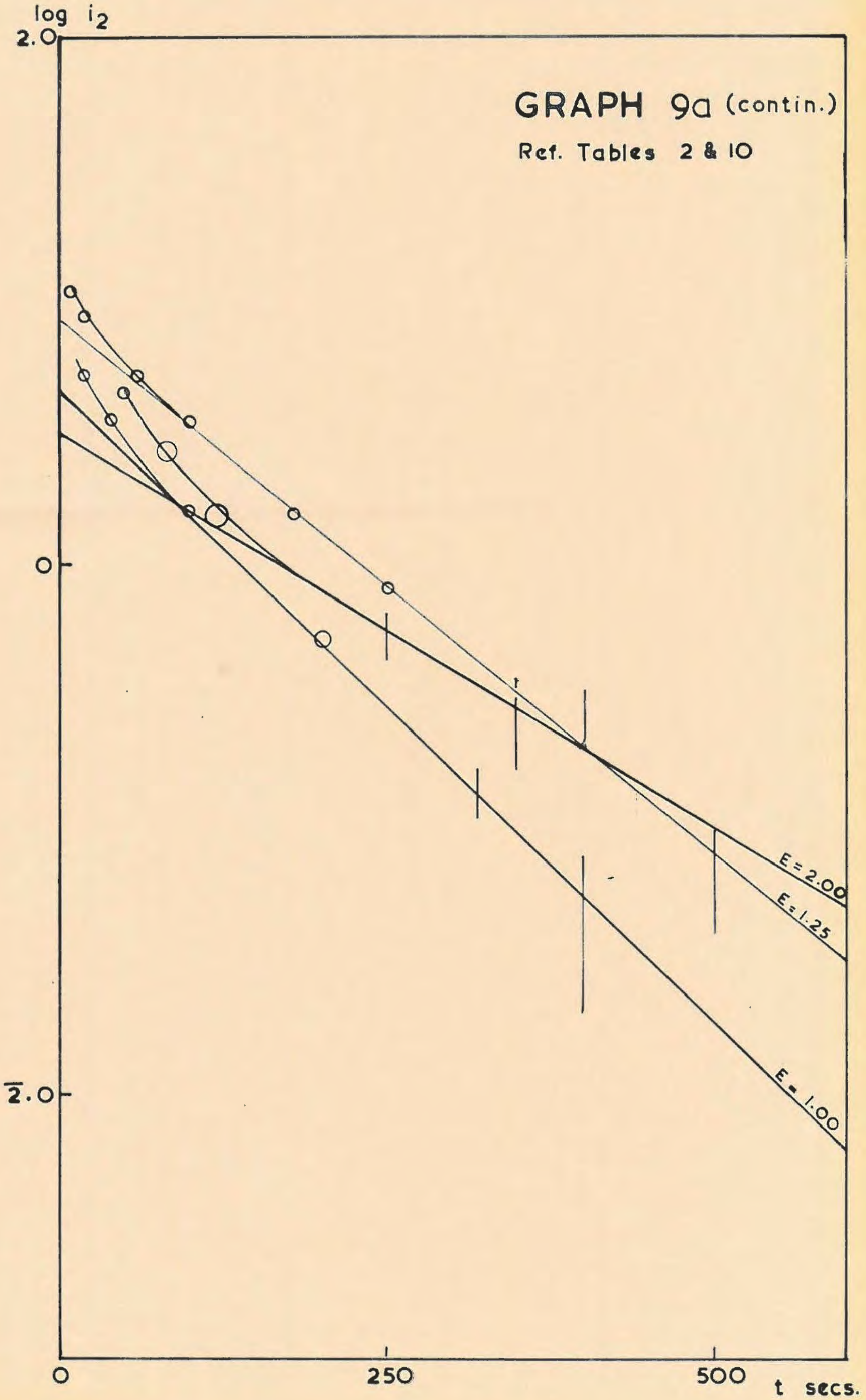
$$C = \frac{E}{R}\,\frac{(b + \alpha_1)(b + \alpha_2)}{b(b - a)} \qquad \ldots\ldots\ldots\ldots(I.3.32)$$

$$D = -\,b \qquad \ldots\ldots\ldots\ldots(I.3.33)$$



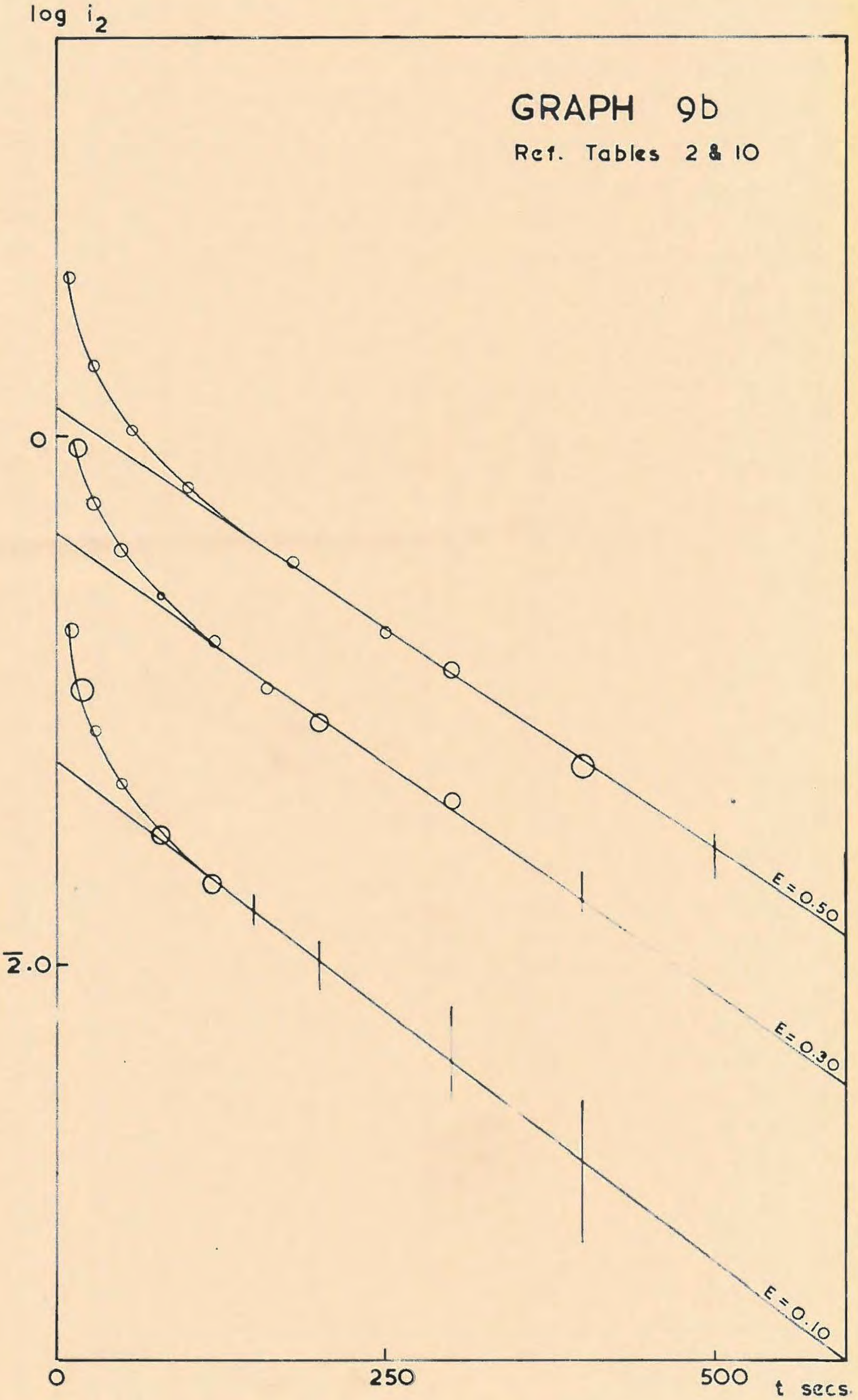
GRAPH 9a

Ref. Tables 2&10



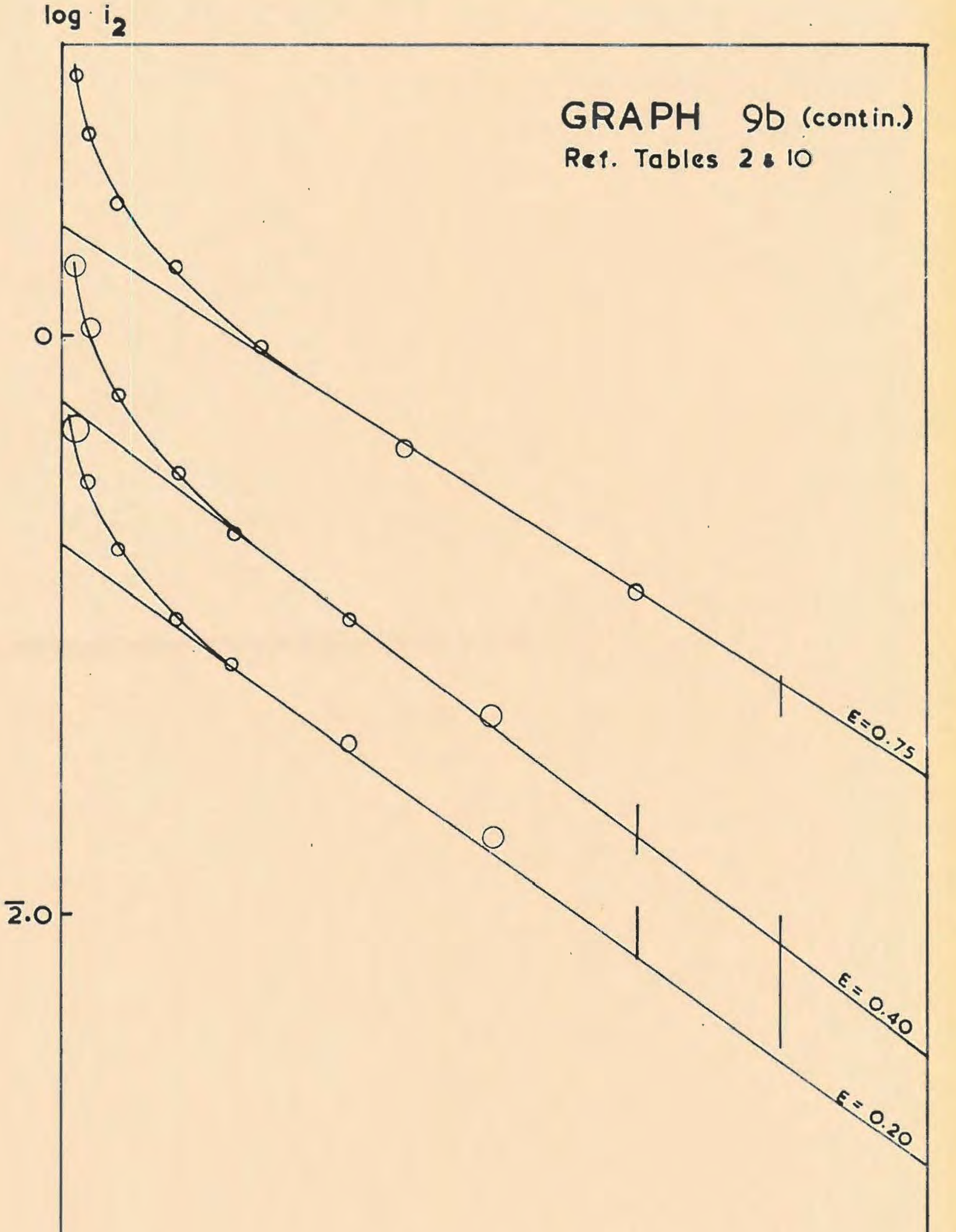
GRAPH 9a (contin.)

Ref. Tables 2 & 10



GRAPH 9b

Ref. Tables 2 & 10



GRAPH 9b (contin.)

Ref. Tables 2 & 10

From (I.3.30) and (I.3.31)

$$(a + \alpha_1)(a + \alpha_2) = A \frac{R}{E} a\ (a - b) = - \frac{R}{E} AB(D - B) \quad (I.3.34)$$

Therefore $a^2 + a(\alpha_1 + \alpha_2) + \alpha_1\alpha_2 = X$

i.e. $$a^2 + S_1 a + S_2 = X \quad \ldots\ldots\ldots\ldots\ldots (I.3.35)$$

where $$X = - \frac{R}{E} AB\ (D - B) \quad \ldots\ldots\ldots\ldots\ldots (I.3.36)$$

$$S_1 = \alpha_1 + \alpha_2 \quad \ldots\ldots\ldots\ldots\ldots (I.3.37)$$

and $$S_2 = \alpha_1\alpha_2 \quad \ldots\ldots\ldots\ldots\ldots (I.3.38)$$

Similarly from (I.3.32) and (I.3.34)

$$(b + \alpha_1)(b + \alpha_2) = C \frac{R}{E} b(b - a) = - \frac{R}{E} CD(B - D) \quad (I.3.39)$$

Therefore $b^2 + b(\alpha_1 + \alpha_2) + \alpha_1\alpha_2 = Y$

i.e. $$b^2 + S_1 b + S_2 = Y \quad \ldots\ldots\ldots\ldots\ldots (I.3.40)$$

where $$Y = - \frac{R}{E} C\ D\ (B - D) \quad \ldots\ldots\ldots\ldots\ldots (I.3.41)$$

S_1 and S_2 may be found by solving (I.3.35) and (I.3.41) by determinants as follows:

$$S_1 = \begin{vmatrix} X - a^2 & 1 \\ Y - b^2 & 1 \end{vmatrix} \div \begin{vmatrix} a & 1 \\ b & 1 \end{vmatrix}$$

$$= \frac{(X - Y) - (a^2 - b^2)}{a - b}$$

$$S_1 = \frac{X - Y}{a - b} - (a + b)$$

$$= - \frac{R}{E} (AB + CD) + (B + D) \quad \text{by (I.3.36) and (I.3.41)}$$

$$= B \left(1 - A \frac{R}{E}\right) + D \left(1 - C \frac{R}{E}\right) \quad \ldots\ldots\ldots\ldots\text{(I.3.42)}$$

$$S_2 = \begin{vmatrix} a & X - a^2 \\ b & Y - b^2 \end{vmatrix} - \begin{vmatrix} a & 1 \\ b & 1 \end{vmatrix}$$

$$= \frac{aY - bX - ab(b - a)}{a - b}$$

$$= \frac{aY - bX}{a - b} + ab$$

$$= \frac{R}{E} \frac{BCD(B - D) + DAB(B - D)}{-(B - D)} + BD \quad \text{by (I.3.36) and (I.3.41)}$$

$$= - \frac{R}{E} B D (A + C) + BD$$

$$= BD\left(1 - A \frac{R}{E}\right) - \frac{R}{E} BDC \quad \ldots\ldots\ldots\ldots\text{(I.3.43)}$$

α_1 and α_2 may be found from S_1 and S_2 as follows: Since by equations (I.3.37) and (I.3.38)

$$S_1 = \alpha_1 + \alpha_2 \quad \text{and} \quad S_2 = \alpha_1 \alpha_2 ,$$

α_1 and α_2 will be the roots of the equation

$$x^2 - S_1 x + S_2 = 0. \quad \ldots\ldots\ldots\ldots\text{(I.3.34)}$$

By solving this equation, using the numerical values of S_1 and S_2 obtained from (I.3.42) and (I.3.43), α_1 and α_2 may be obtained.

