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"Some Investigations on the electrification of interfaces"

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A THESIS

Being an account of research work carried out under the direction of Professor J. E. P. Wagstaff, M.A., D.Sc., at Durham University Science Laboratories during the period:

September, 1946 - September, 1948

and submitted by George William Bloomfield, of University College, in candidature for the Degree of Doctor of Philosophy.

Using a method developed by C. Curry at Durham University, in which the charge on a drop falling under gravity can be measured by the deflection from the vertical in a transverse electric field, experiments were performed to measure the natural charges acquired by water drops in air. These proving unsuccessful, attempts were made to increase the sensitivity of the method by measuring the deflections in an electric field after the drops had fallen into benzene. It was found, however, that these drops acquired a characteristic negative charge, the charge being due to impurities in solution in the water, and being proportional to field intensity and drop radius.

In order to gain more information on the benzene water interface, experiments were performed using benzene drops in aqueous solutions. These drops had a negative charge in distilled water and the drop charge increased to a maximum or "saturation" charge in alkaline solutions. The reasons for attibuting the negative charge to chemical adsorption of hydroxyl ions are given together with a mathematical explanation of the charge - hydroxyl ion concentration curves obtained. Mukherjee's equation for neutralization of charge on colloidal particles was checked by results obtained using benzene drops in Lanthanum Nitrate solutions. Other non conducting drops were found to behave in a similar manner to the benzene drops, and using carbon tetrachloride spheres the charge was found to be proportional to the cube of the radius, over most of the range covered (0.2 - 1.8 m.m. diameter). The charge was also seen to be connected with conditions of turbulence in the liquid round the drops.

Some experiments with pure mercury drops were made and a change in sign of the drop charge from positive to negative was observed in sufficiently large potential gradients, in alkaline and neutral solutions. A possible explanation of this reversal phenomenon is given, and results obtained with neutral salt solutions tend to to verify the simple theory.

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CHAPTER I

Introduction

INTRODUCTION

The separation of electricity which occurs when two phases come into contact, or in other words, the formation of an "electrical double layer," and the relative displacement of these two phases on application of an electric field, give rise to a series of phenomena which have been under observation for many years. These phenomena, which come under the general heading of "electrokinesis," can be conveniently divided into the following four sections:

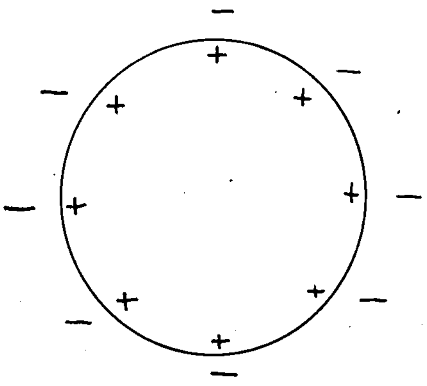
(i) ELECTROPHORESIS including cataphoresis, the motion under the influence of an applied electric field of an isolated particle suspended ina liquid.

(ii) DORN EFFECT, the production of an e.m.f. by the motion of a particle through a stationary liquid.

(iii) ELECTROENDOSMOSIS, the movement of a liquid through a stationary tube under the influence of an electric field, applied across the ends of the tube.

(iv) FLOW OR STREAM POTENTIAL, the potential produced between the ends of a tube by the motion of a liquid through the tube.

It is evident that (ii) and (iv) are the converse effects of (i) and (iii) respectively. Of the above phenomena, electrophoresis and electro-osmosis were the first to be observed, and Quincke[1] in his discussion of them suggested that a charging effect due to separation of electricity took place. Helmholtz[2] was the first to put forward a mathematical explanation of the effects, his work later being amplified by Lamb[3]. Their treatment was based upon the concept of an electrical double layer, forming a parallel plate condenser, one laminar distribution of charge being rigidly attached to the non mobile phase and the other equal and oppositely charged layer residing in the mobile phase. The diagram below illustrates how this idea can be applied to an isolated spherical particle in a liquid, a fixed layer of charge residing on the particle, and a mobile oppositely charged layer collecting in the surrounding fluid.



In this case a transverse electric field will cause the outer negatively charged layer to be pulled towards the positive electrode, and the particle with its immobile positive charge, will be dragged with this outer sheath under the action of viscous forces.

Using these concepts, Helmholtz and Lamb arrived at the equation:

$$u = \frac{\zeta . x . k}{4\pi . \eta} \qquad \text{--------} \qquad 1.$$

where u = the electrophoretic velocity

x = the potential gradient

k = the dielectric constant of the liquid

η = the viscosity of the liquid

ζ = the zeta potential i.e. the potential across the double layer

They made the following four assumptions in their treatment of the problem:

(a) The usual hydrodynamical equations for the motion of a viscous fluid may be assumed to hold both in the bulk of the liquid and within the double layer.

(b) The motion of the fluid round the particle is "streamline", inertia terms in the hydrodynamic equations being neglected.

(c) The applied electric field can be regarded as being superimposed upon the field due to the double layer.

(d) The thickness of the double layer i. e. the distance over which the potential differs appreciably from that of the liquid, is small compared with the radius of curvature at any point on the surface

The formula implies that the electrophoretic velocity of non conducting particles is independent of particle size and particle shape.

Smoluchowski[4], treating the problem in a much more general manner, obtained the same equation, and all subsequent workers have found an equation similar in form, notwithstanding that it is now universally agreed that the double layer is not of the simple "parallel plate" type illustrated. Debye and Huckel[5], using a similar treatment to that devised for the motion of an ion in an electric field obtained the equation,

$$u = \frac{\zeta . X . k}{A \eta} \quad - - - - - - - - \quad 2.$$

in which A is dependent on the particle shape, being 6π for a sphere. Henry[6], however, in a comprehensive treatment of the problem, criticised Debye and Huckel's method and showed that for an insulating particle the constant A in equation (2) should be 4π and independent of particle shape, Debye and Huckel's theory being valid for particles of the same conductivity as the surrounding medium. Other workers, especially Hermans[7] and Booth[8], have considered relaxation effects in the double layer, reviewing the assumption made by Helmholtz to account for these effects, and deriving modified versions of equation (1).

N. K. Adam[8] in his book "The Physics and Chemistry of Surfaces" reviews the possible ways in which such electrical double layers can be formed, and he suggests the following three processes as being the principal causes:

(1) Escape of positive or negative particles from one phase into the other, in the same manner as "thermiomic emission" of electrons takes place from a heated metal. The double layer formed in this manner is usually diffuse, resembling the "space charge" of electrons round a hot wire.

(2) Preferential adsorption of particles of one sign at the interface, neither positive nor negative particles leaving the phases in appreciable amounts, and the double layer forming wholly on one side of the surface.

(3) Orientation of neutral molecules, which contain electrical dipoles at the surface. Most molecules contain such dipoles, and their presence is one of the principal reasons for the orientation of molecules at surfaces. An orientated row of dipoles at a surface is in itself a double layer, but it is not diffuse. It may, however, induce secondary diffuse double layers extending into the phases on either side of the interface, by attracting mobile charged particles.

It was suggested by Professor Wagstaff that measurements should be made on the cataphoretic velocities of air bubbles in water, with a view to obtaining a clearer understanding of the conditions, especially the electrical conditions, existing at the air-water interface. It was expected that the charging of the bubbles would be due to a process similar to one of those outlined by Adam, and listed above.

Quincke[1], in 1861, observed that in an electric field air bubbles in water moved towards the positive electrode, whereas in turpentine they moved towards the negative electrode. As already stated, he attributed these effects to the separation of charge at the bubble surface.

Lenard[9], in his researches on the electrification of water drops fallingin air, observed that distilled water drops after striking a wetted plate were positively electrified, while inthe air surrounding the plate there was a distribution of negative electricity. Professor J. J. Thompson[10] continuing this work showed that the electrification was dependent on the nature of the gas surrounding the drops and also on the presence of electrolytes and organic substances in the drops themselves. He attributed the separation of electricity to the rupture of the double layer of electricity surrounding the drop, the mechanical shock on striking the plate pulling the outer sheath of electricity away from the inner layer, the latter remaining on, and giving the charge to, the drop. He attributed the formation of the double layer to quasi chemical forces existing between the gas and the water.

McTaggart[11] attempted to gain information on the nature of these chemical forces by observing the cataphoretic velocity of air bubbles in water. He used a horizontal tube of circular cross section, kept in rapid smooth rotation about a horizontal axis. In this manner, bubbles of gas could be maintained on the axis of the tube and, on the application of a potential difference between the ends of the tube, the cataphoretic velocity was measured by means of a microscope. The effects of electroendomose in the tube were thought to be negligible and ignored. With the information then available, McTaggart was unable to give an adequate explanation of the negative charge acquired by the air bubbles, but he thought that the effect was due to selective adsorption of the hydroxyl ions in the water; this adsorption being modified in the presence of highly charged positive ions. In a later paper, McTaggart attempted to relate this adsorption effect with Gibb's adsorption equation.

In a similar series of experiments T. Alty[12] improved McTaggart's apparatus and investigated the cataphoresis of bubbles of the inert gases in water, comparing their behaviour with that of air bubbles in water. These experiments were also made in an endeavour to gain more information concerning the quasi chemical forces acting at the gas / water interface. As a result of these and later experiments, Alty concluded that the movement of the gas bubbles under the influence of the electric field was due to a residual electric charge on the bubble and was not a true double layer effect. He observed the charging up effect of such bubbles in water of different purities, and attributed the excess of negative charge as due to ions of impurities in the water rather than to hydroxyl ions, the adsorption being brought about by orientation of the water molecules in the interface, so that the positive poles of the molecules lay inside the water.

Work has also been carried out on the cataphoresis of other non conductors in electrolytic solutions. Mooney[13], and later Miss Newton[14], measured the cataphoretic velocity of oil drops in electrolytic solutions using a vertical closed tube, the velocity being measured with the electric field (a) assisting (b) acting against gravity. Appropriate corrections were made for the electro-endosmotic flow of liquid taking place under the influence of the applied fields. The charges measured were in all cases negative but the results obtained were qualitative rather than quantitative in nature.

The original object of the work described in this thesis was to gain information on the air/water interface, and to see if there is a direct connection between the charges acquired by water drops in air as observed and measured by Professor J. J. Thompson, and on air bubbles in water as investigated by Alty. It was hoped that the charges on the water drops in air could be measured while the drops fell through the air under the action of gravity instead of by splashing on to a wet plate, and that a similar method of charge measurement could be used for the air bubbles in water. If the origin of the charge is preferential adsorption of ions at the interface due to orientation of the water molecules, as suggested by Alty[12], one would expect a direct relationship between the two charges measured in the above manner.