S_1 and S_2 were however not used, since the following approximations (which do not involve S_1 and S_2) were tested numerically and found not to introduce any appreciable error:

Since $S_1 = \alpha_1 + \alpha_2 = B(1 - A\frac{R}{E}) + D(1 - C\frac{R}{E})$ by (I.3.37) and (I.3.42)

and $S_2 = \alpha_1\alpha_2 = BD(1 - A\frac{R}{E}) - \frac{R}{E}BDC$ by (I.3.38) and (I.3.43)

$$= BD(1 - A\frac{R}{E})(1 - C\frac{R}{E}) - \frac{R^2BDAC}{E^2}$$

the approximations that

$$\alpha_1 = B(1 - A\frac{R}{E}) \qquad \ldots\ldots\ldots\ldots\ldots(I.3.45)$$

and

$$\alpha_2 = D(1 - C\frac{R}{E}) \qquad \ldots\ldots\ldots\ldots\ldots(I.3.46)$$

hold. Note that using equations (I.3.45) and (I.3.46) is equivalent to assuming that $\frac{BDACR^2}{E^2}$ is small. It is seen that this value of α_1 (I.3.45) is the same as that found for the previous circuit (equation I.2.20).

R_1 and R_2 may be found from equations (I.3.16) and (I.3.17) as follows:

From (I.3.16)

$$\alpha_1R_1 + \alpha_2R_2 = -R(a + b) - R(\alpha_1 + \alpha_2)$$

$$= R(B + D) - R(\alpha_1 + \alpha_2) \text{ by (I.3.31) and (I.3.33)}$$

$$\ldots\ldots\ldots\ldots(I.3.47)$$

From (I.3.17)

$$R_1 + R_2 = R(\frac{ab}{\alpha_1\alpha_2} - 1)$$

$$= R(\frac{BD}{\alpha_1\alpha_2} - 1) \text{ by (I.3.31) and (I.3.33)} \;.(I.3.48)$$

Solving for R_1 from (I.3.47) and (I.3.48)

$$(\alpha_1 - \alpha_2)R_1 = R(B + D) - R(\alpha_1 + \alpha_2) - R\alpha_2(\frac{BD}{\alpha_1\alpha_2} - 1)$$

and
$$R_1 = \frac{R}{\alpha_1 - \alpha_2} \quad (B + D) - (\alpha_1 + \alpha_2) - \alpha_2(\frac{BD}{\alpha_1\alpha_2} - 1) \qquad \text{.............(I.3.49)}$$

R_2 may be obtained from (I.3.48) using the value of R_1 from (I.3.49):

$$R_2 = R(\frac{BD}{\alpha_1\alpha_2} - 1) - R_1 \qquad \text{.............(I.3.50)}$$

C_1 and C_2 may be found from equations (I.3.10) and (I.3.11):

$$C_1 = \frac{1}{\alpha_1 R_1} \qquad \text{.............(I.3.51)}$$

$$C_2 = \frac{1}{\alpha_1 R_1} \qquad \text{.............(I.3.52)}$$

A, B, C, D, α_1 and α_2 are given in Table 10 and the corresponding R_1, R_2, C_1 and C_2 in Table 2.

Table 10. Ref. Fig. 3b.

Table 2.

E	A x 10^6	B x 10^3	C x 10^6	D x 10^3	α_1 x 10^3	α_2 x 10^3
(a) 0.01N KCl.		Ref. Graph 9a.				
0.10	0.063	3.78	0.123	71.5	3.69	68.2
0.20	0.151	3.42	0.209	20.5	3.32	19.7
0.30	0.282	2.86	0.354	18.2	2.76	17.5
0.40	0.513	2.49	0.616	16.8	2.37	15.9
0.50	0.977	2.76	1.12	15.4	2.56	14.2
0.75	1.445	1.64	2.88	8.88	1.52	7.60
1.00	2.14	0.830	4.68	11.0	0.762	9.05
1.25	4.79	0.369	8.51	9.41	0.316	7.01
1.50	8.51	0.322	4.07	6.50	0.254	5.85
1.80	12.88	0.691	5.75	5.12	0.503	4.52
2.00	20.0	0.115	3.24	6.91	0.0713	6.49
(b) 0.1N KCl.		Ref. Graph 9b.				
0.10	0.0339	1.038	0.0575	8.75	1.033	8.66
0.20	0.0724	0.785	0.191	8.30	0.781	8.26
0.30	0.245	0.738	0.416	8.06	0.730	7.95
0.40	0.479	0.670	0.595	8.80	0.660	8.62
0.50	0.832	0.761	1.26	8.10	0.745	7.83
0.75	1.66	0.807	2.46	7.40	0.783	7.09

(iv) Series resistance and three capacities with leaks (Fig. 3c).

The currents i, i_1, i_2 and i_3 in the branches of this circuit have the directions indicated. Kirchhoff's current relationships for the branches, when transformed, are

$$(R + R_1 + R_2 + R_3)I - R_1I_1 - R_2I_2 - R_3I_3 = \frac{E}{s} \quad .(I.4.1)$$

$$R_1I - (R_1 + \frac{1}{C_1s}) = 0 \quad ...(I.4.2)$$

$$R_2I - (R_2 + \frac{1}{C_2s}) = 0 \quad ...(I.4.3)$$

$$R_3I - (R_3 + \frac{1}{C_3s}) = 0 \quad ...(I.4.4)$$

Solving for I, by determinants, from these four equations, gives

$$I = \frac{E}{s}\frac{\begin{vmatrix} 1 & -R_1 & -R_2 & -R_3 \\ 0 & -(R_1 + \frac{1}{C_1s}) & 0 & 0 \\ 0 & 0 & -(R_2 + \frac{1}{C_2s}) & 0 \\ 0 & 0 & 0 & -(R_3 + \frac{1}{C_3s}) \end{vmatrix}}{\begin{vmatrix} R+R_1+R_2+R_3 & -R_1 & -R_2 & -R_3 \\ R_1 & -(R_1 + \frac{1}{C_1s}) & 0 & 0 \\ R_2 & 0 & -(R_2 + \frac{1}{C_2s}) & 0 \\ R_3 & 0 & 0 & -(R_3 + \frac{1}{C_3s}) \end{vmatrix}}$$

When solved, this determinant has the form

$$I = \frac{E}{R}\,\frac{(s + \alpha_1)(s + \alpha_2)(s + \alpha_3)}{s(s^3 + s^2\beta + s\gamma + \delta)} \qquad \ldots\ldots\ldots\ldots\ldots(I.4.5)$$

where (cf. equations I.3.10 <u>et</u> <u>seq</u>)

$$\alpha_1 = \frac{1}{C_1R_1} \qquad \ldots\ldots\ldots\ldots\ldots(I.4.6)$$

$$\alpha_2 = \frac{1}{C_2R_2} \qquad \ldots\ldots\ldots\ldots\ldots(I.4.7)$$

$$\alpha_3 = \frac{1}{C_3R_3} \qquad \ldots\ldots\ldots\ldots\ldots(I.4.8)$$

$$\beta = \alpha_1(1 + \frac{R_1}{R}) + \alpha_2(1 + \frac{R_2}{R}) + \alpha_3(1 + \frac{R_3}{R}) \ \ldots(I.4.9)$$

$$\gamma = \alpha_1\alpha_2(1 + \frac{R_1}{R} + \frac{R_2}{R}) + \alpha_2\alpha_3(1 + \frac{R_2}{R} + \frac{R_3}{R}) + \alpha_3\alpha_1(1 + \frac{R_3}{R} + \frac{R_1}{R})$$
$$\ldots\ldots\ldots\ldots\ldots(I.4.10)$$

$$\delta = \alpha_1\alpha_2\alpha_3\ (1 + \frac{R_1}{R} + \frac{R_2}{R} + \frac{R_3}{R}) \qquad \ldots\ldots\ldots\ldots\ldots(I.4.11)$$

If the **trinomial in** the denominator of (I.4.5) has as its roots s = a, s = b and s = c, then (I.4.5) may be written

$$I = \frac{E}{R}\,\frac{(s + \alpha_1)(s + \alpha_2)(s + \alpha_3)}{s(s - a)(s - b)(s - b)} \qquad \ldots\ldots\ldots\ldots\ldots(I.4.12)$$

Since $(s - a)(s - b)(s - c) = s^3 + s^2\beta + s\gamma + \delta$

Therefore

$$\beta = -(a + b + c)$$

$$= \alpha_1(1 + \frac{R_1}{R}) + \alpha_2(1 + \frac{R_2}{R}) + \alpha_3(1 + \frac{R_3}{R}) \quad \ldots\ldots\ldots(I.4.13)$$

$$\gamma = ab + bc + ca$$

$$= \alpha_1\alpha_2(1+\frac{R_1}{R}+\frac{R_2}{R}) + \alpha_2\alpha_3(1 + \frac{R_2}{R} + \frac{R_3}{R}) + \alpha_3\alpha_1(1 + \frac{R_3}{R} + \frac{R_1}{R})$$
$$\ldots\ldots\ldots\ldots\ldots(I.4.14)$$

$$\delta = -\ abc$$

$$= \alpha_1\alpha_2\alpha_3(1 + \frac{R_1}{R} + \frac{R_2}{R} + \frac{R_3}{R}) \qquad \ldots\ldots\ldots\ldots\ldots(I.4.15)$$

Equation (I.4.12) may be transformed back to a function of t using f-t pair no 0.11;

$$i = \frac{E}{R}\left[\frac{1}{1 + \frac{R_1}{R} + \frac{R_2}{R} + \frac{R_3}{R}} + \frac{(a + \alpha_1)(a + \alpha_2)(a + \alpha_3)}{a(a - b)(a - c)} e^{at} + \frac{(b + \alpha_1)(b + \alpha_2)(b + \alpha_3)}{b(b - a)(b - c)} e^{bt} + \frac{(c + \alpha_1)(c + \alpha_2)(c + \alpha_3)}{c(c - a)(c - b)} e^{ct} \right]$$

$$= \frac{E}{R + R_1 + R_2 + R_3} + \frac{E}{R}\left[\frac{(a + \alpha_1)(a + \alpha_2)(a + \alpha_3)}{a(a - b)(a - c)} e^{at} + \frac{(b + \alpha_1)(b + \alpha_2)(b + \alpha_3)}{b(b - a)(b - c)} e^{bt} + \frac{(c + \alpha_1)(c + \alpha_2)(c + \alpha_3)}{c(c - a)(c - b)} e^{ct} \right] \qquad \ldots\ldots\ldots\ldots\ldots(I.4.16)$$

(b) <u>To fit the expression (I.4.16) to the data.</u>

The first term $\frac{E}{R + R_1 + R_2 + R_3}$ is the value of i_∞, and equation (I.4.16) has the form

$$i = i_\infty + i_1 + i_2 + i_3 \qquad \ldots\ldots\ldots\ldots\ldots(I.4.17)$$

or $i - i_\infty = i' = i_1 + i_2 + i_3$

$$= A\ e^{-Bt} + C\ e^{-Dt} + G\ e^{-Ht} \qquad \ldots\ldots\ldots(I.4.18)$$

i_∞ is assumed to have the same value as that chosen in analysing the previous twocircuits. Equation (I.4.18) is fitted to the experimental curves in an analagous manner. In this case log $(i_2 + i_3)$ is the log i_2 of the two-condenser circuit. By plotting log $(i_2 + i_3)$ against t and drawing a straight line through the latter points, log i_2 may be obtained. i_1 and i_2 are therefore known and i_3 is obtained by subtracting $(i_1 + i_2)$ from i'. Log A, log C and log are the intercepts on the log i- axis of the straight line portions of the plots of $\log i'$, $\log (i_2 + i_3)$ and $\log i_3$ against t respectively. $-\frac{B}{2.303}$, $-\frac{D}{2.303}$ and $-\frac{H}{2.303}$ are the respective slopes of these straight lines (Graphs 8, 9 and 10 respectively).

(c) Evaluation of α_1, α_2, α_3, R_1, R_2, R_3, C_1, C_2 and C_3 from A, B, C, D, G and H.

Comparing (I.4.16) and (I.4.18) it is seen that

$$A = \frac{E}{R}\,\frac{(a + \alpha_1)(a + \alpha_2)(a + \alpha_3)}{a(a - b)(a - c)} \qquad \text{.............(I.4.19)}$$

$$B = -\,a \qquad \text{.............(I.4.20)}$$

$$C = \frac{E}{R}\,\frac{(b + \alpha_1)(b + \alpha_2)(b + \alpha_3)}{b(b - a)(b - c)} \qquad \text{.............(I.4.21)}$$

$$D = -\,b \qquad \text{.............(I.4.22)}$$

$$G = \frac{E}{R}\,\frac{(c + \alpha_1)(c + \alpha_2)(c + \alpha_3)}{c(c - a)(c - b)} \qquad \text{.............(I.4.23)}$$

$$H = -\,c \qquad \text{.............(I.4.24)}$$

From (I.4.19) and (I.4.20)

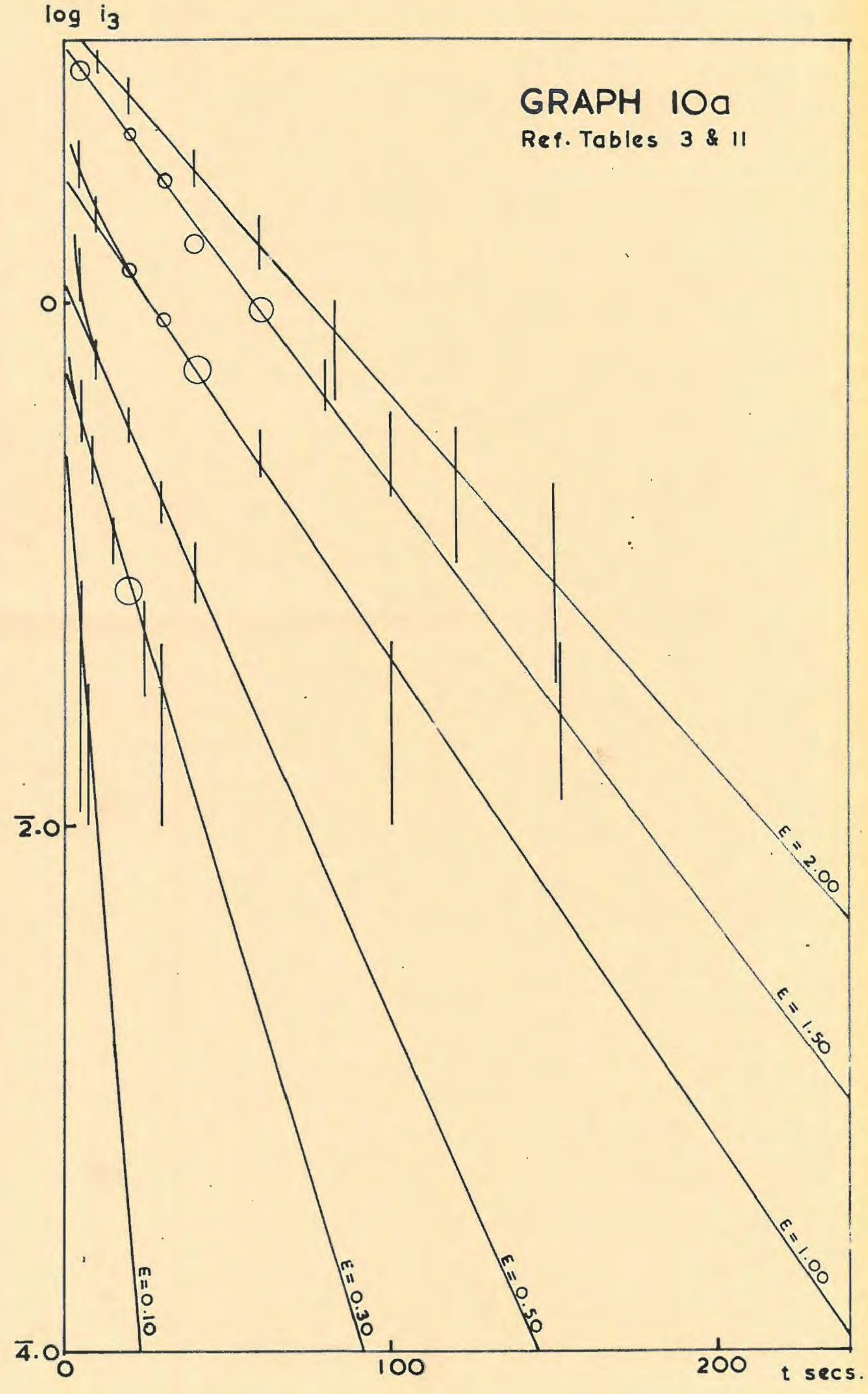
$$(a + \alpha_1)(a + \alpha_2)(a + \alpha_3) = A\,\frac{R}{E}\,a(a - b)(a - c)$$

$$= -\,A\,\frac{R}{E}\,B(B - D)(H - B) \qquad \text{(I.4.25)}$$

Therefore

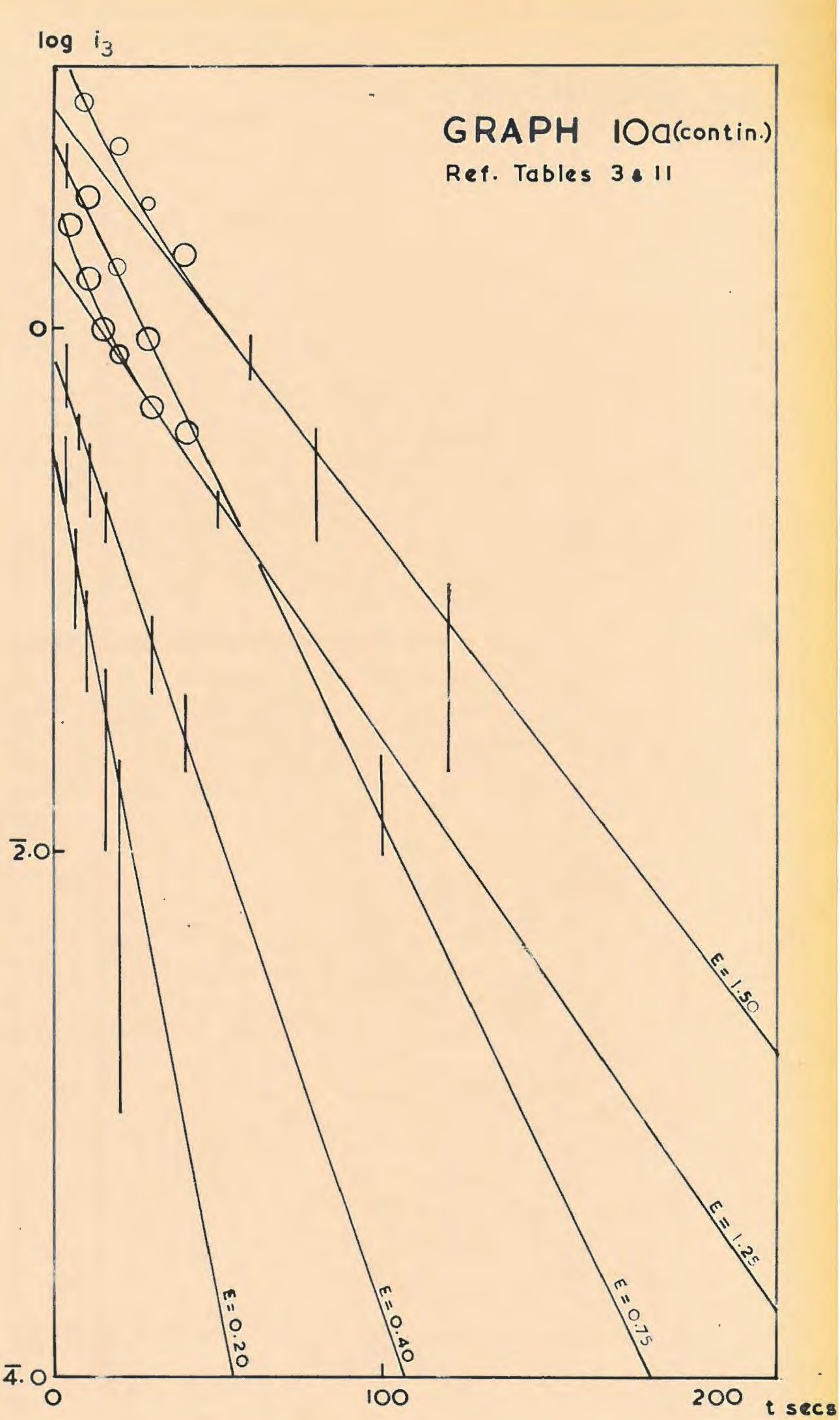
$$a^3 + (\alpha_1 + \alpha_2 + \alpha_3)a^2 + (\alpha_1\alpha_2 + \alpha_2\alpha_3 + \alpha_3\alpha_1)a + \alpha_1\alpha_2\alpha_3 = X$$

i.e. $a^3 + S_1\,a^2 + S_2\,a + S_3 = X$ ......(I.4.26)



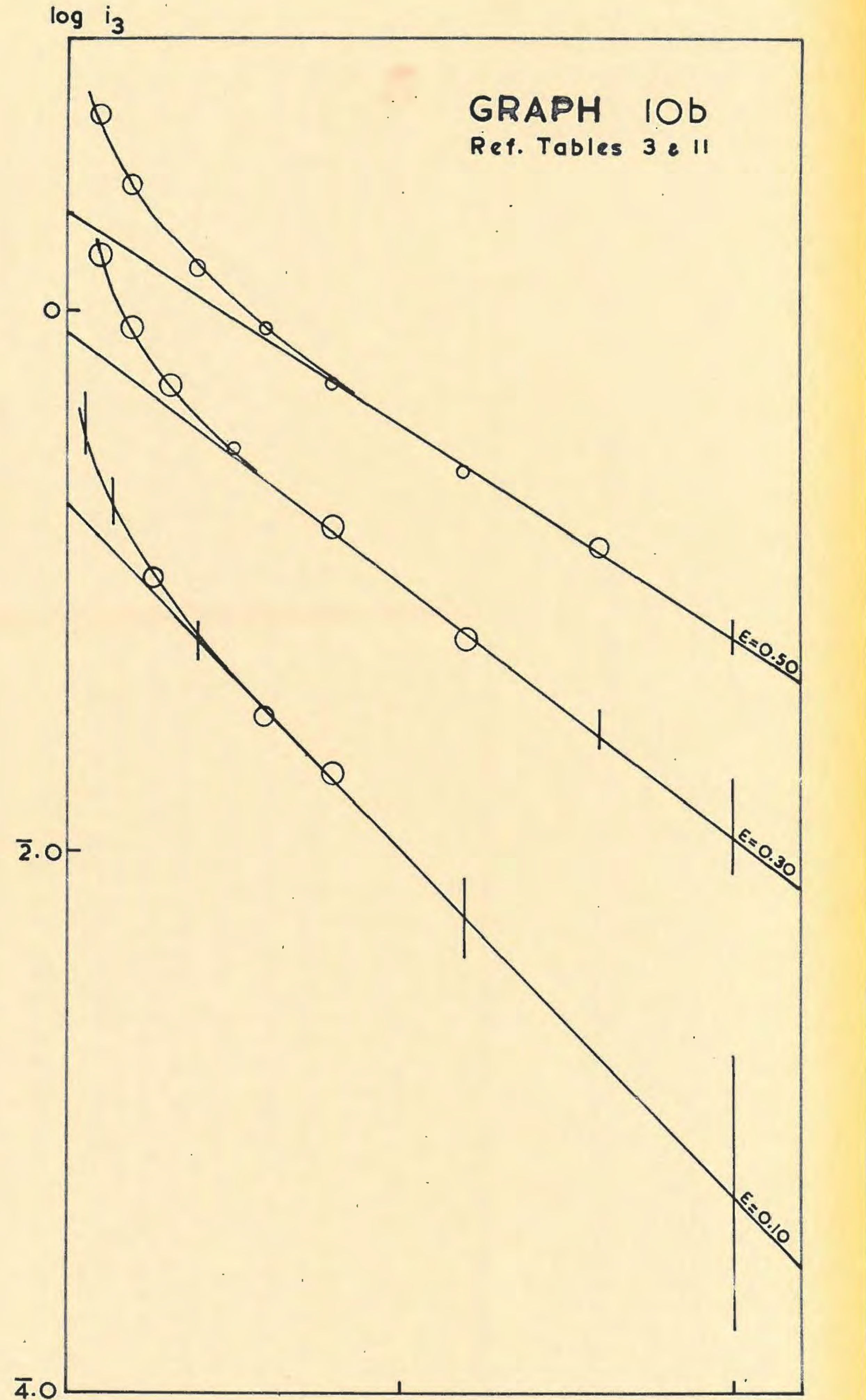
GRAPH 10a

Ref. Tables 3 & 11

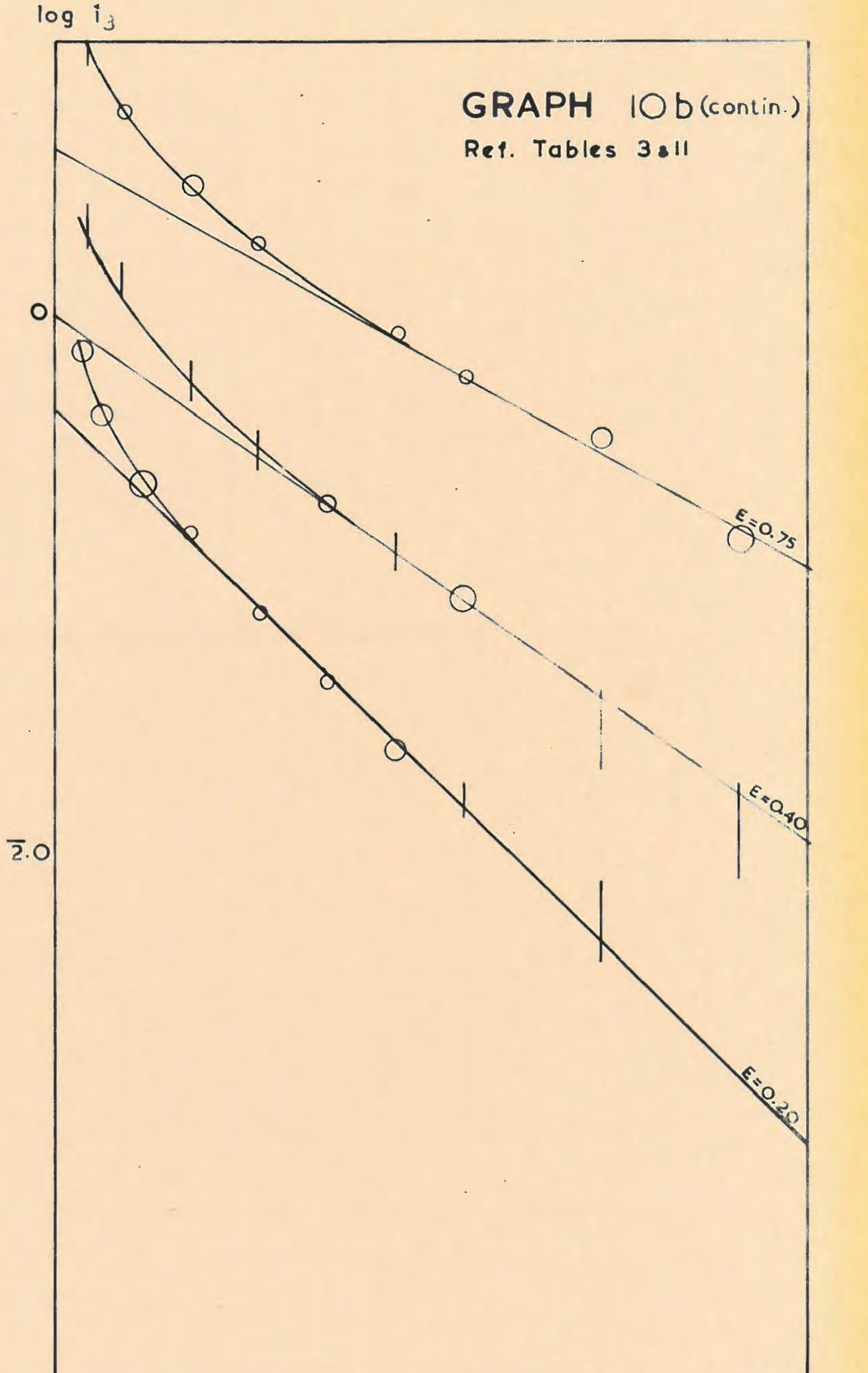


GRAPH 10a(contin.)