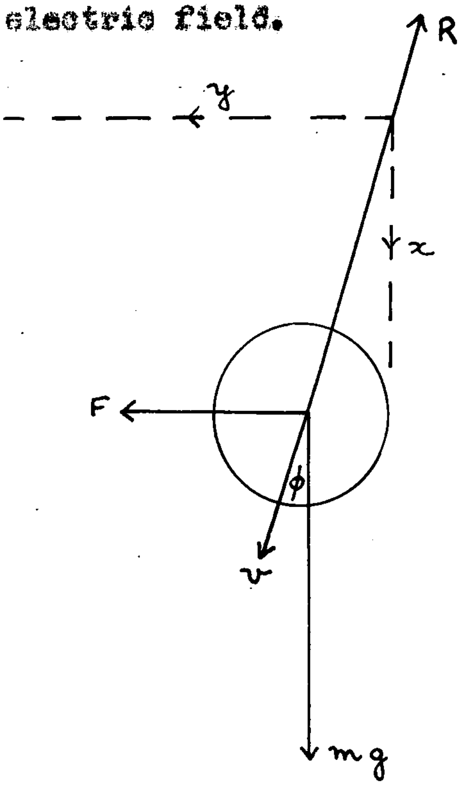
The method of charge measurements adopted, was developed by C. Curry at Durham University for the measurement of charge on mercury drops in electrolytic solutions. It entails the measurement of the deviation from the vertical, of drops falling under gravity, through a transverse electric field, the deviation being measured photographically. The mathematical theory relating drop charge and deflection is given in the next chapter. Making use of this theory, experiments were carried out in an endeavour to measure the charge on water drops falling in air, this later being extended to water drops in benzene and to the measurement of charge on drops of benzene and other liquids in electrolytic solutions.

CHAPTER II

The interpretation of the path of a drop moving through a fluid under the influence of two forces at right angles.

Mathematical theory of the drop path

A charged drop moving under the influence of gravity through a horizontal electric field will be acted upon by two forces mutually at right angles. These are shown in the diagram below and are mg due to gravity acting vertically, m being the weight of the drop in the fluid, and F acting horizontally, due to the electric field.



The drop in motion will also be acted upon by a resistive force R, the magnitude of this force depending upon the conditions of flow of fluid round the drop. If conditions are such that there is streamline fluid flow round the drop then

$$R = 6\pi\eta a v$$

where η = the viscosity of the fluid
a = the radius of the drop
v = the velocity of the drop in the flu

Curry, however, found that such streamline conditions did not hold for mercury drops in sulphuric acid solution, the resistive force under such conditions being proportional to the square of the velocity v and radius a. i.e.

$$R \propto (av)^2$$
$$= kv^2$$

k being constant for drops of radius a.

Using this resistance law, and resolving the velocity, v , into two components v_x and v_y along the vertical x axis and horizontal y axis, Curry gave the following two equations for the movement of a mercury drop in dilute sulphuric acid:

$$m\frac{dv_y}{dt} = F - k(v_y)^2 \text{ - - - - - } 1$$

$$m\frac{dv_x}{dt} = mg - k(v_x)^2 \text{ - - - - } 2$$

Assuming that the vertical terminal velocity was reached before the drop entered the electric field and that this vertical velocity was unaffected by the field, Curry obtained the equations:

$$x = v_x . t \text{ - - - - - - - } 3$$

$$y = \frac{m}{k} . \log_e \left\{ \cosh \sqrt{\frac{kF}{m}} . t \right\} \text{--} 4$$

x and y being the vertical and horizontal displacements respectively, for time t.

If turbulence had not occurred, the motion of the fluid round the drop being streamline, then Stoke's law would apply and the original equations (1) and (2) would become

$$m\frac{dv_x}{dt} = mg - 6\pi\eta a v_x \qquad \text{-----}\ 5.$$

$$m\frac{dv_y}{dt} = F - 6\pi\eta a v_y \qquad \text{-----}\ 6.$$

these leading to

$$x = v_x t \qquad \text{-------}\ 7.$$

$$y = \frac{F}{6\pi\eta a}\left[t - \frac{m}{6\pi\eta a}\left\{1 - e^{-\frac{6\pi\eta a}{m}t}\right\}\right] - 8$$

Curry derived these equations, and used equations (3) and (4) for the interpretation of the paths of the mercury drops in the aqueous solutions. The treatment can be carried a stage further by considering a drop entering the electric field with velocity w where w < the terminal velocity. For such a drop, and for streamline flow of fluid round the drop, we obtain the equations

$$Kx = gt + \left(w - \frac{g}{K}\right)\left(1 - e^{-Kt}\right) \quad \text{---}\ 9$$

$$Ky = \frac{F}{m}\left[t - \frac{1}{K}\left(1 - e^{-Kt}\right)\right] \text{---}10$$

K being the constant $\frac{6\pi\eta a}{m}$

From (9) and (10) we therefore have

$$\frac{x}{t} = \left\{g\cdot\frac{m}{F} - \frac{wKm}{F}\right\}\frac{y}{t} + w \text{ --}11$$

If g is $\gg \frac{wK}{F}$ we may say

$$\frac{x}{t} = \frac{mg}{F}\frac{y}{t} + w \quad \text{----}\ 12$$

This last equation was used for the calculation of F in the experiments with water drops falling in air, described in Chapter 3.

Every attempt to utilize equations (3) and (4) for the interpretation of other drop paths was unsuccessful. On reviewing the work, however, the initial equations (1) and (2) were found to be incorrect. Instead of resolving the velocity of the drop, v, into a horizontal component, v_x, and a vertical component, v_y, and deriving the horizontal and vertical components of the resistive force from v_x and v_y, the force R should be resolved directly.

The equations of motion should therefore be:

$$m\frac{d^2x}{dt^2} = mg - R\cos\phi \quad ----13$$

$$m\frac{d^2y}{dt^2} = F - R\sin\phi \quad --- (14)$$

R and ϕ being shown in the initial diagram. If the resistive force R is proportional to the n'th power of the velocity V i.e.

$R = k_1 v^n$, k_1 being a constant

for drops of radius a, then

$$m\frac{d^2x}{dt^2} = mg - (k_1 v^n)\cos\phi \quad --15$$

$$m\frac{d^2y}{dt^2} = F - (k_1 v^n)\sin\phi \quad --16$$

Under such circumstances equations (1) and (2) would have been

$$m\frac{d^2x}{dt^2} = mg - k_1(v\cos\phi)^n \quad ---17$$

$$m\frac{d^2y}{dt^2} = F - k_1(v\sin\phi)^n \quad --18$$

these differing from (15) and (16) if $n \neq 1$.

Therefore equations (3) and (4) for which n=2, are incorrect. The other equations derived in the case in which streamline flow takes place, and n = 1, are correct.

Consider the problem in a more general manner using equations (13) and (14)

$$m\ddot{x} = mg - R\cos\phi \quad ----13$$

$$m\ddot{y} = F - R\sin\phi \quad ----14$$

Making the assumption that the drop reaches its terminal velocity vertically before entering the field, and also that this velocity $\overline{v_x}$ is unchanged by the horizontal force F, we may say $\ddot{x} = 0$

$$\therefore \; mg = R\cos\phi$$

and substituting this in equation (14) we have

$$\ddot{y} = \frac{F}{m} - g\tan\phi$$

Now $\tan\phi = \dfrac{dy}{dx} = \dfrac{1}{v_x}\cdot\dfrac{dy}{dt}$

$$\therefore \; \ddot{y} + \frac{g}{v_x}\dot{y} = \frac{F}{m}$$

from which we obtain the relationships

$$\dot{y} = \frac{F}{mg}\cdot\overline{v_x}\left\{1 - e^{-\frac{g}{\overline{v_x}}t}\right\} \quad ---19$$

$$y = \frac{F}{m}\left(\frac{\overline{v_x}}{g}\right)^2\left\{e^{-\frac{g}{\overline{v_x}}t} - 1\right\} + \frac{F}{mg}\cdot\overline{v_x}.t \quad ----20$$

Putting $\frac{g}{\bar{v}_x} = \alpha$ and $\frac{F}{m} = \beta$ and remembering that

$x = \bar{v}_x t$

equation (20) becomes

$$y = \frac{F}{mg} \cdot x + \frac{\beta}{\alpha^2}\left\{e^{-\alpha t} - 1\right\} ------21$$

If the terminal velocity $\bar{v}_x$ is small compared with the magnitude of g i.e. if $\bar{v}_x \ll g$, then α is large and $(e^{-\alpha t} - 1)$ very rapidly approaches 0. Under these conditions

$$\frac{\beta}{\alpha^2}\left(e^{-\alpha t} - 1\right)$$

quickly becomes negligible and

$$y = \frac{F}{mg} \cdot x ------22$$

The drop path will thus be slightly curved when the drop first enters the electric field but it will rapidly approach a straight line, of slope

$$\frac{y}{x} = \frac{F}{mg}$$

In Curry's work with mercury drops in dilute sulphuric acid $\bar{v}_x$ was always large and consequently αt never approached a sufficiently large value for

$$e^{-\alpha t} - 1$$

to become negligible. The drops therefore did not have sufficient time between the deflecting plates to enable them to approach straight line paths. We shall see later, however, that with water drops in benzene and benzene drops in water, straight line paths were obtained, as

$\bar{V}x$ was always much smaller than g.

We have seen that by making the assumption

$\ddot{x} = 0$ the path of any drop falling with its terminal velocity through an electric field can be interpreted using equations (21) amd(22) above. An exact knowledge of the constant n in the resistance equation

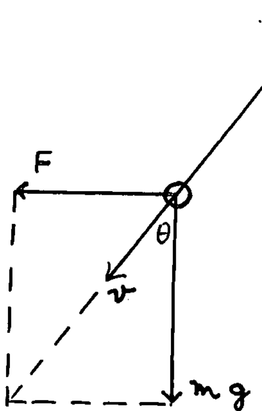
$$R = k v^{n}$$

is not required, providing that n remains constant during the time the drop is under observation.

After some consideration, however, it was decided that the assumption $\ddot{x} = 0$ is not necessarily correct, as the drop may experience a negative acceleration vertically due to the electric field. This becomes obvious if the path of the drop, after an infinite time in the electric field, is considered. The drop will then be travelling with a steady velocity v, say, along a straight line path of slope

$$\frac{y}{x} = \tan\theta = \frac{F}{mg}$$

this being illustrated in the diagram below



Under these steady conditions, the resultant of F and mg will be equal and opposite to the resistance force R. If the resistance law

$$R = k_1 v^n \text{ holds} \quad , \quad n \neq 1$$

then

$$R = k_1 v^n = \left[F^2 + (mg)^2\right]^{\frac{1}{2}}$$

i.e. $$v = \left\{\frac{\left[F^2 + (mg)^2\right]^{\frac{1}{2}}}{k_1}\right\}^{1/n}$$

and the vertical component of this is

$$v_x' = \left\{\frac{\left[F^2 + (mg)^2\right]^{\frac{1}{2}}}{k_1}\right\}^{1/n} \cos\theta$$

When the same drop falls vertically through the liquid in the absence of an electric field, the vertical terminal velocity $\overline{V_x}$ is reached when

$$k_1 (\overline{v_x})^n = mg$$

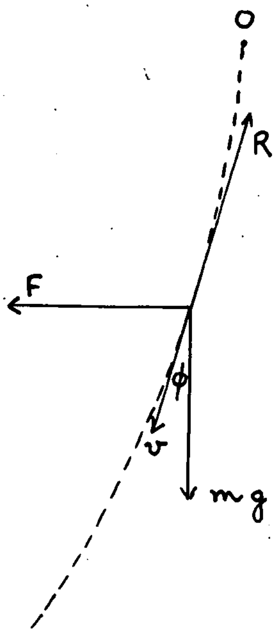
$$\overline{v_x} = \left\{\frac{mg}{k_1}\right\}^{\frac{1}{n}}$$

Unless $n = 1$ $\overline{V_x} \neq V_x'$ and it can easily be shown that $v_x' < \overline{v_x}$. If $F \ll mg$ then $\ddot{x}$ will be small and negative but as F increases, the magnitude of $\ddot{x}$ will increase and the non linear part of the drop path will deviate more and more from that indicated by equation (21), derived by assuming $\ddot{x}$ to be zero. In order to complete the mathematical treatment of the problem, the drop path was therefore considered without making the assumption that $\ddot{x} = 0$. By means of the formulae produced, it should be possible to analyse large deflections in an electric field of those quickly moving drops which do not have time to attain straight line paths. Thus although the formulae derived below were not of direct use for the paths photographed in the work done for this thesis, they should enable curved paths such as those of mercury drops in aqueous solutions to be interpreted correctly and accurately.