Ref. Tables 3 & 11



GRAPH 10b
Ref. Tables 3 & 11



GRAPH 10b (contin.)

Ref. Tables 3 & 11

where $X = -\frac{R}{E} AB(B - D)(H - B)$ ....(I.4.27)

$$S_1 = \alpha_1 + \alpha_2 + \alpha_3 \qquad \text{.............(I.4.28)}$$

$$S_2 = \alpha_1\alpha_2 + \alpha_2\alpha_3 + \alpha_3\alpha_1 \qquad \text{.............(I.4.29)}$$

$$S_3 = \alpha_1\alpha_2\alpha_3 \qquad \text{.............(I.4.30)}$$

Similarly from (I.4.21) and (I.4.22)

$$(b + \alpha_1)(b + \alpha_2)(b + \alpha_3) = C \frac{R}{E} b(b - a)(b - c)$$

$$= - C \frac{R}{E} D(B - D)(D - H) \quad \text{.(I.4.31)}$$

Therefore $b^3 + S_1 b^2 + S_2 b + S_3 = Y$ ....(I.4.32)

where $Y = -\frac{R}{E} CD(B - D)(D\ )\ H)$ ....(I.4.33)

Similarly from (I.4.23) and (I.4.24)

$$(c + \alpha_1)(c + \alpha_2)(c + \alpha_3) = G \frac{R}{E} c(c - a)(c - b)$$

$$= - \frac{R}{E} GH(H - B)(D - H) \quad \text{..(I.4.34)}$$

Therefore $c^3 + S_1 c^2 + S_2 c + S_3 = Z$ ....(i.4.35)

where $Z = -\frac{R}{E} GH(H - B)(D - H)$ ....(I.4.36)

S_1, S_2 and S_3 may be found by solving (I.4.26), (I.4.32)and (I.4.35) by determinants, to give the following:

$$S_1 = B(1 - A\tfrac{R}{E}) + D(1 - C\tfrac{R}{E}) + H(1 - G\tfrac{R}{E}) \quad ....(I.4.37)$$

$$S_2 = BD(1 - A\tfrac{R}{E}) + DH(1 - C\tfrac{R}{E}) + HB(1 - G\tfrac{R}{E}) - \tfrac{R}{E}(BDC + DGH + HAB) \quad ....(I.4.38)$$

$$S_3 = BDH(1 - A\tfrac{R}{E}) - \tfrac{R}{E}\,BDH(C + G) \quad ....(I.4.39)$$

Again the approximations that

$$\alpha_1 = B(1 - A\tfrac{R}{E}) \quad ....(I.4.40)$$

$$\alpha_2 = D(1 - C\tfrac{R}{E}) \quad ....(I.4.41)$$

and $\alpha_3 = H(1 - G\tfrac{R}{E})$ apply. ....(I.4.42)

It is therefore unnecessary to solve for α_1, α_2 and α_3 from S_1, S_2 and S_3.

R_1, R_2 and R_3 may be obtained from equations (I.4.13), (I.4.14) and (I.4.15), since in these equations β, γ and δ are known (since a, b, c are known) and α_1, α_2 and α_3 are known from equations (I.4.40), (I.4.41) and (I.4.42). The relations (I.4.28), (I.4.29) and (I.4.30) between α_1, α_2 and α_3 are also used. R_1, R_2 and R_3 are given by the following determinants:

$$R_1 = R\,\frac{\begin{vmatrix} (B + D + H - S_1) & \alpha_2 & \alpha_3 \\ (BD+DH+HB-S_2) & \alpha_2(\alpha_1 + \alpha_3) & \alpha_3(\alpha_1 + \alpha_2) \\ (\frac{BDH}{S_3} - 1) & 1 & 1 \end{vmatrix}}{-(\alpha_1 - \alpha_2)(\alpha_2 - \alpha_3)(\alpha_3 - \alpha_1)}$$

............(I.4.43)

$$R_2 = R \frac{\begin{vmatrix} \alpha_1 & (B + D + H - S_1) & \alpha_3 \\ \alpha_1(\alpha_2 + \alpha_3) & (BD + DH + HB - S_2) & \alpha_3(\alpha_1 + \alpha_2) \\ 1 & (\frac{BDH}{S_3} - 1) & 1 \end{vmatrix}}{-(\alpha_1 - \alpha_2)(\alpha_2 - \alpha_3)(\alpha_3 - \alpha_1)} \quad \ldots\ldots\ldots\ldots\ldots (I.4.44)$$

$$R_3 = R \frac{\begin{vmatrix} \alpha_1 & \alpha_2 & (B + D + H - S_1) \\ \alpha_1(\alpha_2 + \alpha_3) & \alpha_2(\alpha_1 + \alpha_3) & (BD+DH+HB-S_2) \\ 1 & 1 & (\frac{BDH}{S_3} - 1) \end{vmatrix}}{-(\alpha_1 - \alpha_2)(\alpha_2 - \alpha_3)(\alpha_3 - \alpha_1)} \quad \ldots\ldots\ldots\ldots\ldots (I.4.45)$$

Also, by (I.4.6), (I.4.7) and (I.4.8)

$$C_1 = \frac{1}{\alpha_1 R_1} \quad \ldots\ldots\ldots\ldots\ldots (I.4.46)$$

$$C_2 = \frac{1}{\alpha_1 R_1} \quad \ldots\ldots\ldots\ldots\ldots (I.4.47)$$

$$C_3 = \frac{1}{\alpha_1 R_1} \quad \ldots\ldots\ldots\ldots\ldots (I.4.48)$$

G, H, α_1, α_2 and α_3 are given in Table 11. (See Table 10 for A, B, C, D). The corresponding values of R_1, R_2, R_3, C_1, C_2 and C_3 are given in Table 3.

Table 11. Ref. Fig. 3c.

Table 3.

E	G x 10^6	H x 10^3	α_1 x 10^3	α_2 x 10^3	α_3 x 10^3
(a) 0.01N KCl.		Ref. Graph 10a.			
0.10	0.220	328	3.69	68.2	301
0.20	0.350	151.8	3.32	19.7	142.0
0.30	0.550	96.7	2.76	17.5	90.1
0.40	0.793	84.5	2,37	15.9	78.2
0.50	1.212	65.0	2.56	14.2	59.1
0.75	1.861	42.9	1.52	7.60	38.9
1.00	2.95	42.7	0.762	9.05	37.9
1.25	5.75	61.8	0.316	7.01	51.1
1.50	9.12	38.8	0.254	5.85	29.9
1.80	11.02	40.3	0.503	4.52	31.0
2.00	11.80	33.4	0.0743	6.49	25.9
(b) 0.1N KCl.		Ref. Graph 10b.			
0.10	0.191	54.5	1.033	8.66	53.2
0.20	0.436	57.2	0.781	8.26	55.5
0.30	0.830	43.6	0.730	7.95	42.0
0.40	0.975	40.8	0.660	8.62	39.5
0.50	2.34	36.7	0.745	7.83	34.5
0.75	3.94	32.1	0.783	7.09	29.9

(v) Series resistance, capacity and capacity with leak (Fig. 3d).

(a) To obtain the current expression.

The currents i and i_2 have the directions indicated. Kirchhoff's current relationships, when transformed, are

$$\left(R + R_2 + \frac{1}{C_1 s}\right)I \quad - \quad R_2 I_2 \;=\; \frac{E}{s} \qquad \text{..........(I.5.1)}$$

$$R_2 I \quad - \quad \left(\frac{1}{C_2 s} + R_2\right)I_2 \;=\; 0 \qquad \text{..........(I.5.2)}$$

Solving for I in the same manner as before, gives

$$I = \frac{E}{R}\,\frac{(s + \alpha_2)}{s^2 + s\beta + \gamma} \qquad \text{.............(I.5.3)}$$

where $\alpha_2 = \dfrac{1}{C_2 R_2}$ ....(I.5.4)

$$\alpha_1 = \frac{1}{C_1 R} \qquad \text{.............(I.5.5)}$$

$$\beta = \alpha_1 + \alpha_2 + \alpha_2 \frac{R_2}{R} \qquad \text{.............(I.5.6)}$$

$$\gamma = \alpha_1 \alpha_2 \qquad \text{.............(I.5.7)}$$

If the binomial in the denominator of (I.5.3) has as its roots s = a and s = b, then (I.5.3) may be written

$$I = \frac{E}{R}\,\frac{(s + \alpha_2)}{(s - a)(s - b)} \qquad \text{.............(I.5.8)}$$

Since $(s - a)(s - b) = s^2 + s\beta + \gamma$

therefore $\beta = -(a + b) = \alpha_1 + \alpha_2 + \alpha_2 \dfrac{R_2}{R}$ ......(I.5.9)

$$\gamma = ab = \alpha_1 \alpha_2 \qquad \text{............(I.5.10)}$$

Equation (I.5.8) transforms (f-t pair no. 1.107) to

$$i = \frac{E}{R} \quad \frac{(a + \alpha_2)}{a - b} e^{at} + \frac{(b + \alpha_2)}{b - a} e^{bt} \quad \text{........(I.5.11)}$$

(b) To fit the expression (I.5.11) to the data.

Equation (I.5.11) has the form

$$i = i_1 + i_2 \qquad \text{.............(I.5.12)}$$

$$= A e^{-Bt} + C e^{-Dt} \qquad \text{.............(I.5.13)}$$

Equation (I.5.13) is fitted to the experimental data in the same manner as equation (I.3.20), the only difference being that in this case i replaces i'. A, B, C and D may be obtained from the intercepts and slopes of the plots of log i and log i_2 against t in the same way as before (Graphs 11 and 12).

(c) Evaluation of α_1, α_2, R, R_2, C_1 and C_2 from A, B, C and D.

Comparing (I.5.11) and (I.5.13) it is seen that

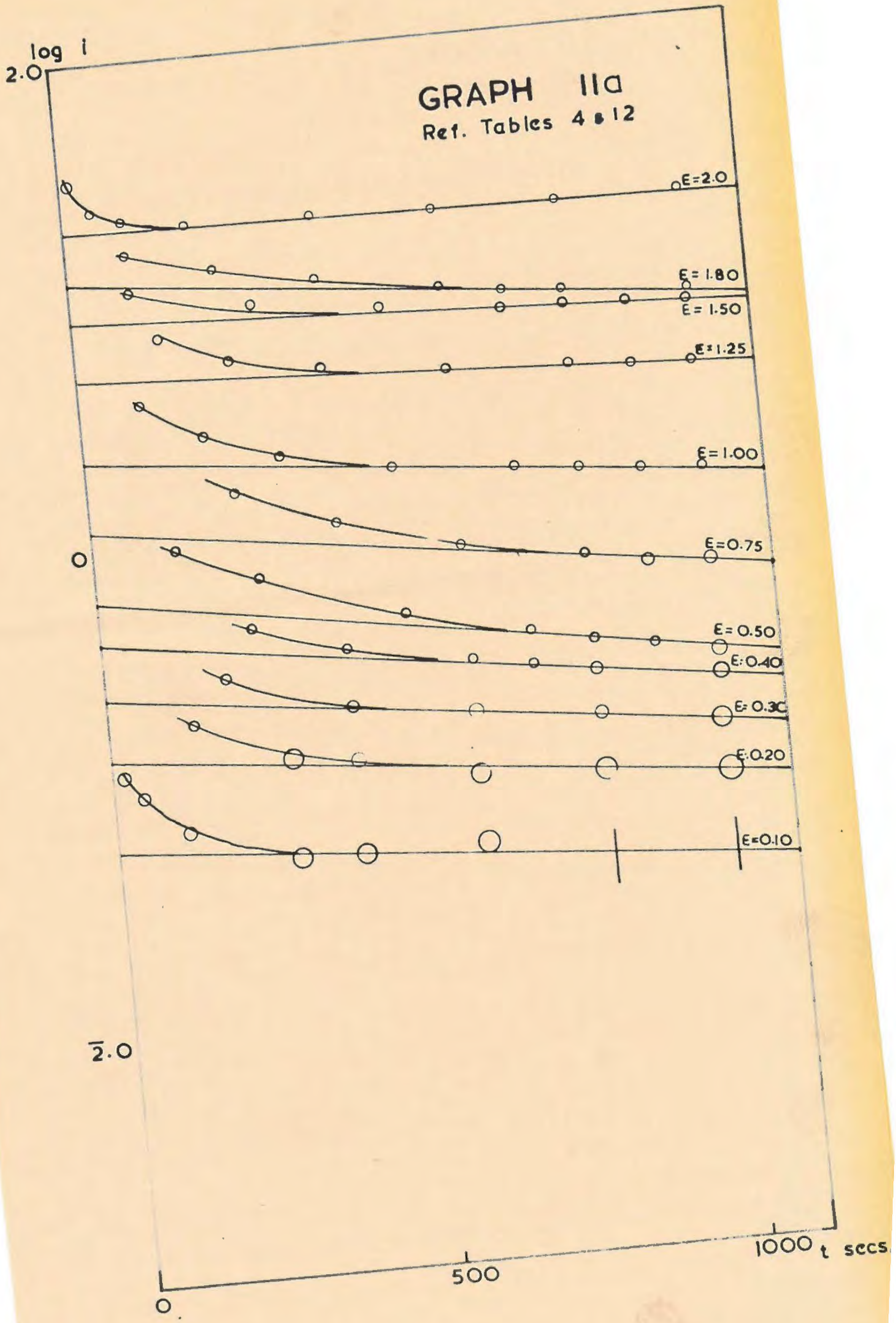
$$A = \frac{E}{R} \frac{(a + \alpha_2)}{(a - b)} \qquad \text{.............(I.5.14)}$$

$$B = - a \qquad \text{.............(I.5.15)}$$

$$C = \frac{E}{R} \frac{(b + \alpha_2)}{(b - a)} \qquad \text{.............(I.5.16)}$$