In the following treatment, n in the resistance law

$$R = k v^{n}$$

is assumed to be 3/2. This was found to be the case for the water drops used in benzene and for the benzene drops in water, although any empirically determined value of n can be substituted in the equations. Consider the drop moving along the curved path as shown in the diagram below



Measuring the distance along the drop path s, from the origin O, we have

$$\dot{s} = v \quad \text{and}$$

$$R = k_1 v^{3/2}$$

Resolving tangentially

$$m v \frac{dv}{ds} = m g \cos\phi + F \sin\phi - k_1 v^{3/2} \quad ----23.$$

Resolving normally

$$m v^2 \frac{d\phi}{ds} = F \cos\phi - m g \sin\phi \quad ------24.$$

Dividing (23) by (24) to eliminate ds

$$\frac{1}{v}\frac{dv}{d\phi} = \frac{g\cos\phi + \frac{F}{m}\sin\phi - \frac{k_1}{m} v^{3/2}}{\frac{F}{m}\cos\phi - g\sin\phi}$$

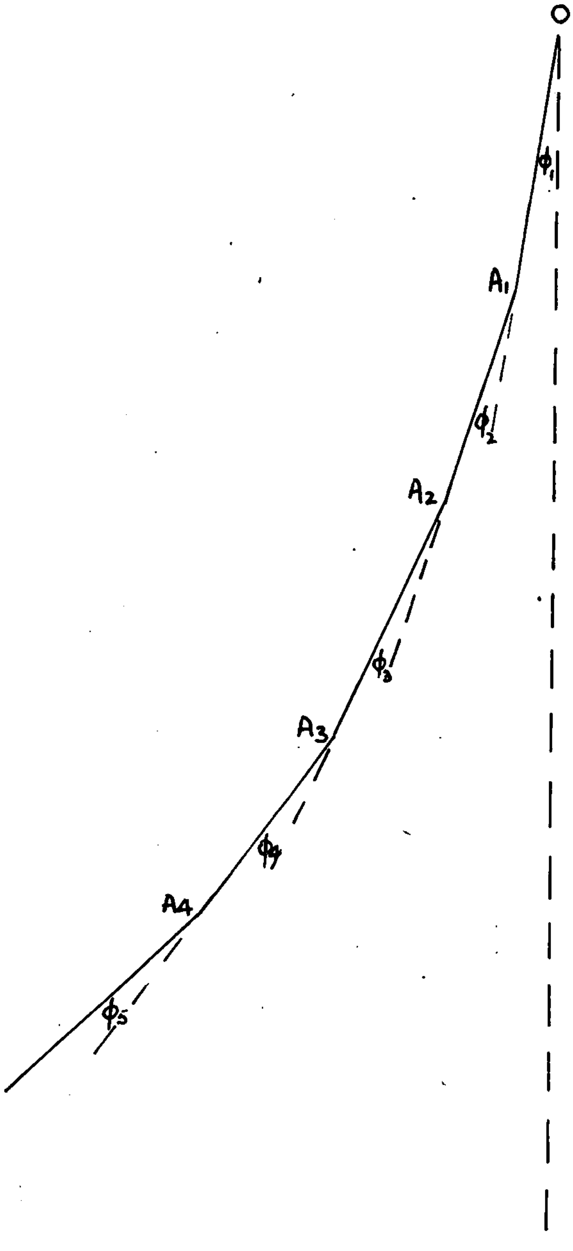
$$\frac{dv}{d\phi}\left(\frac{F}{m}\cos\phi - g\sin\phi\right) - v\left(g\cos\phi + \frac{F}{m}\sin\phi\right) = -\frac{k_1}{m} v^{5/2}$$

$$\frac{d}{d\phi}\left\{ v\left(\frac{F}{m}\cos\phi - g\sin\phi\right)\right\} = -\frac{k_1}{m} v^{5/2}$$

$$v\left\{\frac{F}{m}\cos\phi - g\sin\phi\right\} = -\frac{k_1}{m}\int_0^{\phi} v^{5/2}\, d\phi + v_0 \frac{F}{m} \quad ------25$$

Where V_0 is the velocity when t = 0, $\phi = 0$ usually being the terminal velocity.

Equation (25) must be solved numerically in the manner described by Piaggio[15] and outlined below. The path can be considered as parts of the sides of a polygon


O
ϕ_1
A_1
ϕ_2
A_2
ϕ_3
A_3
ϕ_4
A_4
ϕ_5

ϕ_1 = angle OA_1 makes with the vertical

ϕ_2 = angle A_1A_2 makes with OA_1

ϕ_3 = angle A_2A_3 makes with A_1A_2

etc

$$\therefore \int_0^{\phi} v^{5/2}\,d\phi = v_1^{5/2}\phi_1 + v_2^{5/2}\phi_2 + v_3^{5/2}\phi_3 + \ldots \text{ etc}$$

where V_1 is the average velocity along OA_1

V_2 is the average velocity along A_1A_2 etc

OA_1 , A_1A_2 etc are taken sufficiently small for a good approximation to be made.

An alternative but probably equally as laborious method would be to start from the equations

$$\ddot{x} = g - \frac{k_1}{m} v^{3/2}\cos\phi = g - \frac{k_1}{m} v^{1/2}\dot{x} \quad ---26$$

$$\ddot{y} = \frac{F}{m} - \frac{k_1}{m} v^{3/2}\sin\phi = \frac{F}{m} - \frac{k_1}{m} v^{1/2}\dot{y} \quad ---27$$

$$\therefore \dot{x}\ddot{x} = g\dot{x} - \frac{k_1}{m} v^{1/2}\dot{x}^2$$

$$\dot{y}\ddot{y} = \frac{F}{m}\dot{y} - \frac{k_1}{m} v^{1/2}\dot{y}^2$$

and adding these equations

$$\dot{x}\ddot{x} + \dot{y}\ddot{y} = g\dot{x} + \frac{F}{m}\dot{y} - \frac{k_1}{m} v^{5/2}$$

$$\therefore \frac{d}{dt}\left\{\frac{\dot{x}^2 + \dot{y}^2}{2} - gx - \frac{F}{m}y\right\} = -\frac{k_1}{m} v^{5/2}$$

$$gx + \frac{F}{m}y - \frac{1}{2}v^2 = +\frac{k_1}{m}\int v^{5/2}\,dt - \frac{1}{2}v_0^2$$

------ 28.

This will be capable of numerical solution in a manner similar to that described for equation (25) above

Summarizing the above work, we may therefore say that unless a drop moving under the influence of gravity and an horizontal electric field has sufficient time in the field to enable it to reach a straight line path, the analysis of the path and the derivation of F will become most tedious. The approximation that $\ddot{x}$ is zero is not very satisfactory and the values of F obtained from the curved tracks using the equations derived from this approximation, will not be accurate, especially if the deflections are large. In such experiments the aim must therefore be to produce sufficiently large fields to allow the drop under observation sufficient time to approach the condition of non acceleration for which the drop path is a straight line of slope.

$$\tan \theta = \frac{F}{mg}$$

This will obviously entail the use of large cells, especially where the drops under observation have high terminal velocities.

The determination of charge from the value of F calculated from the drop path.

If the conditions under which the drop collects its charge are favourable toward the formation of a complete double layer then the Helmholtz equation relating cataphoretic velocity with potential gradient would be expected to hold. The determination of the horizontal velocity in the electric field should therefore give a direct measurement of ζ, the zeta potential across the double layer. It must be remembered that with such a double layer, the net charge on the drop, and the liquid immediately surrounding it, will be zero. Wagstaff[16] has also shown that a spherical drop of radius a, surrounded by a double layer of thickness d, is acted on in an electric field by a force F where

$$F = \frac{1}{3} \cdot \frac{a^2 \zeta}{d} \cdot \frac{dV}{dy}$$

$\frac{dV}{dy}$ being the potential gradient in e.s.u. and ζ the zeta potential across the double layer. The function $\frac{\zeta}{d}$ can therefore be derived from either F, the force acting on the drop, or from Vy the horizontal velocity attained in the electric field.

If, however, the conditions of charge formation are such that the outer sheath of charge in the double layer is either incomplete, or even non existent, these equations derived assuming a complete double layer, will not be valid. The drop will then possess an excess of charge of one sign, q e.s.u., and the force, F, acting on it will be given by the equation.

$$F = q \cdot \frac{dV}{dy} \quad \text{-----------} \quad 29$$

Alty[12] in his work with air bubbles in water assumed such a formula to hold, as the movement of the air bubbles in electric fields, determined experimentally, did not agree with the Helmholtz formula and were consequently attributed to the existence of an excess of charge on the bubbles. Any disturbance or turbulence in the liquid round the drop will upset and tend to remove, either completely or partially, the outer portion of the double layer providing that it is of the diffuse type and due to attraction of ions from the liquid. As pointed out in Chapter I, one of the essential assumptions underlying the Helmholtz formula is that the motion of the liquid round the drop is streamline, disturbance of the double layer then being at a minimum. It is therefore most probable that drops falling through a liquid under the influence of gravity, and attaining terminal velocities in excess of the limiting velocity for which streamline flow takes place, are unable to attract all the outer layer of charge which completes the formation of the double layer, owing to the disturbances and turbulence occurring in the liquid immediately surrounding the drop. In such cases, the assumption that the force in an electric field is due to an excess of charge on the drop therefore seems to be more reasonable than attributing the movement to distortion of a double layer.

In the experiments performed using liquid drops in electrolytic solutions it was therefore necessary to de-

determine the type of liquid motion taking place round the drops, this being done by measuring the terminal velocity of drops of different radii through the liquid. Such measurements showed that the law

$$R == k\,v^{3/2}$$

holds good, and in in no case were sufficiently small drops used for Stoke's law to apply. For this reason, therefore, the movement in the electric field was attributed to an excess of charge q on the drop given by the formula

$$F = q.E \qquad \text{where} \quad E = \frac{dV}{dy} \ \text{e.s.u.}$$

In the experiments described, using water drops in air, equations (11) and (12) above, derived assuming streamline flow, were found to fit the experimental results, but as will be seen, the method was not sufficiently sensitive for the measurement of natural charges on the water drops, and consequently the above consideratons had no direct bearing on the measurements made.

Derivation of the resistance law in force

It can easily be shown, by the method of dimensions, that the resistive force R, for drops of radius a, and mass m, falling through a liquid with terminal velocity v, is given by the equation:

$$R = mg = A(a v_x)^n$$

where $A \propto \rho^{n-1} \eta^{2-n}$ being constant between certain limits of a, for a given liquid of density ρ and viscosity η, n being constant over these limits of a and lying between 1 and 2.

We therefore have

$$\log_{10}(mg) = n \log_{10}(a v_x) + \log_{10} A \quad --- 30$$

By plotting $\log_{10}(mg)$ against $\log_{10}(a v_x)$ over the range of radii in use, the value of n in force can therefore be obtained. Obviously for extremely small drops for which streamline flow takes place n will be unity. Using this method Allen[17] found n to be 3/2 for small air bubbles (0.08 m.m.—0.8 m.m. diameter) in water. For benzene and similar liquid drops in water, and for water drops in benzene, n was also found to be 3/2, the range of diameters used being 0.3 m.m. to 2m.m. As mg $\propto a^3$, we also have the relationship

$$\underline{V_x \propto a}$$

Chapter III

The charges on water drops falling through air.

The apparatus used in the first series of experiments is shown diagramatically in fig 1. PP were 3" x 2" rectangular copper plates cut from $^1/_{16}$" copper sheeting. These were mounted 2 cms. apart, symetrically and vertically, by means of two rods L, L which screwed into nuts soldered centrally on the backs of the plates, and passed through two rubber bungs R,R. These rubber insulators were securely fixed in two diametrically opposite holes drilled in a circular tin case, C , of diameter 4" and depth 3". The 2" long ½" diameter copper tube S was soldered into a hole drilled in the case vertically above and midway between the deflecting plates and this tube together with the case was earthed. An inch diameter hole drilled in the base of thecase served as an outlet.

Voltages were applied to PP by means of the arrangement shown in fig 2., voltages up to 1800 volts being obtained from a chain of H.T. batteries. The arrangement shown enabled either plate to be earthed, the other being raised to a high positive potential with respect to earth.

Water drops were formed at the end of a fine capillary, drawn out from a thin glass tube. The smallest drops conveniently obtained by this method were of the order of 2 m.m. diameter, as below a certain value of, r, the capillary radius, decreasing r does not affect the drop radius but only the rate of formation. Filtered distilled water passed from a glass reservoir through rubber tubing to the dropper and the rate of formation of the drops could be conveniently regulated by adjusting the height of the reservoir. The dropper was initially earthed by means of a copper plate dipping into the water in the reservoir, and the end of the capillary was placed in the centre of the screening tube S. This prevented any charge from being induced on the drops, while forming, by the high voltages applied to the deflecting plates.

The optical system used for drop illumination was similar to that used by Curry and is illustrated in fig. 3. A "pointolite" was used as the source and the light concentrated into a vertical parallel beam of diameter slightly less than that of the screening tube S by means of a concave mirror. The falling drops were highly illuminated between the plates in this vertical light beam, appearing as bright streaks of light on the ground glass screen of the camera, this being a double extension f/3.5 plate camera, taking 9 x 12 cm. plates. Using aperture f/3.5, with very high speed panchromatic plates (Ilford H.P.3.,34^{0}), actual size photographs were obtained at double extension, the drop paths appearing on these photographs as well defined lines.

The timing of the drops in their fall was arranged by means of a light interrupter B, this being a sectored disc driven by a high speed synchronous motor. The disc had three vanes as shown in fig. 4 and interrupted the light beam M, three times per revolution. An intermittent illumination of the drops at constant known frequency was thus obtained, and the drop paths were indicated on the photograph as a series of equally spaced bright lines. Figs. 21 to 24 illustrate the type of photograph obtained using this procedure. The frequency of the light interrupter was accurately measured using the stroboscope effect, by illuminating the rotating disc with light from an helium tube of frequency equal to that of an electrically maintained tuning fork, the frequency of the fork being measured directly with a Rayleight motor.

Experimental procedure

With the above arrangement, observations were made on water drops of 2 m.m. diameter, falling vertically between the plates. With the screen S and the dropper both at earth potential there was no dectable deflection when the drops passed through the highest electric field available, indicating that the charge on the drops formed under these conditions, was too small to be detected.

In order to check the method, charges of known magnitude were therefore given to the drops by applying known voltages of magnitude 100-2000 volts between the dropper and screen as illustrated in fig. 5. A voltage V applied between the screen and the dropper in this manner induced a charge $\frac{Va}{300}$ e.s.u. on a drop of radius a falling from the end of the dropper.

The drops so charged were deflected in the electric field and the magnitude of the charge was experimentally determined in each case from the deflection in fields of known strength. Photographs 84-92 were obtained in this manner the drop paths being photographed on either side of the vertical. The information relating to these photographs is given in table 1 below

Distance between deflecting plates = 2.54 cms.

Time intervals on photographs = .001[illegible]85 second

TABLE I

Photograph	Voltage between scree and dropper "V"	Voltages between deflecting plates	Radius of drop "a" cms.	mg for drop in dynes
84	198	1862	.1176	7.025
85	420	1862 ,1047	.1172	6.95
86	618	1862 ,1047	.1164	6.79
87	816	1862 ,1047	.115	6.56
88	1047	1862 , 816	.113	6.28
89	1245	1862 ,1047, 618	.1112	5.93
90	1430	1862 ,1245, 618	.1091	5.615
91	1615	1862 ,1245, 618	.106	5.13

Equation 12 given in Chapter 2 was found to fit the photographed paths of the water drops extremely well. The equation is

$$\frac{x}{t} = \frac{mg}{F}\,\frac{y}{t} + \omega \quad ----- \quad 12.$$

and it was derived theoretically, assuming that there was streamline flow of fluid round the drop

$\frac{y}{t}$ plotted against $\frac{x}{t}$ as obtained by means of a travelling microscope from photographs 84-91 gave good straight line curves in each case, and Graph 1 shows these curves obtained from the paths of the drops with 1862 volts between the deflecting plates. Such good agreement with equation 12 indicates that for the velocities observed there must be streamline air flow round the drops.

From graph 1 the value of F, the horizontal force on the drop, was obtained in each case using the relationship

$$\frac{F}{mg} = \frac{d\left(\frac{y}{t}\right)}{d\left(\frac{x}{t}\right)}$$

If X is the electric field intensity and e the charge on the drop then

$$F = Xe$$

X was equal to $\frac{1862 \text{ volts}}{2.54 \text{ cms.}}$ in every case so that e in e.s.u was calculated directly from the value of F obtained. The value of e obtained in this manner is compared with $\frac{Va}{300}$ e.s.u, the charge induced on the drop for different values of V, in table II below

TABLE II

Voltage between Screen and dropper "V"	Radius of drop in cms "a"	$\frac{Va}{300}$ e.s.u.	$\frac{d(y/t)}{d(x/t)}$ from graph 1	m g for drop in air	$e = \frac{mg\frac{d(y/t)}{d(x/t)}}{X}$ in esu
198	.1176	0.07766	.02906	7.025	0.0837
420	.1172	0.1641	.0594	6.95	0.1681
618	.1164	0.2396	.0865	6.79	0.2395
816	.115	0.3128	.1183	6.56	0.322
1047	.1135	0.3956	.147	6.28	0.3799
1245	.1112	0.4616	.195	5.93	0.4650
1430	.1091	0.5203	.2259	5.615	0.5180
1615	.106	0.57066	.27	5.13	0.5670

Table II shows that there is good agreement between the values $\frac{Va}{300}$ and e, as calculated from the drop deflection, over the range covered. It therefore appears that though the deflection method is not sufficiently sensitive to measure the small "natural" charges acquired by the water drops in air it is capable of good accuracy with the larger induced charges.

It was noticed in the above experiments that the radius of the drop on leaving the dropper was affected by the voltages applied between screen and dropper. In these experiments it was therefore necessary to measure the mass of the drop for each voltage used between screen and dropper; this being done by collecting and weighing 50 drops. The drop radius for each voltage, obtained by the method of weighing, is given in tables I and II. Though this dependence of drop mass on voltage between screen and dropper was not of importance with regard to the main problem under investigation, measurements of the effect were made for different rates of formation i.e. for different heights of the reservoir above the dropper. A summary of the results obtained together with a discussion of them is given in the appendix, this being done to prevent the discussion from interferring with the trend of the main problem.

Attempts were made to increase the sensitivity of the method, in the hope that the natural charges acquired by the water drops would then be measurable. Increased sensitivity could be obtained by (1) decreasing the mass of the drop and thereby reducing the vertical force mg (2) increasing the electric field intensity in order to increase F, the horizontal force acting on the drop.

In order to obtain smaller drops a water dropper of the type described by Lane[18] was constructed. In this type of dropper, drops forming at the tip of an hyperdermic needle were blown off by a steady blast of air before they could attain their full size. The stream of air was directed vertically downwards, parallel to the axis of the needle, through a small circular hole, the needle being accurately fixed at the centre of this hole. The air blast assisted gravity to overcome the surface tension forces which caused the drop to adhere to the tip of the needle, and was supplied by a constant speed electrically driven blower. Regulating the flow of air through the jet, by means of an "air bleed" in the air reservoir supplying the jet, enabled the drop size to be controlled, drops varying in diameter from 0.2 mm. to 3 m.m. being possible

The diameter of the drops in use was obtained by collecting a sample of them in a vaselined glass trough containing light oil, the measurements being made with a microscope fitted with a scale in the eyepiece. Drops of water up to 3 m.m. diamter retained their spherical shape in the oil, evaporation not being possible and coalescing with the glass being prevented by the vaseline. This method of measurement was both simple and rapid, and it was the only one that could be used for the smaller drops, the rate of formation then being so rapid that it was impossible to measure the weight, or volume, of a known number of drops.

A difficulty encounted with the Lane type dropper was especially obvious when the stronger air blasts were used to obtain the smaller drops. The direction of emission was found to vary from drop to drop, and when the tip of the needle was viewed under a microscope the drops before leaving were seen to be in violent oscillation, any small irregularity in the air flow causing the direction of emission to vary. Though this effect was one which was never fully overcome it was minimized by having the jet fed from a large air reservoir, this smoothing out the small irregularities in the supply from the blower. The drops were also allowed to fall through a metre of air before entering the electric field, this ensuring that they fell vertically on reaching the deflecting plates.

In order to increase F, the horizontal force on the drop in the electric field, highervoltages were used, these being obtained by means of a Whimshurst machine. As corona occurred at these high voltages with the rectangular deflecting plates, highly polished circular plates, 12 cms. in diameter and 1 cm. thick, were constructed, all sharp edges being avoided and the cross section of the plates being made as in fig. 6 These plates were mounted on insulating rods of 3 cms. diameter, by means of 0 B.A. metal plugs as shown in the diagram, and were clamped vertically and parallel distant 3 cms. apart.

The voltage applied to the deflecting plates by the Whimshurst machine was measured by means of a capacity bridge arrangement shown in fig 7. With the switch in position 1-2, the Whimshurst machine charged condenser C_1, this being connected directly across the circular plates. C_1 was a high grade Muirhead porcelain insulated 25,000 volt condenser of capacity 0.001 u.F. On switching the key to position 1-3 the charge on C_1 was shared by condenser C_2, the latter being a Muirhead 1500 volt 0.025 UF condenser, and the voltage across C_2 was measured by an electrostatic 0-600 voltmeter. R was a megohm resistance inserted to prevent heavy sparking taking place when position 1-3 was made.