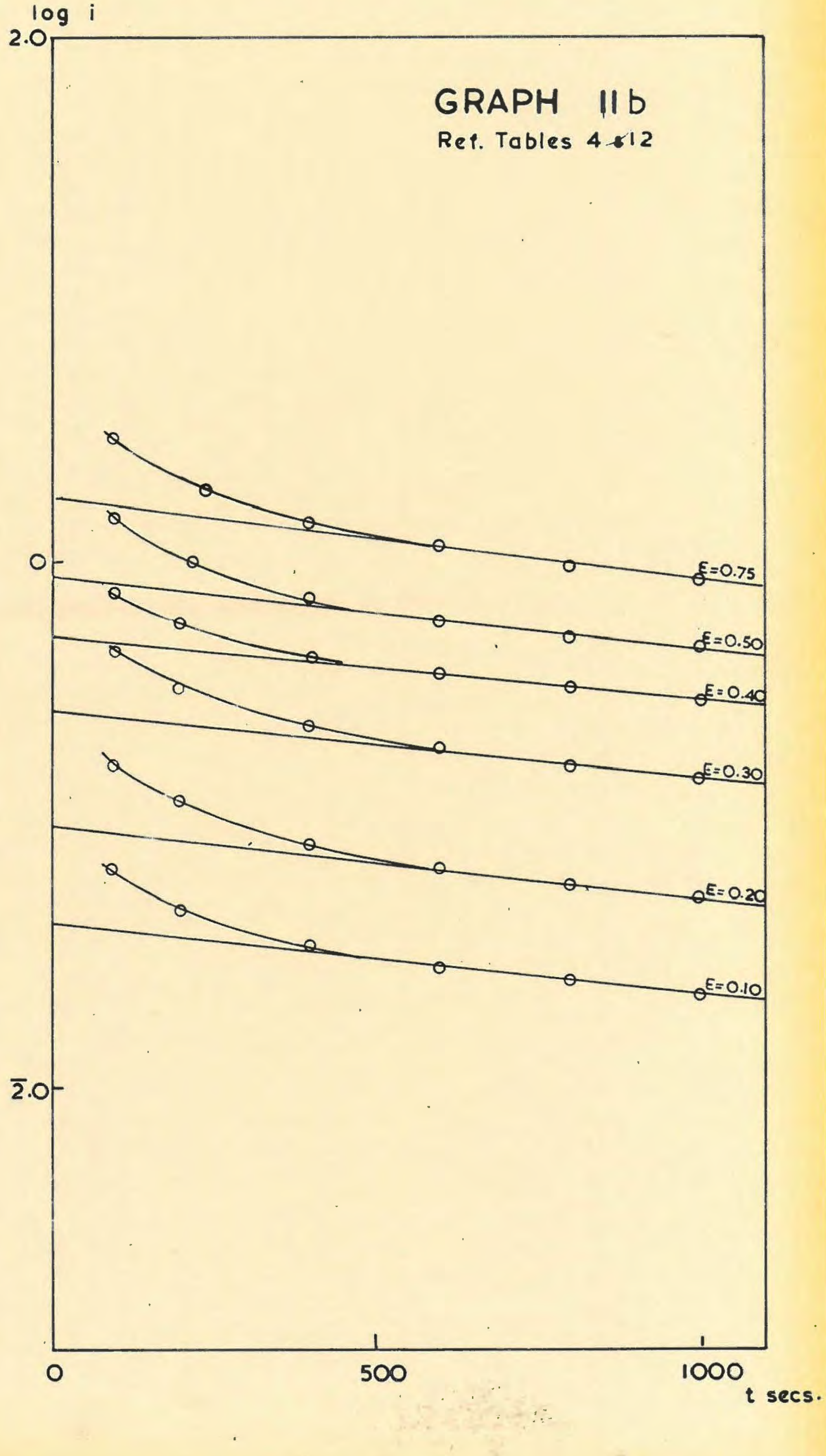
$$D = - b \qquad \text{.............(I.5.17)}$$