If V_1 was the voltage supplied by the Whimshurst machine, then the charge initially acquired by C_1 would be 0.001 V_1 coulombs. On connecting C_2 in parallel with C_1, the voltage across C_1 dropped to V_2, the charge remaining constant so that

$$0.001\ V_1 = 0.026 V_2$$

$$\underline{V_1 = 26\ V_2}$$

Thus with the 600 volt electrostatic voltmeter across C_2 it was possible to measure 15,600 volts across C_1.

Great care was taken to prevent leakage of charge from the assembly, all sharp points being avoided, the shortest possible leads being used and a clean paraffin wax block used for the switch. With these precautions it was possible to charge C_1 to a steady high potential which only very gradually leaked away. The sphere spark gap on the Whimshurst was adjusted to spark at a voltage below 25,000 volts and so protected C_1 from over load. Key K was a mercury in wax key which was used to discharge the apparatus after each voltage measurement.

Using the above high voltage system to obtain fields of the order 7,500 volts/ cm, drops of diameter 0.2 m.m diameter were allowed to fall between the plates. These drops while forming were screened from the high voltages by a copper tube, both the tube and dropper being earthed. These small drops were noticeably deflected to the negative plate indicating a positive charge on the drop, but it was not possible to make any quantitative measurements, as with the optical system in use the paths of these very small drops could not be consistently photographed

An alternative method of reducing "mg" was therefore considered, the object being to increase the sensitivity without using drops too small to be photographed.

The principle of the method is to allow the water drops to fall from the air into a column of non conducting liquid of slightly lower density than that of water,and to measure the charge by deflection in this non conductor. With such an arrangement, the water drops will be in the transverse electric field a much longer time than when falling in air due to the viscosity of the liquid, and alsothe effective vertical force acting on the drop will be much smaller. Benzene, toluene and xylene have densities of 0.88 grams c.c. at 20^{0}C so that the effective weight of a water drop in these liquids will be 0.12 m, where m is the mass of the drop in air. As benzene is also an extremely good conductor, the use of high voltage gradients is still possible.

It was hoped that the charge on the drop, measured in the benzene,would be the same as the charge acquired by the water drop in air, as transference of ions to or from the drop in such a non conductor as benzene should be negligible.

An account of the experiments made with water drops in benezene is given in the next chapter.

Chapter IV

The measurement of charge on water drops in benzene

Construction of cell

Several glass cells were constructed before a satisfactory type was developed. The construction of this cell is shown in fig. 8 and a photograph of the actual cell used is shown in fig 9. The four main walls of the cell were 10" x 4" glass plates, of thickness 1/16", cut and ground accurately rectangular. An 1/8" diameter hole was drilled centrally in two of these plates. Two 4" x 2" copper deflecting plates were mounted over these holes on two 1¼" lengths of ½" diameter glass tubes, the end of these being ground at right angles to the axis of the tube. The deflecting plates were cut from ⅛" thick copper sheeting and a thin copper wire was soldered centrally to the back of each plate and passed along the mounting tubes through the holes in the cell walls. The ½" diameter glass tubes thus supported the deflecting plates vertically and parallel, distant 3.5. cm. apart, and also prevented the benzene in the cell from coming into contact with the soldered connections at the back of each plate.

The top of the cell consisted of a glass plate drilled centrally, with a 6" long ½" diameter tube fitting through the hole and cemented perpendicular to the plate. This tube projected 2½" into the cell, that is within $\frac{1}{2}$" of the top of the deflecting plates, being directly above with its axis vertical and midway between them. A glass plate with an $\frac{1}{2}$" hole drilled in the centre and fitted with an outlet tube and tap was used as the base. The complete cell was mounted with the base resting on a wooden stool.

Gelatine was the cement used for the joints, this being made up in warm water, and applied warm to the surfaces. It set rapidly and hardened, to give a clean robust joint insoluble in benzene.

In use, the cell was filled with benzene, the upper level being $\frac{1}{2}$" from the top of the vertical tube. The drops under observation were formed above the surface of the benzene and allowed to fall into the tube, any oscillations set up in the drop on breaking the surface being completely damped in the tube. On reaching the deflecting plates the drops were therefore falling centrally and vertically, the 15 cm. column of benzene being also quite adequate for the drops to attain their vertical terminal velocity before entering the electric field.

The deflecting plates were mounted away from the cell walls to prevent disturbance of the benzene between the plates by electro endosmotic flow. Earlier cells had been constructed with the deflecting plates cemented directly onto the cell walls and distant 3 cms. apart, the object being to decrease the size of the cell and the amount of benzene required to fill it. With this type of cell, the drop paths photographed were modified by electro-endosmosis of the benzene along the cell walls and between the plates, this occurring when the high deflecting voltages were applied. The type of drop path photographed with such a cell had a characteristic curvature near the deflecting plates as shown in Fig. 25. Many attempts were made to analyse this type of curve until the streaming of the benzene along the cell walls was observed. The motion of the benzene, as indicated by a suspension of lycopodium powder, usually took the form of a double spiral as illustrated in Fig. 10 and Fig. 11.

The possibility of electro-endosmotic flow occurring with benzene had not been considered up to this time, chiefly because of the results obtained by Fairbrother and Balkin who found very small flow effects occurring at the benzene /glass interface, under the influence of potential gradients. They even found this to be the case with benzene made artificially impure, and they attributed it, and a similar effect for carbon tetrachloride, to the fact that molecules of such substances have extremely small electric moments. That electro-endosmosis occurred in our experiments may be due to either (a) much higher voltage gradients being used than in Fairbrother and Balkin's experiments, or (b) the cell being constructed of soft glass whereas Fairbrother and Balkin examined the hard glass/benzene and quartz/benzene interfaces.

Mounting the plates away from the cell walls, in the manner ~~described~~ above reduced the flow effects to a minimum, and even at the highest voltages used there was no disturbance of the benzene between the plates.

The dropper

A glass capillary dropper of the type already described, earthed and well screened by an earthed tube, was used, the drops forming in the centre of the screen. Drops of diameter 2-3 m.m. were obtained in this manner, and for experiments in which smaller water drops were required the Lane type dropper, suitably earthed and screened, was used.

Method of drop illumination

The method described previously using a vertical, highly concentrated, parallel beam of light between the plates to illuminate the drops as they fell was not successful in these experiments, as too much light was blocked by the screening used. As an alternative the drops were illuminated by a 100 watt electric bulb situated behind and slightly above the cell. Extraneous light was prevented from falling on the camera by means of a screen placed so that only the partof the cell under observation was photographed, and the heat component of the radiation was removed by a water cell placed between the lamp and the cell. The arrangement was then as shown in Fig. 12.

The timing of the drop was as before, the vanes of a rotating disc interrupting the light from the electric lamp. A time of 0.0727 second was represented by one dash length on the photographs.

Voltage Supply and Screening

The voltages used were obtained from three 2000 volt , 250 m.A. motor generators wired in series, and controlled by a rheostat fitted on the motor side. Steady D.C. voltages between 1000 and 6000 volts were obtained in this manner. The voltage was measured by a 0-6000 volts electrostatic voltmeter and could be reversed by a switiching arrangement shown in Fig. 13, the high voltages always being disconnected from the cell before the reversing key was switched. As benzene is such a good non-conductor the generators were running on very light load throughout the experiments, and they maintained very steady D.C. voltages.

Ample screening was provided to prevent charges being induced on the drops forming at the dropper, by the high voltages in use. The dropper and the 15 cm. column of benzene was surrounded by a half inch diameter earthed copper tube S and further screened from the high voltages in use by the 9" x 12" earthed copper sheet N, the tube and sheet resting on a wooden stool, and completely covering the top of the cell as shown in Fig. 14. The leads carrying the high voltages from the generators to the reversing key were screened polythene cable, the outer screening being earthed, and the voltage supply centre tapped to earth across two 10 meghom resistances, as shown in Fig. 13. All unscreened connections and leads lay underneath the 9" x 12" earthed plate.

Experimental procedure used with water drops in benzene.

With the experimental arrangements as outlined above the following experiments were performed, the water drops falling from the air into the benzene. Photographs of the drop paths were taken on Ilford H.P.3 plates, the F/3.5 camera being used at double extension. The method devised by Curry was used for the examination of the photographs, the plates under examination being illuminated by a lantern and the enlarged image focused on a sheet of paper pinned on to a drawing board. The image of the drop paths was traced on the paper, and the measurements were made on the enlarged tracing. The magnification was usually of the order 25-30, but this was not needed in the calculations, as the slope of the straight line paths was all that was required. The type of photographs obtained in this series of experiments is shown in Figs. 26-28 and it can be seen that the drop paths became straight lines after the first centimetre or so between the plates. The horizontal force F acting on the drop in each case, was obtained from the relationship

$$\frac{E}{m'g} = \frac{y}{x} = \tan \theta$$

m' being the weight of the water drop in benzene.

Drops of distilled water of diameter 1.95 m.m. were first usedand they fell slowly and centrally between the copper plates. Voltages between 0-6000 volts were applied in turn between the plates and the drops of water in every case movedtowards the positive plate. Deflections of the drops were photographed for deflection voltages between 0-6000 volts and the magnitude of F the horizontal force on the drop calculated in each case. F was found to be proportional to the $(\text{voltage gradient})^2$ and not to voltage gradient as expected. Table III below gives a series of results for drops of this diameter falling through electric fields of different intensities.

$$m'g = \frac{4}{3} \pi \times (.0975)^3 \times 0.12\, g$$

$$= \underline{0.4575 \text{ dynes}}$$

TABLE III

Photograph Number	Voltage Gradient	(Voltage gradient)^2	$\tan \theta = \frac{y}{x}$	$F = m'g \tan \theta$ dynes
175	2.20	4.84	.045	2.06×10^{-2}
	3.350	11.22	.11	5.03×10^{-2}
	3.450	11.9	.115	5.26×10^{-2}
	4.250	18.06	.18	8.24×10^{-2}
	4.375	19.14	.2	9.16×10^{-2}
	5.780	33.41	.35	16.0×10^{-2}

Graph 2 was drawn from the above result relating $\tan \theta$ and E^2, the square of the voltage gradient in e.s.u., and as can be seen it is a straight line graph passing through the origin. This indicates that the charge on the water drop in benzene is zero in the absence of an electric field, but in an electric field the drop acquires a charge proportional to the field intensity.

By means of the Lane dropper, water drops between 0.8 and 2 m.m. were produced and the drop paths of these photographed in fields of different intensities. For each drop size used, $\tan\theta$ and therefore F was found to be proportional to E^2, the square of the field intensity. The drops in each case fell through 15 cms. of benzene before reaching the deflecting plates. Table IV below shows the results obtained with such drops and graph 3 shows the relationship between $\tan\theta$ and E^2 in each case.

TABLE IV

Photograph Number	Diameter of drop in m.m.	Voltage Gradient in e.s.u.	E^2	$\tan\theta$	$F = m'g \tan\theta$
177	1.1	2.4	5.76	.125	1.125×10^{-2}
		3.25	10.56	.225	1.845
		3.70	13.69	.3	2.46
178	1.6	2.5	6.25	.08	2.02
		4.3	18.49	.25	6.32
		4.8	23.04	.315	7.96
179	0.82	2.45	6.003	.28	0.953
		2.85	8.123	.35	1.19
		3.1	9.60	.42	1.43

If q is the charge on a drop of water, of radius a, in a field of intensity E E.S.U., then

$$F = q.E.$$

But in all the above results $F \propto E^2$

$\therefore q = kE$, where k is a constant which may vary with the drop radius. We therefore, see that the charge on a water drop in benzene is directly proportional to the field intensity and is zero when the field is zero.

Graph 3 shows the relationship between $\tan\theta$ and E^2 for different size drops, so that $\tan\theta$ can be obtained directly for each drop radius and these values are given in table V below:-

TABLE V

Radius of drop a in cms.	$1/a^2 \times 10^{-2}$ cm.$^{-2}$	$\tan\theta/E^2$ e.s.u.$^{-2}$
.041	5.94×10^2	.045
.055	3.3×10^2	.0225
.08	1.56×10^2	.01375
.0975	1.05×10^2	.0095

Now $\tan\theta \propto \frac{F}{a^3}$, and as

$F = kE^2$,

$$\frac{\tan\theta}{E^2} \propto \frac{k}{a^3}$$

Graph 4 derived from the results in table 5 above, shows that there is a linear relationship between $\frac{\tan\theta}{E^2}$ and $\frac{1}{a^2}$ so that

$$k \propto a$$

The charge acquired by a drop of water in an electric field in benzene is therefore proportional to the radius of the drop, a , and the intensity of the field E. i.e.

$$\underline{q = A' a. E.}$$

A' being a constant. The order of charge acquired i.e. the value of A' can easily be obtained from the above results. A' is found to be 0.515 e.s.u. charge/ cm. radius/ e.s.u. field intensity.

- The complete screening of the dropper ensured that no charges were induced on the drops, by the voltages applied to the deflecting plates while they were forming at the tip, so that any deflection of the drop in the electric field must have been due to other causes. That this was so was also proved by alterations made in the earthing of the voltage supply. The earthed centre tapping was removed and the positive plate earthed. The drops of water in the benzene still moved towards the positive plate and the deflection was of exactly the same magnitude This was again the case when the negative side of the voltage supply was earthed. Thus, as the deflection towards the positive plate was of the same magnitude when the voltage supply was (a) centre tapped to earth (b) positive side earthed (c) negative side earthed, it was evident that induced charges on the drop, if any, were extremely small.

That the charge was not induced at the dropper was also seen to be true, when a drop reached the positive plate and on collision acquired a positive charge. Under the influence of the field the drops then moved towards the negative plate but once it left the positive plate it quickly lost its positive charge, regained the negative charge and moved back towards the positive plate. Thus, in some cases, the drop made a series of "hops" down the positive electrode. Figs. 26-28, which are prints from photographs taken of this phenomena, show the effect at different field intensities.

This effect also makes it quite obvious that the method is of little use for the measurement of charges acquired by the water drops in the air, before entering the benzene, as these charges are immediately modified when the drop enters the electric field.

As charges induced on the drops while forming at the dropper could not explain the charging of the water drops in the electric field, other possibilities were examined. Benzene and water are slightly soluble in each other at room temperature, benzene being 0.15% soluble in water at 20° C, so that solution of one phase in the other may have occurred during the passage of the drop through the benzene. In order to see if the acquisition of charge in the electric field was due to this solution effect, saturated solutions of benzene in water, and water in benzene, were prepared. This was done by having the benzene and distilled water in contact with each other for two or three weeks, the mixture being thoroughly shaken at frequent intervals. Using these solutions, measurements of charge on water drops in benzene were made in the following sequence, drops of 1.95 m.m. diameter being used in each case:

(a) Drops of distilled water in benzene which had been redistilled and was therefore free from water.

(b) Drops of distilled water in benzene saturated with water.

(c) Drops of distilled water saturated with benzene in benzene saturated with water

(d) Drops of distilled water saturated with benzene in benzene free from water.

The charge acquired by the drops in the electric fields was the same in all the above cases and identical with the charges acquired by the distilled water drops of this diameter listed in Table III above. This indicates that solution of one or both phases in the other has little if any effect on the charge acquired by the water drops in the electric field in the benzene.

In the above experiments distilled water drops were used, no special precautions being taken to rid the water of any impurities. The purity and conductivity of the water was therefore uncertain, especially as it had been in contact with soft glass for long periods before use. In order to see if the charges acquired could be attributed to the presence of impurities in the water, a reservoir and capillary tubing dropper of hard glass were constructed. By having an hard glass conductivity cell serving as the reservoir, the conductivity of the water could also be measured while the dropper was in use, any errors which would occur by transferring the water to a separate dropper being eliminated. The system used is shown in fig. 15.

A was an hard glass conductivity cell containing two parallel platinized platinum discs, 1.5 cms. diameter and distant 0.6 cms. apart. Connection to these discs was by thin platinum wire fused into the sides of the 4 cm. diameter bulb of the cell. The dropper D was joined directly to this cell by a 20 cm. length of capillary tubing, and tap, as shown. The short length of 1 cm. diameter tube BC contained a few pieces of hard glass fragments as "clinker". A ground glass stopper fitted the top of the cell and the two tubes in this stopper were used for steaming out the cell, or alternatively the pressure inside the cell was reduced by connecting a filter pump to one of the tubes, the other being closed by a tap. The cell and dropper were mounted on a wooden baseboard which could be clamped in a retort stand.

The cell was first thoroughly cleaned, using strong chromic acid followed by weak solutions of caustic soda and nitric acid. Whereas care was taken to prevent any of the chromic acid coming into contact with the platinized electrodes, the capillary and dropper were left two or three days in contact with this strong cleaning agent. After thorough washing with distilled water, the cell was steamed out for 12 hours, the condensed steam flowing through the capillary dropper and washing that in turn. An hard glass boiler containing distilled water with a trace of potassium permanganate and pure nitric acid was used to provide the steam. This in effect gave the cell a thorough washing with boiling conductivity water.

A quantity of distilled water was further purified by redistillation three times in an hard glass distilling apparatus. The cell and dropper were rinsed with a sample of this water and then filled. The resistance between the platinized electrodes was measured by a Mullard, 50 cycle, A.C. bridge. The resistance measured in this manner gave a direct value of the conductivity of the water as the cell constant of the cell, C, had been previously determined by means of a standard potassium chloride solution. If R is the resistance in ohms measured in this manner, the specific resistance of the water σ, is

$$\sigma = R.\frac{A}{l} \text{ ohm. cm.}$$

where A is the area of the electrodes

ℓ is the distance between the electrodes.

$\therefore$ σ = C.R where C is the cell constant. With the cell in use C was 4·5 . The specific conductance of the water, K, will therefore be

$$K = \frac{1}{CR} \text{ ohm}^{-1} \text{ cm}^{-1}$$

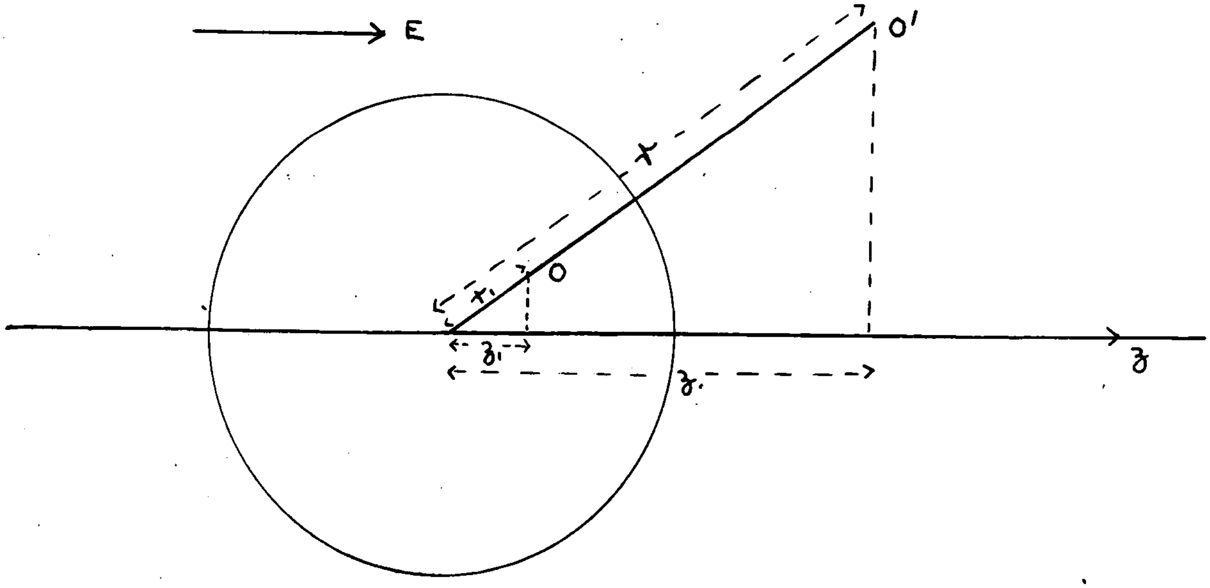
The conductance of the redistilled water when it was first inserted was measured in this manner and it was then boiled in the cell under reduced pressure, using a small gas flame to heat tube C D. The object of boiling was to drive off any air remaining in the conductivity water after redistillation and especially to remove any dissolved carbon dioxide. The glass clinker in tube C D prevented any serious "bumping" during the boiling, and reducing the pressure by means of a filter pump enabled the boiling to be carried out at 35° C. Arrangements were made so that any air entering the cell after the water had been boiled did so as small bubbles through a fine jet in strong caustic soda solution, this preventing carbon dioxide from coming into contact with the water.

The resistance of the air free water prepared in the above way was found to be 90,000 ohms at 20°C, inthe cell. The calculated specific conductance at this temperature was therefore 2.47×10^{-6} ohm^{-1} cm^{-1}. Drops of this purer water of diameter 1.95 m.m. were dropped into the benzene and fell between the deflecting plates. Voltages up to 6000 volts were applied between the deflecting plates but there was no detectable deflection of the drops,

The water in the cell was next saturated with air, this being drawn through the cell for two hours, by way of the capillary dropper. The resistance of the water in the cell after air and carbon dioxide saturation was a little less, dropping to 87,000 ohms, this being equivalent to a specific conductance of 2.55×10^{-6} $\text{ohm}^{-1}\text{cm}^{-1}$ at 20° C. Even so, drops of this water were not appreciably deflected in the highest voltage gradients available.

Distilled water drops of uncertain purity from the original soft glass dropper still acquired the large negative charges in the benzene, so that the reduction in charge acquired by the purer water drops was therefore due to the removal of impurities from the water. A sample of the impure distilled water contaminated with soft glass and impurities from rubber tubing was found to have a specific conductance of 1.2×10^{-5} ohm^{-1} cm^{-1}. Thus all the charges acquired by the water drops in the previous experiments must have been due to the presence of impurities in the water. That some of these impurities were ionized is indicated by the higher conductance of the impure water.

Let us consider the movement of an insulated spherical drop of radius, a, in an electric field of intensity E. If there are ionized impurities in the water drop, then under the influence of the strong electric fields the positive and negative ions will migrate to opposite sides of the drop, forming an electric doublet in the insulating benzene. The drop will have zero net charge unless the positive or negative ions penetrate the water/benzene interface under the influence of the electric field and leave the drop with an excess of ions of one sign. There will, however, be a surface distribution of charge on the sphere due to the polarization effect and the potentials inside and outside the sphere due to the surface distribution of charge are related in the following manner.