Since equations (I.5.14) and (I.5.16) contain only

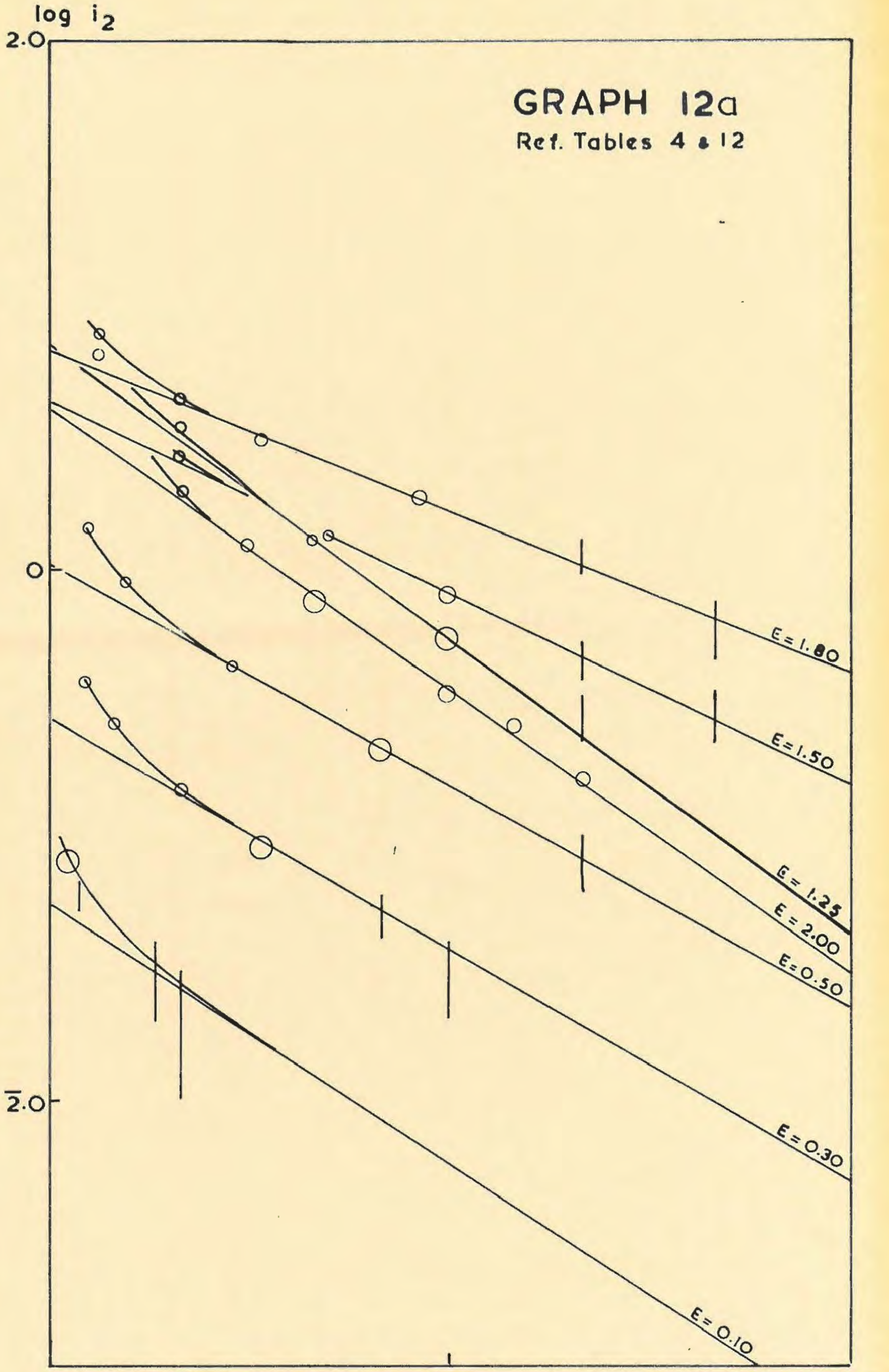


GRAPH IIa

Ref. Tables 4 & 12

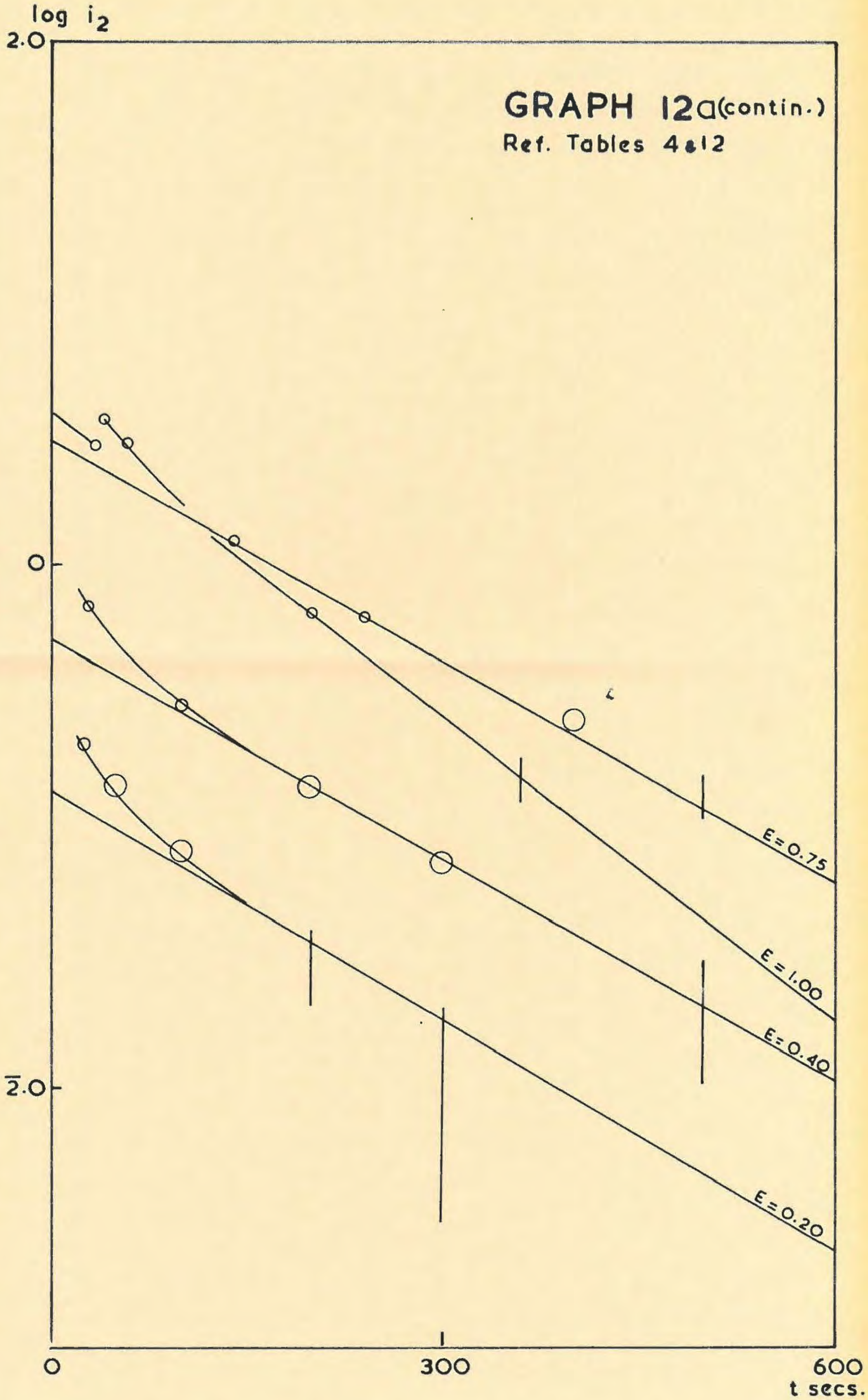

GRAPH 11b

Ref. Tables 4 & 12



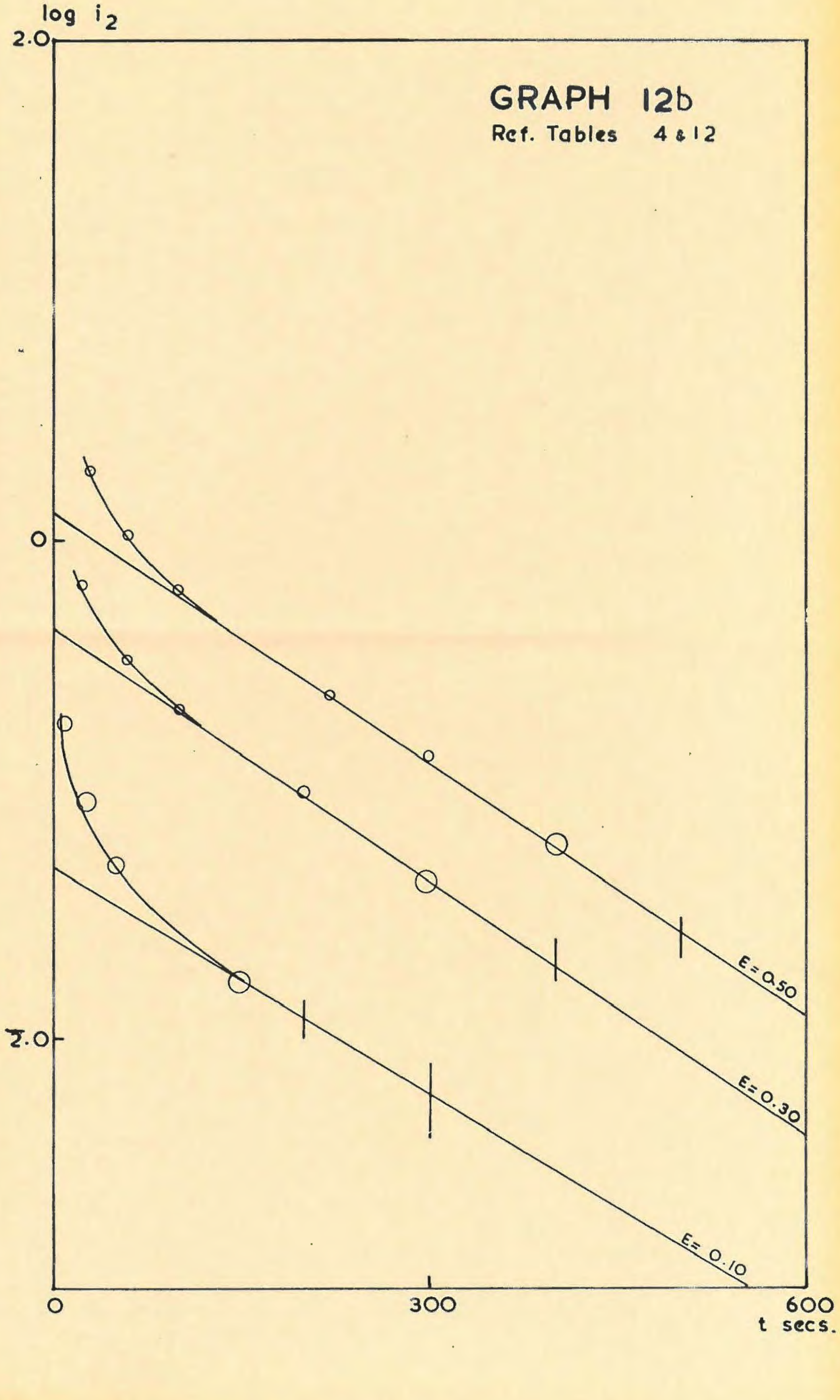
GRAPH 12a

Ref. Tables 4 & 12



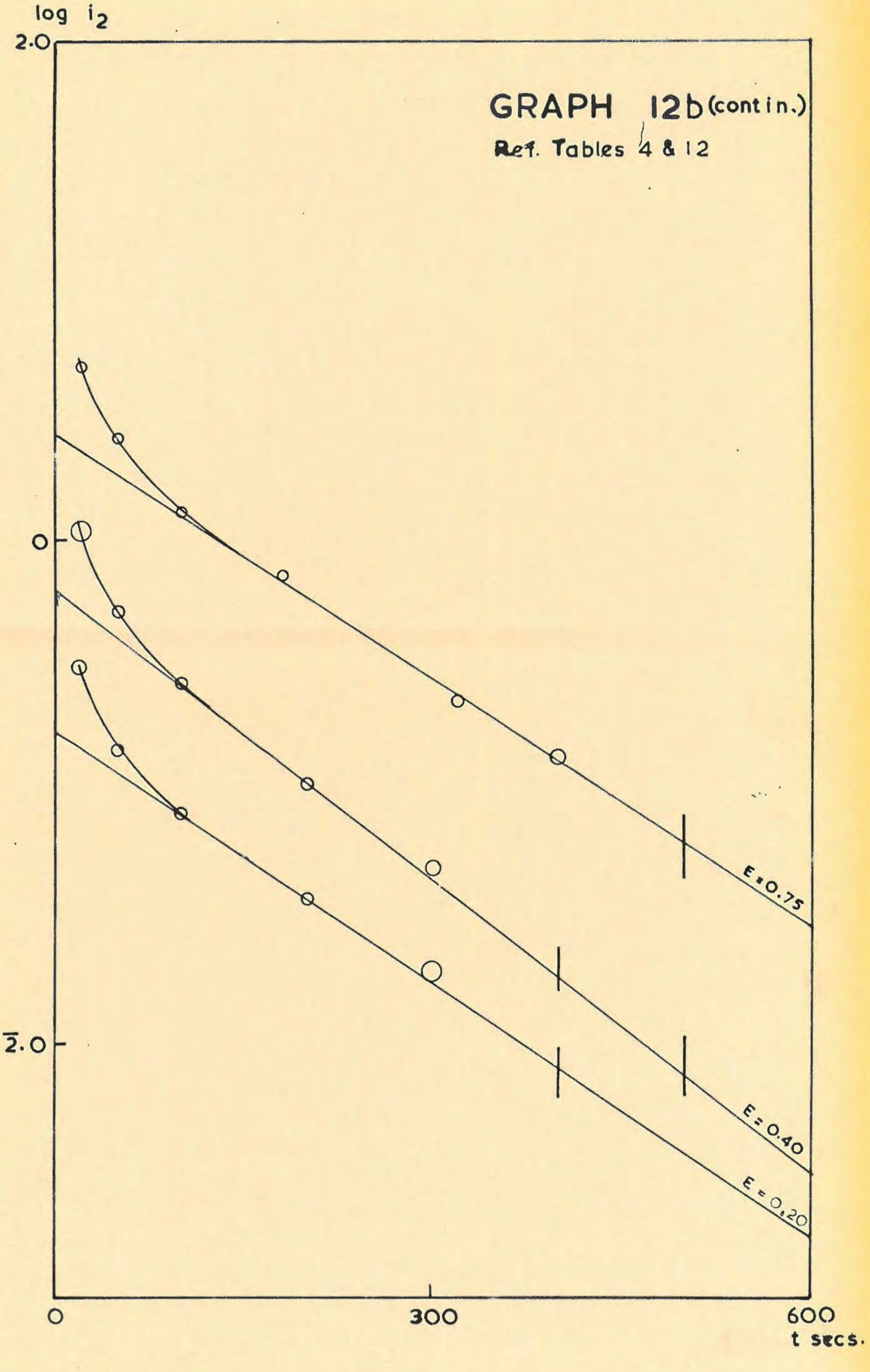
GRAPH 12a(contin.)

Ref. Tables 4 & 12



GRAPH 12b

Ref. Tables 4 & 12



GRAPH 12b (contin.)

Ref. Tables 4 & 12

R and α_2 as unknowns, they may be solved for from these equations. The values obtained for R should agree with the measured resistance. From (I.5.14) and (I.5.16):

$$\frac{A}{C} = -\frac{(a + \alpha_2)}{(b + \alpha_2)}$$

$$\alpha_2(\frac{A}{C} + 1) = -a - b\frac{A}{C}$$

$$= B + \frac{AD}{C} \text{ from (I.5.15) and (I.5.17)}$$

Hence $\alpha_2 = \dfrac{BC + AD}{A + C}$ ....(I.5.18)

R is the resistance as measured at zero time. It will therefore be given by $\frac{E}{i_0}$, where i_0 is the current at $t = 0$. On putting $t = 0$ in (I.5.13) it is seen that

$i_0 = A + C$ ....(I.5.19)

therefore

$R = \dfrac{E}{A + C}$ ....(I.5.20)

From (I.5.10) and (I.5.18)

$\alpha_1 = \dfrac{ab}{\alpha_2} = \dfrac{BD}{\alpha_2}$ ....(I.5.21)

From (I.5.9)

$R_2 = (B + D) - (\alpha_1 + \alpha_2)\dfrac{R}{\alpha_2}$ ....(I.5.22)

From (I.5.5) and (I.5.4)

$C_1 = \dfrac{1}{\alpha_1 R}$ ....(I.5.23)

$C_2 = \dfrac{1}{\alpha_1 R_1}$ ....(I.5.24)

A, B, C, D, α_1 and α_2 are given in Table 12.

Table 12. Ref. Fig. 3d.
Table 4.

E	A $\times 10^6$	B $\times 10^3$	C $\times 10^6$	D $\times 10^3$	$\alpha_1 \times 10^3$	$\alpha_2 \times 10^3$
(a) 0.01N KCl.		Ref. Graphs 11a, 12a.				
0.10	0.061	0.489	0.055	7.59	0.882	4.20
0.20	0.142	0.581	0.133	6.85	1.04	3.81
0.30	0.253	0.671	0.269	6,70	1.25	3.54
0.40	0.419	0.738	0.519	6.58	1.45	3.59
0.50	0.624	0.888	1.03	6.43	1.92	2.98
0.75	1.20	0.729	2.94	6.50	1.97	2.40
1.00	2,37	0.565	3.89	9.02	1.35	3.77
1.25	5.25	0.334	7.08	8.55	0.745	3.83
1.50	8.81	0.265	4.30	5.68	0.385	3.91
1.80	12.8	0.567	6.61	4.68	0.810	3.28
2.00	20.8	0.111	4.09	8.28	0.132	6.94
(b) 0.1N KCl.		Ref. Graphs 11b, 12b				
0.10	0.042	0.639	0.049	0.703	1.26	3.56
0.20	0.098	0.661	0.171	0.765	1.58	3.20
0.30	0.267	0.595	0.436	0.785	1.39	3.35
0.40	0.513	0.576	0.617	0.883	1.18	4.32
0.50	0.871	0.682	1.24	0.768	1.47	3.57
0.75	1.700	0.716	2.75	0.751	1.63	3.31

Appendix II.

Analysis of Non-linear Circuit (Fig. 4a).

R' varies with E in the manner given by equation (6.1.5):

i.e. $$R_t = \frac{K}{E_C}$$

Now $$i_R = \frac{E_C}{R_t} = \frac{E_C^2}{K} = K' E_C^2 \qquad \text{.............(II.1)}$$

where $$K' = \frac{1}{K} \qquad \text{.............(II.2)}$$

The circuit may now be analysed as follows:

$\frac{V - V_1}{R_1}$ = current flowing into node through R_1,

$C \frac{dV_1}{dt}$ = current flowing out of node through C,

and $\frac{V_1}{R}$ = current flowing out of node through R.

Since the same current flows into and out of the node,

$$\frac{V - V_1}{R_1} - C \frac{dV_1}{dt} - \frac{V_1}{R} = 0 \qquad \text{.............(II.3)}$$

which may be re-written as

$$C \frac{dV_1}{dt} + \frac{V_1}{R} + \frac{V_1}{R_1} - \frac{V}{R_1} = 0 \qquad \text{.............(II.4)}$$

On making the sunstitution $R = K/E_C = K/V_1 = 1/K'V_1$, equation (II.4) becomes

$$C \frac{dV_1}{dt} + K'V_1^2 + \frac{V_1}{R_1} - \frac{V}{R_1} = 0 \qquad \text{.............(II.5)}$$

This is a first order differential equation in V_1, the solution to which is obtainable by the standard method as follows:

$$t = -A\int \frac{dV_1}{V_1^2 + BV_1 - BV} + \text{constant} \quad \text{.........(II.6)}$$

$$= A\int \frac{dV_1}{(BV + \frac{B^2}{4}) - (V_1 + \frac{B}{2})^2} + \text{constant} \quad \text{......(II.7)}$$

where $A = \frac{C}{K'}$ ....(II.8)

$B = \frac{1}{K'R_1}$ ....(II.9)

The integral in (II.7) may be written in the form $\int \frac{dx}{a^2 - x^2}$ which has the solution $\frac{1}{a} \tanh^{-1} \frac{x}{a}$ or $\frac{1}{2a} \log \frac{(a + x)}{(a - x)}$ if $a > x$. The solution of (II.7) therefore is

$$t = \frac{A}{D} \tanh^{-1} \frac{B/2 + V_1}{D} + \text{constant} \quad \text{.........(II.10)}$$

$$\text{or} \quad t = \frac{A}{2D} \log_e \frac{D + (B/2 + V_1)}{D - (B/2 + V_1)} + \text{constant} \quad \text{.....(II.11)}$$

where $D = \frac{B}{2} (1 + \frac{4V}{B})^{\frac{1}{2}}$ ....(II.12)

The value of the constant term in each solution may be found by putting $V_1 = 0$ at $t = 0$. On including the value of the constant term and substituting back for A and B, equation (II.11) becomes

$$t = \frac{C}{2K'D} \log_e \frac{2V + V_1(2DK'R_1 - 1)}{2V - V_1(2DK'R_1 + 1)} \quad \text{.............(II.13)}$$

Using the approximation that $(1 + \frac{4V}{B})^{\frac{1}{2}} = 1 + \frac{2V}{B}$

i.e. $D = \frac{B}{2} + V$ ....(II.14)

equation (II.13), may be written

$$t = \frac{C}{2K'D} \log_e \frac{V}{V - V_1} \times \frac{B + V + V_1}{B + V} \quad \ldots\ldots\ldots\ldots\ldots (II.15)$$

V, V_1 ($= E - i_t R_1$), B and K' in this equation are all known and therefore C may be calculated. Equation (II.15) may be re-written

$$\log_{10} \frac{V}{B + V} + \log_{10} \left(\frac{B + 2V}{iR_1} - 1\right) = \frac{0.868K'D}{C} t \quad (II.16)$$

A graphical method of finding C is therefore by plotting $\log_{10} \left(\frac{B + 2V}{iR_1} - 1\right)$ against t, when a straight line of slope $\frac{0.868K'}{C}$ and intercept $\log_{10} \frac{V}{B + V}$ should be obtained.

Appendix III.

Calculation of the Diffusion Coefficient of HCl.

The diffusion coefficient of HCl did not appear to be available in the literature, but the diffusion coefficient of KCl was known to be 1.91×10^{-5} cm^2/sec. for 0.01N solution and 1.86×10^{-5} cm^2/sec. for 0.1N KCl (13). If the value 1.9×10^{-5} cm^2/sec. be taken, assuming it to be independent of concentration, the diffusion coefficient of HCl may be calculated by means of the equation relating diffusion coefficient to the the equivalent conductance at infinite dilution (14).

$$D = 2000\ R\ T\ \frac{\bar{M}}{C}\ (1 + C\ \frac{\partial \ln y_{\pm}}{\partial C}) \qquad \ldots\ldots\ldots\ldots.(III.1)$$

where

$$\bar{M} = 1.074 \times 10^{-20} \times \frac{\lambda_1^0\ \lambda_2^0\ c}{\nu_1\ |z_1|\ \Lambda^0} + \Delta\bar{M}' + \Delta\bar{M}'' \quad .(III.2)$$

λ_1^0, λ_2^0 and Λ^0 are the limiting equivalent conductances of the ions 1 and 2 and the diffusing electrolyte (which ionises to give ions 1 and 2) respectively. $C\ \frac{\partial \ln y_{\pm}}{\partial C}$, $\bar{M}'$ and $\bar{M}''$ are correction terms for ionic interaction, and since the order of D is all that is required, they may be neglected. If D_{HCl} and D_{KCl} are respectively the diffusion coefficients of HCl and KCl, it is readily seen from equations (III.1) and (III.2) that

$$\frac{D_{HCl}}{D_{KCl}} = \frac{\lambda^0_{H^+}\ \lambda^0_{Cl^-}\ \Lambda^0_{KCl}}{\lambda^0_{K^+}\ \lambda^0_{Cl^-}\ \Lambda^0_{HCl}} \qquad \ldots\ldots\ldots\ldots.(III.3)$$

$$= \frac{350 \times 150}{73.5 \times 426}$$

$$= 3.2 \times 10^{-5}\ \text{cm}^2/\text{sec.}$$

This is in good agreement with the figures given by Conway (15): 3.34×10^{-5} cm^2/sec. for concentration 0 and 3.07×10^{-5} cm^2/sec. for concentration o.05N.