If O and O' in the diagram are inverse points i.e. $r_1 r' = a^2$

then $$V_o' = \frac{a}{r} V_o$$

where Vo and Vo' are the potentials at O and O' respectively due to the surface charges on the drop.

If a field of intensity E acts parallel to the z axis as shown, and we have the origin as the centre of the sphere

$$-\frac{\partial V}{\partial z} = E$$

$$V = -Ez$$

V being the potential at any point due to the field.

If the sphere has a potential C, this will be the potential over the whole of the inside.

The potential inside at O due to the distribution of electricity on the surface of the sphere must therefore be

$$V_o = C + Ez_1$$

i.e. the total potential at O = C + Ez_1 - Ez_1 = C.

The potential outside the sphere at the inverse point O' due to the distribution of charge on the surface of the sphere will therefore be

$$V_{o'} = \frac{a}{r} V_o$$

$$= \frac{a}{r}(C + Ez_1)$$

$$= \frac{a}{r}(C + r_1 \cos\theta . E)$$

$$= \frac{a}{r}\left(C + \frac{Ea^2\cos\theta}{r}\right)$$

The total potential outside at O' is Vo' - Ez

$$= \overline{V_{o'}} = \frac{a}{r}\left(C + \frac{Ea^2\cos\theta}{r}\right) - Er\cos\theta$$

Now the resultant intensity at the surface of the sphere $E_a = 4\pi\sigma$ where σ is the surface density of charge at the surface.

$$\therefore \quad 4\pi\sigma = -\left\{\frac{\partial V_0'}{\partial r}\right\}_{r=a}$$

$$= \left\{\frac{Ca}{r^2} + \frac{2Ea^3\cos\theta}{r^3} + E\cos\theta\right\}_{r=a}$$

$$= \frac{C}{a} + 3E\cos\theta$$

$$\therefore \quad \sigma = \frac{C}{4\pi a} + \frac{3E\cos\theta}{4\pi}$$

$\therefore$ the total charge on the sphere, q,

$$= \frac{C \times 4\pi a^2}{4\pi a}$$

$$\underline{= C.a}$$

This result means that a sphere of potential C and of radius a, moving into a transverse electric field with its centre along the line V = 0 collects a charge, q, given by the equation

$$\underline{q = C.a}$$

This is in agreement with the experimental results, in so far as the charge acquired in the electric field is proportional to the drop radius, a. It is difficult to see, however, why the water drop in the electric field should acquire a potential $C \neq 0$ with respect to the benzene surrounding it.

The arrangement was such that the drop of water from an earthed dropper fell midway between two plates which were at potentials $+\frac{V}{2}$ and $-\frac{V}{2}$ respectively i.e. the field was centre tapped to earth. The drop at earth potential would thus be falling with its centre along the line $V = 0$, so that unless its potential was altered in the electric field, C would be 0 and the drop would pass through the field uncharged and undeflected. This was found to be the case for drops of purified water in the benzene.

In order to explain the results obtained with the impure water drops, the potential C across the water - benzene interface must therefore become negative in the electric field and the magnitude of C must increase in proportion to E, the field intensity. It is difficult to see why such a relationship should exist. Alternatively the drop may acquire the negative charge in the electric field, by the loss of positive ions of the impurities in solution, across the water benzene interface, in such a way as to leave the drop with a negative charge. It is still difficult to explain why the negative charge acquired, in this way should be proportional to drop radius, a, and field intensity E.

To see if more information could be obtained on the conditions existing at the water - benzene interface, in order to throw more light on the above results, a series of experiments on benzene drops in water and aqueous solutions were performed. An account of these is given in the next chapter. Although some interesting results were obtained with benzene drops in water, they were not, however, of direct use in arriving at an adequate explanation of the above work.

CHAPTER 5

The measurement of charge on benzene and other nonconducting drops in aqueous solutions.

Construction of cell and dropper.

As benzene is less dense than water, the arrangement of the cell constructed for this series of experiments was such as to allow the benzene drops to rise vertically through the water and midway between two platinum deflecting plates. A more robust cell than the type used in the previous experiments was constructed, 2.5 m.m. thick window glass being used and this was cemented with a shellac cement, put on under heat. The cement was 80% shellac and 20% wood tar, and it gave a robust joint insoluble in water and benzene and resistant to weak acid and alkaline solutions. The construction is shown in Fig. 16, and Fig. 17 is a photograph of the actual cell used.

The cell was 25 cms. high, 10.5 cms. wide and 5 cms. deep, the platinum deflecting plates mounted vertically in the cell being 10.3 cms. long, and 2.5 cms. wide and situated 3.05 cms. apart. These plates consisted of 0.01 cms. thick platinum foil cemented onto rectangular glass plates of the same area. A 3m.m. diameter hole was drilled in the centre of each of these glass plates to enable soldered connections to be made to the platinum with the fine copper leads from the D.C. voltage supply. The deflecting plates were again mounted in position by means of two 3.5 cms. lengths of centimetre diameter glass tubing, these also serving to prevent the liquid in cell from coming into contact with the soldered connections and copper connecting wires. The cell constant $C = \frac{A}{l}$ was calculated from the dimensions of the plates and found to be 8.44cms. Using this value of C the conductivity of the aqueous solutions were calculated from the resistance between the plates measure by a 50 cycle Mullard bridge.

The fine thin walled capillary at which the benzene drops formed was cemented into a wider tube fitting over a hole drilled in the centre of the base, the tip of the capillary being vertically below and midway between the plates. The benzene drops rose through 8 cms. of water before entering the electric field. Supply of benzene to the dropper was from the reservoir as shown, the height of benzene being sufficient to ensure the regular formation of benzene drops at the rate of one a minute. This rate of formation could be speeded up if necessary by applying pressure with a cycle pump through tube E in the top of the reservoir. Drops formed by the fine capillary in the above manner were of the order of 2 m.m. diameter. In use, the tap to the benzene reservoir was turned on and pressure applied until a steady stream of drops formed at the end of the capillary. This pressure was removed when it was seen that the benzene drops were forming steadily and evenly, and the drops allowed to form under the head of benzene at the rate of one a minute. The diameter of these drops when on the point of leaving the capillary tip was measured by means of a microscope fitted with a scale in the eye-piece. The horizontal and vertical dimensions were taken and the mean used as the diameter of the free drop in the solution. With drops of the order of 1·5m.m. to 2 m.m. diameter there was a difference of 10% in the horizontal and vertical diameters measured in this manner but in the initial experiments the object was not to get an exact value of the diameter, but to check that drops of the same size formed throughout the series of observations. The terminal velocity of the drop rising vertically, as measured from the photographs, was also used as a check for consistency of drop diameter.

The same dropper was used throughout the initial experiments, but as has been observed by other workers[17,20] thin walled capillaries are not dependable for producing drops of a consistent size. The changes in drop diameter observed in these experiments were not serious however, the capillary delivering drops of the same size over long periods of time. The changes that occurred did so from one experiment to the next rather than during the series of observations making up an experiment. Thus, by making use of the microscope to give a direct reading of drop diameter, and from measurements on terminal velocity, the results obtained were easily corrolated.

The top of the cell was a fitted glass plate which could be removed when it was necessary to fill the cell, and the cell could be emptied by means ofthe exit tube in the base. The cell and dropper were mounted as a complete unit on a wooden stool and baseboard.

Voltage Supply.

D.C. voltages up to 760 volts were available from a bank of H.T. batteries, the voltage across the cell and the current flowing being measured by a voltmeter and milliam meter connected as shown in fig. 18. Provision was also made to measure the resistance of the solution in the cell between the platinum deflecting plates by means of a Mullard 50 cycle A.C. bridge. The Pohl commutator, P_2 in the diagram, enabled the plates to be used for this conductivity test or to be connected to the D.C. voltage supply. This arrangement was found to be most convenient, as the conductivity of the solution in the cell was directly measureable before and after the D.C. voltages were applied. This value of the conductivity, as will be explained later, was a measurement of the ionic concentration of the solution, providing that the mobilities at 20°C of the ions present were known. Key K was a press key, inserted so that the D.C. deflecting voltages could be applied for the minimum time necessary i.e. while the drop being photographed was between the plates. Any gassing of the electrodes due to electrolysis was therefore reduced to a minimum. Commutator P_1 enabled the deflecting voltages to be reversed so that a deflection on either side of the vertical could again be photographed.

Drop Illumination and Interpretation of Photographs

The system illustrated in fig. 3 was again used, a vertical, parallel beam of light of 4cms. diameter being produced by reflection of a pointolite beam from a concave mirror above the cell. A light interupter of the usual rotating sectored disc type was again employed to time the drops moving through the water.

Photographs of the drop paths were taken on Ilford H.P. 3 plates, using the F/3·5 camera at double extension as before. In all the experiments discussed in this chapter the drops in the electric fields quickly acquired straight line paths, no appreciable curvature being noticeable. This indicated that the equilibrium charge was quickly reached and also that the horizontal terminal velocity was very rapidly attained. The slope, tanθ, of the drop paths was again a direct measurements of the horizontal force F on the drop as

$$\tan\theta = \frac{F}{m'g}$$

Because of the excellent photographs obtained and the good straight line paths acquired, tan θ was measured directly from the photographic plates by means of a microscope fitted with a scale in the eye-piece, only the horizontal deflection at the top of the field being measured as the drops traversed the same fixed length of field in each case.

Figs. 29 to 35 show the type of photographs obtained in the above manner, the deflections in all cases being towards the positive plate, showing the drops to be charged negatively.

Drops of Benzene in Water.

The diameter of the benzene drops throughout this series of experiments was constant and equal to 1·95 m.m.

The first object was to see if the negative charges acquired by the benzene drops in water was affected by the volage gradient between the plates. The cell was filled with water which had been purified by redistillation in hard glass apparatus and photographs 365 - 371, given in table VI below, taken. The resistance between the plates as measured by the Mullard bridge, for water of this purity, was 5×10^4 ohms, from which the specific conductivity was calculated to be $2{\cdot}37 \times 10^{-6}$ ohm^{-1} cm^{-1}. Tan θ was measured for each voltage gradient and the values are listed.

TABLE VI

Photograph Number	Voltage between Plates	Current m. amps	Tan θ	Charge on drop $q = \frac{\tan\theta . m'g}{E}$ e.s.u.
365	360	7·2	/	/
366	474	9·5	/	/
367	62	1·2	·0097	·0653
368	125	2·5	·0136	·0454
369	184	3·7	·01757	·0399
370	244	5·0	·01815	·0310
371	300	6·1	·01815	·0252

Graphs 5 and 6 drawn from the results shown in this table show the relationship between tan θ and voltage gradient, and charge on drop and voltage gradient, respectively. It can be seen from graph 5 that tan θ increased with increase in voltage gradient up to 50 volts/ cm., above which tan θ did not increase. Indeed as the voltage gradient increased above 100 volts/ cm. the drop paths became very erratic as though the charge on the drop was unsettled and unstable. Photographs 365 and 366 shown in figs. 34 and 35 illustrate the type of paths obtained with such fields. It is to be noticed in these photographs that the drops traversed fully one third of the field before showing any deflection from the vertical, indicating that the charge on the drop was very small during this period.