Appendix IV.

Data used in the Analysis of Charge Curves.

In the following tables:

E is in volts, t in seconds, and i in μAmps.

Pages 80 to 90 refer to 0.01N KCl and pages 91 to 96 to 0.1N solution.

All logs are to base 10.

i' is given by $(i_t - i_\infty)$ (Ref. Fig. 3a, Graphs 8).

i_2 (column 4) is given by $(i' - i_1)$, where i_1 is obtained from the linear part of the plot of log i' against t. (Ref. Fig. 3b, Graphs 9).

i_3 (column 5) is given by $(i' - i_1 - i_2)$, where i_1 and i_2 are obtained from the linear portions of the plots of log i' and log i_2 against t respectively.

i_2 (column 6) is given by $(i_t - i_1)$, where i_1 is obtained from the linear part of the plot of log i against t. (Ref. Fig. 3d, Graphs 11 and 12).

(a) 0.01N KCl. E = 0.10

t	i_t	i'	i_2	i_3	i_2
0	2.65	2.61	2.56	2.44	2.59
3	0.40 ± 0.05	0.35	0.29	0.19	0.30
5	0.23 ± 0.03	0.19	0.13	0.04	0.17
7	0.19 ± 0.02	0.15	0.09	0.02	0.13
10	0.16 ± 0.01	0.12	0.06	0.00	0.10
13	0.15	0.11	0.05		0.09
16	0.14	0.10	0.04		0.08
20	0.13	0.09	0.03		0.07
25	0.12	0.08	0.02		0.06
30	0.11	0.07	0.01		0.05
40	0.10	0.06	0.01		0.04
50	0.10	0.06	0.01		0.04
60	0.09	0.05	0.00		0.03
80	0.09	0.05			0.03
100	0.08	0.04			0.02
120	0.07	0.03			0.01
150	0.06	0.02			0.00
250	0.06	0.02			
300	0.05	0.01			
400	0.05	0.01			
600	0.05	0.01			
800	0.04	0.00			
1000	0.04				

$\Xi = 0.20$

t	a i_t	i'	i_2	i_3	i_2
0	5.3	5.2	5.0	4.8	5.2
4	0.8 ± 0.2	0.7	0.5	0.3	0.7
7	0.55 ± 0.05	0.45	0.30	0.12	0.41
10	0.47 ± 0.03	0.39	0.24	0.07	0.33
13	0.43 ± 0.02	0.35	0.21	0.05	0.29
16	0.40	0.32	0.18	0.03	0.26
20	0.37 ± 0.01	0.29	0.15	0.01	0.23
25	0.34	0.26	0.12	0.00	0.20
30	0.33	0.25	0.11		0.19
40	0.31	0.23	0.10		0.17
50	0.28	0.20	0.07		0.14
60	0.26	0.18	0.06		0.12
80	0.23	0.15	0.04		0.10
100	0.21	0.13	0.02		0.08
120	0.20	0.12	0.02		0.07
140	0.19	0.11	0.02		0.06
160	0.18	0.10	0.01		0.05
200	0.16	0.08	0.00		0.03
250	0.14	0.06			0.02
300	0.13	0.05			0.01
400	0.12	0.04			
600	0.10	0.02			
800	0.09	0.01			
1000	0.08	0.00			

$\Xi = 0.30$

t	i_t	i'	i_2	i_3	i_2
0	7.96	7.84	7.56	7.71	
4	1.6 ± 0.2	1.5	1.2	1.3	
6	1.1 ± 0.1	1.0	0.7	0.8	
9	0.95 ± 0.05	0.85	0.55	0.70	
12	0.85 ± 0.03	0.73	0.46	0.60	
15	0.78	0.66	0.39	0.53	
20	0.71	0.59	0.33	0.46	
25	0.66	0.54	0.28	0.41	
30	0.62 ± 0.02	0.50	0.24	0.37	
35	0.59	0.47	0.22	0.34	
40	0.55 ± 0.01	0.43	0.18	0.30	
50	0.51	0.39	0.14	0.26	
60	0.48	0.36	0.13	0.23	
80	0.42	0.30	0.08	0.18	
100	0.39	0.27	0.06	0.15	
120	0.36	0.24	0.04	0.13	
140	0.34	0.22	0.03	0.11	
160	0.32	0.20	0.02	0.09	
200	0.29	0.17	0.01	0.07	
250	0.26	0.14	0.00	0.05	
300	0.24	0.12		0.03	
400	0.20	0.08		0.00	
600	0.17	0.05			
800	0.15	0.03			
1000	0.13	0.01			

B = 0.40

t	i_t	i'	i_2	i_3	i_2
0	10.6	10.4	9.9	9.3	10.2
5	2.0 ± 0.2	1.8	1.3	0.7	1.6
10	1.6 ± 0.1	1.4	0.9	0.4	1.2
15	1.36 ± 0.05	1.20	0.70	0.21	0.94
20	1.23 ± 0.03	1.07	0.58	0.13	0.81
30	1.08	0.92	0.44	0.06	0.67
40	0.98 ± 0.02	0.82	0.35	0.03	0.57
50	0.90	0.74	0.28	0.00	0.49
60	0.84	0.68	0.23		0.44
80	0.75	0.59	0.17		0.35
100	0.68	0.52	0.12		0.29
120	0.62	0.46	0.08		0.23
140	0.59 ± 0.01	0.43	0.07		0.21
160	0.55	0.39	0.04		0.18
200	0.50	0.34	0.02		0.14
250	0.45	0.29	0.01		0.10
300	0.41	0.25	0.00		0.07
400	0.35	0.19			0.03
500	0.31	0.15			0.02
600	0.28	0.12			0.01
700	0.25	0.09			
800	0.23	0.07			
900	0.22	0.06			
1000	0.20	0.04			

$\Xi = 0.50$

t	i_t	i'	i_2	i_3	i_2
0	13.3	13.1	12.1	11.0	12.7
5	3.5 ± 0.3	3.3	2.3	1.3	2.9
10	2.8 ± 0.1	2.6	1.6	0.6	2.2
15	2.5 ± 0.05	2.3	1.4	0.5	1.9
20	2.28	2.08	1.17	0.34	1.66
30	1.98 ± 0.03	1.78	0.89	0.17	1.38
40	1.77	1.57	0.70	0.09	1.17
60	1.49 ± 0.02	1.29	0.46	0.00	0.90
100	1.18	0.98	0.24		0.60
140	0.99	0.79	0.13		0.44
180	0.86	0.66	0.07		0.33
200	0.81	0.61	0.05		0.29
250	0.71	0.51	0.02		0.21
300	0.62	0.42	0.00		0.14
350	0.57	0.37			0.11
400	0.52	0.32			0.08
500	0.45	0.25			0.05
600	0.39 ± 0.01	0.19			0.03
700	0.35	0.15			0.01
800	0.30	0.10			0.00
900	0.28	0.08			
1000	0.25	0.05			

E = 0.75

t	i_t		i'	i_2	i_3	i_2
0	19.9		19.6	18.2	15.3	18.7
5	6.9	± 0.3	6.6	5.2	2.4	5.7
10	5.8	± 0.15	5.5	4.1	1.5	4.6
15	5.2	± 0.1	4.9	3.5	1.0	4.0
20	4.9	± 0.05	4.6	3.2	0.8	3.7
30	4.40		4.1	2.7	0.5	3.22
40	4.00		3.7	2.4	0.4	2.82
50	3.60		3.39	2.07	0.21	2.53
60	3.42		3.12	1.83	0.13	2.27
80	3.04	± 0.04	2.74	1.48	0.06	1.91
100	2.77		2.47	1.24	0.06	1.65
140	2.29	± 0.03	1.99	0.84		1.20
180	1.96		1.66	0.59		0.91
240	1.63	± 0.02	1.33	0.35		0.62
320	1.32		1.02	0.17		0.36
400	1.13		0.83	0.09		0.24
450	1.03		0.73	0.04		0.16
500	0.96		0.66	0.03		0.13
600	0.82		0.52	0.00		0.04
700	0.73		0.43			0.01
800	0.67		0.37			
900	0.62		0.32			
1000	0.59		0.29			

E = 1.00

t	i_t	i'	i_2	i_3	i_2
0	26.5	26.1	24.0	19.3	24.1
5	10.4 ± 0.7	10.0	7.9	3.4	8.0
10	8.9 ± 0.3	8.5	6.4	2.2	6.5
15	8.1 ± 0.1	7.7	5.6	1.6	5.7
20	7.6	7.2	5.1	1.3	5.3
30	6.69	6.29	4.20	0.81	4.36
40	6.06	5.66	3.57	0.55	3.74
60	5.15	4.75	2.71	0.27	2.86
100	3.93 ± 0.05	3.53	1.58	0.03	1.69
150	3.20 ± 0.04	2.80	0.89		1.01
200	2.76	2.34	0.52		0.64
240	2.53	2.13	0.36		0.45
280	2.34 ± 0.03	1.94	0.23		0.31
320	2.20	1.80	0.14		0.21
360	2.09	1.69	0.09		0.15
400	2.00	1.60	0.05		0.10
450	1.90	1.50	0.01		0.06
500	1.83	1.43	0.00		0.04
600	1.71	1.31			0.02
700	1.60	1.20			
800	1.51	1.11			
900	1.43 ± 0.02	1.03			
1000	1.38	0.98			

E = 1.25

t	i_t	i'	i_2	i_3	i_2
0	33.2	32.7	27.9	19.4	27.0
5	18 ± 1	18	13	5	13
10	16.1 ± 0.3	15.6	10.8	3.1	10.9
15	15.3 ± 0.2	14.8	10.0	2.6	10.1
20	14.0	13.5	8.8	1.7	8.8
30	12.6 ± 0.1	12.1	7.4	0.9	7.4
40	11.5	11.0	6.3	0.4	6.3
60	10.3	9.8	5.1	0.2	5.1
100	8.44 ± 0.07	7.94	3.35	0.02	3.37
140	7.33	6.83	2.31		2.32
180	6.52 ± 0.05	6.02	1.55		1.58
200	6.20	5.70	1.28		1.29
250	5.65	5.15	0.81		0.82
300	5.29	4.79	0.52		0.55
350	5.04	4.54	0.36		0.37
400	4.87	4.37	0.27		0.28
450	4.67	4.17	0.14		0.15
500	4.52	4.02	0.07		0.08
600	4.30	3.80	0.00		
700	4.16	3.66			
800	4.02 ± 0.04	3.52			
900	3.89	3.39			
1000	3.79	3.29			

$E = 1.50$

t	i_t	i'	i_2	i_3	i_2
0	39.8	39.2	30.7	26.6	31.0
5	20.6 ± 0.7	20.0	11.5	7.5	11.8
10	19.1 ± 0.4	18.5	10.0	6.1	10.3
15	17.8 ± 0.3	17.2	8.7	5.0	9.0
20	16.9 ± 0.2	16.3	7.9	4.3	8.1
30	15.3 ± 0.1	14.7	6.3	2.9	6.5
40	13.8	13.2	4.8	1.6	5.1
60	12.67	12.07	3.71	0.92	4.0
80	11.85	11.25	2.95	0.49	3.22
100	11.26	10.66	2.42	0.28	2.67
120	10.84	10.24	2.05	0.17	2.31
150	10.28 ± 0.07	9.68	1.57	0.02	1.83
180	9.93	9.33	1.29		1.53
210	9.63	9.03	1.09		1.31
250	9.28	8.68	0.85		1.04
300	8.92	8.32	0.59		0.79
350	8.62	8.02	0.43		0.58
400	8.38	7.78	0.30		0.45
500	7.97 ± 0.06	7.37	0.13		0.28
600	7.68	7.08	0.08		0.18
700	7.38	6.78	0.00		0.05
800	7.12	6.52			
900	6.94	6.34			
1000	6.74	6.14			

E = 1.30

t	i_t		i'	i_2	i_3	i_2
0	47.8		47.1	34.2	28.4	35.1
5	29	± 1	28	15	9	16
10	26.4	± 0.5	25.7	12.8	7.3	14.7
15	24.9	± 0.4	24.2	11.6	6.2	12.3
20	23.5	± 0.3	22.8	10.2	5.0	10.9
30	21.6	± 0.2	20.9	8.3	3.3	9.0
40	20.0		19.3	6.8	2.1	7.5
60	18.1	± 0.15	17.4	5.1	0.8	5.8
80	17.1		16.4	4.2	0.3	4.9
100	16.3		15.6	3.6	0.1	4.3
120	15.7		15.0	3.1	0.0	3.8
140	14.9		14.2	2.5		3.1
160	14.7		14.0	2.5		3.1
200	14.2		13.5	2.3		2.8
240	13.3		12.6	1.7		2.2
280	12.7		12.0	1.4		1.8
360	11.8		11.1	1.1		1.4
400	11.3		10.6	0.8		1.1
500	10.2		9.5	0.4		0.6
600	9.3	± 0.1	8.6	0.1		0.2
700	8.6		7.9	0.0		
800	8.2		7.5			
900	7.6		6.9			
1000	7.2		6.5			

E = 2.00

t	i_t		i'	i_2	i_3	i_2
0	53		52	32	29	32
5	34	± 1	33	13	10	13
10	32		31	11	8	11
20	30		29	9	6	9
30	27.5	± 0.5	26.5	6.5	3.9	6.8
40	26.3		25.5	5.7	3.2	5.6
50	25.1	± 0.4	24.3	4.5	2.2	4.5
60	24.4		23.6	3.8	1.7	3.8
80	23.2	± 0.3	22.4	2.6	0.7	2.6
100	22.5	± 0.2	21.7	2.0	0.4	1.9
120	22.0		21.2	1.5	0.1	1.5
150	21.6	± 0.1	20.8	1.2	0.1	1.2
200	21.08		20.28	0.78		0.76
250	20.75		19.95	0.54		0.52
300	20.47		19.67	0.39		0.33
350	20.25		19.45	0.26		0.25
400	20.07		19.27	0.22		0.16
500	19.63		18.83	0.00		0.00
600	19.46		18.66			
700	19.21		18.41			
800	19.05		18.25			
900	18.82		18.02			
1000	18.62		17.82			

(b) 0.1N KCl. E = 0.10

t	i_t	i'	i_2	i_3	i_2
0	7.70	7.69	7.66	7.60	7.66
3	0.5 ± 0.1	0.5	0.5	0.4	0.5
5	0.35 ± 0.05	0.34	0.31	0.25	0.31
7	0.29 ± 0.04	0.28	0.25	0.20	0.25
10	0.22 ± 0.01	0.21	0.18	0.13	0.18
13	0.19	0.18	0.15	0.10	0.15
16	0.17	0.16	0.13	0.08	0.13
20	0.15	0.14	0.11	0.06	0.11
25	0.13	0.12	0.09	0.04	0.09
30	0.119 ± 0.002	0.109	0.076	0.032	0.078
40	0.101	0.091	0.059	0.019	0.060
50	0.090	0.080	0.048	0.012	0.050
60	0.082	0.072	0.040	0.000	0.042
80	0.073	0.063	0.031	0.002	0.033
100	0.065	0.055	0.025	0.001	0.026
120	0.060	0.050	0.020		0.022
150	0.055	0.045	0.016		0.017
200	0.048	0.038	0.010		0.012
300	0.040	0.030	0.005		0.006
400	0.035	0.025	0.003		0.003
600	0.028	0.018	0.000		0.000
800	0.025	0.015			
1000	0.022	0.012			

E = 0.20

t	i_t	i'	i_2	i_3	i_2
0	15.4	15.4	15.3	15.1	15.3
4	1.0 ± 0.1	1.0	0.9	0.7	0.9
7	0.69 ± 0.05	0.67	0.60	0.42	0.59
10	0.57 ± 0.04	0.55	0.48	0.30	0.47
13	0.49 ± 0.03	0.47	0.40	0.23	0.39
16	0.44 ± 0.02	0.42	0.35	0.18	0.34
20	0.40 ± 0.01	0.38	0.31	0.15	0.30
25	0.349 ± 0.003	0.329	0.258	0.103	0.253
30	0.316	0.296	0.225	0.077	0.220
40	0.270 ± 0.002	0.250	0.179	0.043	0.174
50	0.241	0.221	0.150	0.024	0.145
60	0.221	0.201	0.132	0.016	0.128
80	0.193	0.173	0.104	0.006	0.100
100	0.172	0.152	0.084	0.000	0.081
120	0.158	0.138	0.072		0.067
140	0.147	0.127	0.061		0.058
160	0.136	0.116	0.051		0.049
200	0.122	0.102	0.039		0.037
250	0.108	0.088	0.028		0.025
300	0.099	0.079	0.021		0.020
400	0.084	0.064	0.010		0.008
600	0.067	0.047	0.001		0.001
800	0.058	0.038			
1000	0.052	0.032			

$E = 0.30$

t	i_t	i'	i_2	i_3	i_2
0	23.1	23.1	22.9	22.5	22.8
3	3.1 ± 0.2	3.1	2.9	2.5	2.8
5	2.2 ± 0.16	2.2	2.0	1.6	1.9
7	1.8 ± 0.12	1.8	1.6	1.2	1.5
10	1.53 ± 0.08	1.50	1.26	0.88	1.27
16	1.15 ± 0.06	1.12	0.88	0.52	0.89
20	1.03 ± 0.04	1.00	0.76	0.41	0.77
25	0.91 ± 0.02	0.88	0.64	0.30	0.65
30	0.82	0.79	0.55	0.23	0.56
40	0.72	0,69	0.45	0.15	0.46
50	0.633 ± 0.01	0,603	0.369	0.093	0.375
60	0.581 ± 0.005	0.551	0.318	0.062	0.324
80	0.505	0.475	0.246	0.028	0.251
100	0.453	0.423	0.198	0.013	0.202
120	0.416	0.386	0.163	0.006	0.167
140	0.384	0.354	0.135	0.001	0.138
160	0.360	0.330	0.114		0.117
200	0.333	0.293	0.084		0.096
250	0.294	0.264	0.061		0.064
300	0.267	0.237	0.042		0.043
400	0.231	0.201	0.019		0.021
600	0.191	0.161	0.003		0.004
800	0.165	0.135			
1000	0.149	0.119			

E = 0.40

t	i_t	i'	i_2	i_3	i_2
0	30.8	30.8	30.3	29.7	30.3
5	3.3 ± 0.4	3.3	2.8	2.2	2.8
10	2.3 ± 0.2	2.3	1.8	1.3	1.8
15	1.86 ± 0.15	1.82	1.34	0.82	1.36
20	1.58 ± 0.1	1.54	1.07	0.56	1.08
30	1.27 ± 0.06	1.23	0.76	0.30	0.77
40	1.12 ± 0.02	1.08	0.61	0.19	0.62
50	1.01	0.97	0.51	0.13	0.51
60	0.94 ± 0.01	0.90	0.44	0.09	0.45
80	0.821	0.781	0.326	0.030	0.332
100	0.750	0.710	0.263	0.013	0.268
120	0.693 ± 0.005	0.653	0.209	0.000	0.215
140	0.652	0.612	0.175		0.182
160	0.616	0.576	0.147		0.149
200	0.561	0.521	0.103		0.105
250	0.510 ± 0.004	0.470	0.064		0.069
300	0.479	0.439	0.048		0.050
400	0.426	0.386	0.020		0.020
500	0.389 ± 0.003	0.349	0.005		0.008
600	0.362	0.322	0.001		
700	0.341	0.301			
800	0.322	0.282			
900	0.306	0.266			
1000	0.286	0.246			

E = 0.50

t	i_t	i'	i_2	i_3	i_2
0	38.5	38.5	37.7	36.5	37.6
5	7.1 ± 0.5	7.1	6.3	5.1	6.2
10	4.8 ± 0.2	4.8	4.0	2.9	3.9
15	3.9 ± 0.1	3.9	3.1	2.0	3.0
20	3.36 ± 0.03	3.31	2.50	1.45	2.50
30	2.71 ± 0.02	2.65	1.84	0.86	1.86
40	2.33	2.27	1.46	0.55	1.48
60	1.87 ± 0.01	1.82	1.03	0.25	1.03
80	1.64	1.59	0.80	0.13	0.81
100	1.47	1.42	0.64	0.06	0.65
140	1.242 ± 0.007	1.192	0.43	0.01	0.448
180	1.09	1.04	0.32		0.31
220	0.985	0.935	0.227		0.230
250	0.923	0.873	0.181		0.183
300	0.845	0.795	0.131		0.086
350	0.778	0.729	0.088		0.058
400	0.723	0.673	0.056		0.025
500	0.646 ± 0.005	0.596	0.026		
600	0.577	0.527	0.002		
700	0.539	0.489			
800	0.503	0.453			
900	0.469 ± 0.004	0.419			
1000	0.445	0.395			

$E = 0.75$

t	i_t		i'	i_2	i_3	i_2
0	57.7		57.6	55.9	53.4	56.0
.5	13.4	± 1	13.3	11.6	9.2	11.7
10	9.5	± 0.4	9.4	7.8	5.5	7.8
15	8.0	± 0.3	7.9	6.3	4.1	6.3
20	6.6	± 0.2	6.5	4.9	2.8	4.9
30	5.4	± 0.05	5.3	3.7	1.8	3.7
40	4.6	± 0.04	4.5	2.9	1.1	2.9
50	4.15	± 0.03	4.07	2.49	0.81	2.53
60	3.81		3.73	2.15	0.58	2.19
80	3.32		3.24	1.69	0.34	1.72
100	2.90	± 0.02	2.82	1.30	0.14	1.32
140	2.48		2.40	0.92	0.05	0.95
180	2.21		2.13	0.71		0.72
240	1.86		1.78	0.42		0.42
320	1.58	± 0.007	1.50	0.22		0.23
400	1.41		1.33	0.13		0.14
450	1.33		1.25	0.10		0.10
500	1.24		1.16	0.05		0.06
600	1.13		1.05	0.03		0.03
700	1.02		0.94	0.00		
800	0.95		0.87			
900	0.88		0.80			
1000	0.83		0.75			

Appendix V.

Discharge Current Values.

In the following tables:

E is in volts, t in seconds and i in μAmps.

Section (a) (pages 98 and 99) and Section (b) (page 100) contain data for 0.01 and 0.1N KCl solutions respectively.

(a) 0.01N KCl.

E	0.10	0.20	0.30	0.40	0.50	0.75
t	i	i	i	i	i	i
2	0.45					
3					3.5	
4	0.20	0.7	1.3			5.0
5				1.8	2.2	
6	0.13		0.7			
7		0.35			1.7	3.1
8	0.10			1.15		
10	0.09	0.29			1.30	2.5
11				0.90		
13	0.08	0.20				2.0
15			0.40	0.69	1.00	
16	0.07	0.18				1.75
20	0.06	0.16	0.31	0.55	0.82	1.49
25	0.05	0.14		0.48	0.69	1.30
30	0.04	0.14	0.23	0.41	0.58	1.13
35		0.13	0.21	0.37		1.03
40	0.04	0.11	0.18	0.33	0.48	0.91
45		0.10	0.17	0.31		
50	0.04	0.09	0.16	0.28	0.40	0.76
60	0.03	0.08	0.13	0.24	0.35	0.65
70	0.03	0.07	0.12	0.21	0.31	0.57
80	0.02	0.06	0.10	0.19	0.27	0.51
90					0.25	0.46
100	0.02	0.05	0.09	0.16	0.23	0.41
120	0.01	0.05	0.07	0.14	0.19	0.36
140					0.17	0.31
150	0.01	0.05	0.06	0.12		
160					0.15	0.28
180					0.14	0.26
200	0.00	0.04	0.04	0.09	0.13	0.23
230						0.21
250		0.04	0.04	0.08	0.10	
260						0.19
300		0.03	0.04	0.07	0.09	0.17
400		0.02	0.03			0.14
500		0.02	0.02			0.11
600						0.09
800						0.08
1000						0.06

(a) continued.

E	1.00	1.25	1.50	1.80	2.00
t	i	i	i	i	i
4	7.25	11	15	19	
5					19
6	5.4				
7		8.2	12.0	14.9	
8	4.0				
10	3.6	6.8	9.8	12.2	17.7
13		5.7	8.4	10.5	
15	2.95				
16		5.0	7.4	9.1	
20	2.47	4.25	6.5	8.1	16.0
25	1.95	3.7	5.6	7.1	
30	1.65	3.20	5.0	6.3	14.6
35	1.50	2.85	4.45	5.6	
40	1.30	2.55	4.00	5.1	13.6
45	1.15	2.30	3.65	4.8	
50	1.05	2.10	3.38	4.4	12.8
55		1.94	3.11	4.2	
60		1.79	2.91	3.9	12.1
65				3.7	
70	0.74	1.56	2.57	3.5	11.5
80	0.66	1.39	2.30	3.25	11.0
90	0.58	1.24	2.10	2.80	10.50
100	0.52	1.13	1.92	2.67	10.00
110		1.03	1.77	2.49	
120	0.44	0.95	1.63	2.33	9.15
140	0.38	0.81	1.43	2.11	
150					7.99
160	0.33	0.70	1.28	1.93	
200	0.26	0.56	1.06	1.64	6.62
250	0.21	0.47	0.88	1.38	5.63
300	0.17	0.39	0.73	1.21	4.93
350					4.48
400	0.13	0.28	0.56	0.97	4.08
500	0.11		0.45	0.80	3.58
600	0.08	0.20	0.39	0.68	3.27
700				0.59	3.03
800	0.06	0.13	0.29	0.52	2.82
900					2.69
1000	0.05	0.12	0.24	0.42	2.56

(b) 0.1N KCl.

E	0.10	0.20	0.30	0.40	0.50	0.75
t	i	i	i	i	i	i
3	0.30	1.5	2.3	3.7		20.2
5	0.16	1.0	1.4	2.1	5.7	13.6
7	0.14	0.7		1.6	4.3	10.6
10	0.117	0.55	0.8	1.24	3.25	7.9
13	0.095	0.43	0.67	0.90	2.53	
15						5.7
16	0.082	0.38	0.55	0.78	2.07	
20	0.070	0.31	0.46	0.64	1.70	4.4
25	0.062	0.26	0.365	0.53	1.34	3.45
30	0.052	0.228	0.31	0.418	1.11	2.8
35	0.046	0.195	0.27	0.364	0.95	
40	0.043	0.179	0.24	0.329	0.83	2.18
45		0.164	0.22	0.292		
50	0.036	0.151	0.17	0.264	0.648	1.72
60	0.032	0.132	0.164	0.225	0.541	1.346
70	0.028	0.116	0.139	0.194	0.464	1.166
80	0.025	0.105	0.125	0.171	0.410	1.036
90	0.024	0.010	0.114			
100	0.023	0.009	0.104	0.139	0.329	0.823
120	0.020	0.074	0.087	0.116	0.202	0.682
140	0.017		0.075	0.098	0.232	0.584
160	0.016	0.058	0.066		0.201	
170						0.480
180	0.015	0.054	0.059	0.075		
190					0.164	
200	0.015	0.043	0.052			0.404
220				0.060	0.141	
230	0.012		0.044			
240		0.039				
250						0.321
260	0.012			0.046	0.117	
300	0.011	0.035	0.035	0.040	0.097	0.265
350	0.009		0.032	0.033	0.082	
400	0.008	0.025	0.025	0.028	0.069	0.196
500	0.004	0.023		0.019	0.051	0.151
600		0.016	0.016	0.015	0.039	0.122
700				0.012		0.105
800		0.016	0.011	0.008	0.024	0.087
900						
1000		0.013	0.008	0.007	0.016	0.069

REFERENCES.

(1) Bronsted & Nielsen, Trans. Far. Soc. 31, 1478, (1935).

(2) Acree, Bennett, Gray & Goldberg, J. Phys. Chem. 42, 871, (1938).

(3) Jones & Christian, J. A. C. S. 57, 272, (1935).

(4) Jones & Josephs, J. A. C. S. 50, 1049, (1928).

(5) Gledhill, Dissertation, Yale University, (1949).

(6) Gardner & Barnes, "Transients in Linear Systems," Wiley, New York, (1942).

(7) Newbery, Trans. Roy. Soc. S. Africa, (in press).

(8) Scarpa & Denina, Zeit. Phys. Chem. 449, 137,(1927).

(9) Ilkovic, Coll. Czech. Chem. Comm. 11, 498, (1934).

(10) Harned, Chem. Revs. 40, 461, (1947).

(11) Kolthoff & Lingane, "Polarography", Interscience Publishers,(1941).

(12) Fliva & Kontecky, Coll. Czech. Chem. Comm. 18, 7, (1953).

(13) Harned & Nuttall, J. A. C. S. 69, 736, (1947).

(14) Harned & Owen, "The Physical Chemistry of Electrolytic Solutions",Reinhold(1943).

(15) Conway, "Electrochemical Data", Elsevier, (1952).