Graph 6 shows the decrease in charge on the drop in water of this purity as the voltage gradient increased, and it is evident from this curve that for voltage gradients above 150 volts / cm. the charge is small and approaching zero. In the field free water the charge on the drop is negative, and by producing the curve of graph 6 back to the zero voltage gradient axis, the order of this charge is seen to be 0·086 e.s.u. Graph 6 makes it obvious that the voltage gradients used to measure the charge on the benzene drops are themselves altering the magnitude of charge. In order to obtain values approaching the correct magnitude, gradients as small as possible will therefore need to be used in water of this purity.

If the charge on the benzene drop is attributed to selective adsorption at the benzene / water interface, of negative ions from the water, it is evident that when the drop enters an electric field of sufficiently high intensity some of adsorbed ions are removed from the surface and migrate towards the positive electrode. If the field intensity is sufficiently great all the negative ions are forcibly removed leaving the drop with zero charge and this seems to be the state of affairs in photographs 365 and 366.

Although the water used in the above experiments was purer than distilled water, the greater part of the ions in solution must have been due to impurities present, these probably being dissolved out from the cement used to assemble the cell and also from the soft glass plates used in its constuction. There would, however, be H^+ and OH^- ions present, due to the partial dissociation of the water. Kohlrausch and Heydweiller[26] gave the dissociation as

$$[H^+]\,[OH^-] = 0{\cdot}6 \times 10^{-14}\ N \text{ at } 18^\circ\ C,$$

this value being determined from conductivity measurements on water of extreme purity, and this relationship must be satisfied in all aqueous solutions at 18°C. In neutral solutions, the

$[H^+]$ and $[OH^-]$ are equal and

$$[H^+] = [OH^-] = 0{\cdot}8 \times 10^{-7}\ N$$

Therefore, if the negative charge observed on the benzene drops was due to selective adsorption of negative ionsas suggested, the ions adsorbed could have been either OH^- ions, present due to partial dissociation of the water, or negative ions from the dissolved impurities. In order to see if the charge on the benzene

drop increased as the impurities increased the above experiment was repeated using distilled water with a much higher conductivity, the concentration of the OH^-

ions being the same but the concentration of negative ions from the impurities being much greater. Water of conductivity 9·16 x 10^{-6} ohm^{-1} cm^{-1} was used and photographs 372 - 379, listed in table VII, below were taken.

TABLE VII

Photograph Number	Voltage applied between plates	Tan θ	Charge an drop q $q = \frac{m'g \tan\theta}{E}$ e.s.u.
372	61	·0135	·086
373	61, 180	·01135, ·0329	·086, ·0762
374	239, 121	·0408, ·0227	·071, ·0784
376	295	·0606	·0856
377	350	·0606	·072
378	405	·059	·0608
379	462	·0635	·0574

Graphs 7 and 8 were drawn from the above results and show how tan θ varies with voltage gradient, and how charge on the drop varies with voltage gradient respectively. Graph 7 shows that in water of this purity, tan θ increases almost in proportion to voltage gradient up to 100 volts / cm but if the field is increased above this valve tan θ is little affected. Graph 8 indicates that there is a decrease in charge as the voltage gradient increases but this decrease is small compared with that observed in the purer water. The magnitude of the negative charge on the benzene drop in the field free water obtained from graph 8 is 0.086 e.s.u., this being in exact agreement with the value derived from graph 6 for the benzene drops in the purer water. Thus, although the concentration of negative ions due to impurities has increased more than threefold, this being obvious from the relative values of the specific conductivities of the waters used , the charge on the benzene drops in the absence of an electric field is the same in each. That this is so indicates that it is the hydroxyl ions from the dissociated water molecules which are adsorbed giving the negative charge to the benzene drop, and not the negative ions from the impurities.

As the charge on the drop in the less pure water was not so readily affected by the higher potential gradients up to 100 volts / cm, the great number of ions present per c.c., due to the impurities, must have helped to "screen" the drop from the influence of the field and so prevented the adsorbed hydroxyl ions from leaving the surface of the benzene. As the voltage gradient was increased beyond 100 volts / cm this screening action became less effective and the charge on the benzene drop decreased.

The above photographs were exposed using water free from benzene and benzene free from water, so that solution of one phase in the other was possible. In orderto see if such an effect made any difference to the charge obtained, the experiments were repeated using water saturated with benzene and benzene drops saturated with water. The results obtained in these experiments were identical with those given above, this indicating that if solution did occur, it had little effect on the charge acquired by the drop.

In the following series of experiments no attempt was made to change the water or aqueous solutions in use as they became saturated with benzene, and benzene saturated with water was used in the dropper.

Drops of benzene in Alkaline and other Aqueous Solutions

As the above experiments indicated that the OH^- ions present in water were responsible for the negative charge on the benzene drops, the effect of increasing and decreasing the concentration of the OH^- ions on the magnitude of the charge acquired was investigated. As very weak solutions of alkalis and acids were used, it was found most convenient to start each series of experiments with distilled water in the cell, and to increase the concentration by adding drops of a $N/_{10}$ solution of the electrolyte in use.

Measurement of the resistance of the solution between the platinum plates in each case enabled the conductivity to be calculated in the manner already described and using this value, the concentration of the ions in solution was obtained making use of the ionic mobilities listed below. The mobilities of the following ions at 18° C are given in Kaye and Laby's "Physical and Chemical Constants":

H^+	330	OH^-	180
Na^+	45	Cl^-	68
NH_4^+	66	NO_3^-	64
$\frac{1}{2}Ba^+$	55	$\frac{1}{2}SO_4^{--}$	71
$\frac{1}{3}La^{+++}$	57		

The conductivity of a completely ionized solution is proportional to the sum of the mobilities of the positive and negative ions in solution. Thus a solution of H_2SO_4 and a solution of the same normality of HCl, assuming complete dissociation, will have conductivities in the ratio

$$\frac{(U+ \; + \; U-)_{H_2SO_4}}{(U+ \; + \; U-)_{HCl}}$$

Where U+ and U- are the mobilities of the positive and negative ions. This ratio for sulphuric acid and hydrochloric acid will therefore be

$$\frac{330 + 71}{330 + 68} = \frac{401}{398}$$

Similarly equal concentration solutions of Na OH and H_2SO_4 will have conductivities in the ratio

$$\frac{45 + 180}{330 + 71} = \frac{225}{401}$$

assuming complete dissociation in each solution.

The resistance between the plates when the cell was filled with a $N/_{1000}$ solution of sulphuric acid was found to be $1\cdot9 \times 10^2$ ohms. By making use of this value, the ionic concentration of any solution can be calculated from the resistance measured between the plates, providing the ions in solution and their mobilities are known. Thus a solution of NaOH with resistance R ohms in the cell must have an ionic concentration of

$$\frac{1\cdot9 \times 10^2 \times 401}{R \times 225} \quad . \quad N/_{1000}$$

$$= \frac{3\cdot386 \times 10^2}{R} \quad . \quad N/_{1000}$$

It is to be noted that this value will be the concentration of the ions in solution and will not give any indication of undissociated NaOH in solution. We have assumed that the $N/_{1000}$ sulphuric acid with cell resistance $1\cdot9 \times 10^2$ ohms was completely dissociated, and with a solution of such a strong electrolyte of this concentration, this can be assumed to be correct.

The distilled water with which each set of experiments was started was assumed to contain none of the electrolyte to be used so that a small "end correction" was subtracted from the value of the concentration calculated in each case. This correction was always of the order 1×10^{-5}.N.

Benzene drops of diameter 1·5 m.m. were first used in solutions of NH_4OH and H_2SO_4 and the charge on the drop derived from the deflectious in fields of 40 volts/cm and 80 volts/cm. The results obtained and the value of the charge calculated for each concentration are given in tables VIII and IX below.

NH_4OH solutions TABLE VIII

Photograph No.	Resistance x10^4 ohms	Conc. Calculated x10^{-5}N	Conc. -"end correction" x10^{-5}N	Voltage Applied	Tan θ	Charge $q=\frac{m'g\tan\theta}{E}$ in e.s.u
384	3·2	1·0	10^{-2}	121	·0136	·0212
385				240	·02665	
386	1·865	1·7	0·7	121	·01985	·0309
387				239	·04025	
388	1·02	3·1	2·1	121	·0312	·0487
389				237	·0624	
390	·64	4·9	3·9	121	·04025	·064
391				235	·0828	
392	·40	7·92	6·92	120	·0448	·078
393				230	·093	
394	·25	12·75	11·75	119	·0453	·078
395				227	·093	
396	·097	32·8	31·8	60	·0221	·078
397				118	·0453	

H_2SO_4 solutions TABLE IX

Photograph No.	Resistance x10⁴ ohms	Conc. Calculated x10⁻⁵N	Conc. -"end correction" x10⁻⁵N	Voltage Applied	Tan θ	Charge $q=\frac{m'g\tan\theta}{E}$ in e.s.u.
400	2·38	0·798	10-2	121	·0136	·0212
401				238	·0266	
402	1·39	1·366	0·566	121	·0136	·0212
403				236	·0272	
404	0·85	2·235	1·435	120	·013	·0203
405				235	·025	
406	0·505	3·76	2·96	120	·0145	·0195
407				231	·024	
408	0·255	7·45	6·65	120	·0107	·0167
409				228	·02	
410	0·17	10·05	10·05	119	·0096	·0149
411				222	·019	
412	0·075	25·3	24·5	60	·0062	·00966
413				114	·012	
414	0·130	14·6	13·8	117	·0085	·0133

Graph 9 was drawn from the results in table VIII and shows the relationship between drop charge and hydroxyl ion concentration in the NH_4OH solution. The charge increased steadily as the concentration of the OH^- ions increased until a maximum, or "saturation", charge was reached with solutions of concentration greater than 7×10^{-5}N. Increasing the NH_4OH concentration above this value had little effect on the drop charge.

Graph 10 produced from the results in table IX, shows that the drop charge is reduced by adding H_2SO_4 i.e. by reducing the hydroxyl ion concentration. It appears from this curve that in sufficiently high acid concentrations the drop charge will become zero, this probably occurring when no hydroxyl ions are present in solution.

Graph 11 shows the drop charge acquired over the whole range of acid and alkaline solutions covered, this being done as the two sets of results are obviously closely connected. Graph 12 was produced connecting the results in another manner, drop charge being plotted against the calculated pH values of the NH_4OH and H_2SO_4 solutions used, the pH value being related to OH^- ion concentration in the form

$$\log_{10}\left[OH^-\right] = pH - 14$$

Benzene drops of 2·0 m.m. diameter were then used in NaOH and HCl solutions. The results obtained are given in tables X and XI below.

NaOH Solutions TABLE X

Photograph No.	Resistance $\times 10^4$ ohms	Conc. Calculated $\times 10^{-5}$ N	Conc. -"end correction" $\times 10^{-5}$ N	Voltage Applied	Tan θ	Charge $q = \frac{m'g \tan\theta}{E}$ e.s.u.
433	2·75	1·23	·01	121	·0215	·0794
434	2·05	1·64	·41	121	·026	·096
435				238	·051	
436	1·58	2·14	·91	120	·0312	·152
437				236	·0611	
438	0·98	3·46	2·23	120	·0436	·161
439				234	·0861	
440	0·65	5·23	4·0	120	·0553	·204
441				232	·110	
442	0·455	7·45	6·22	120	·0595	·220
443	0·291	11·58	10·35	120	·060	·221
444	0·208	16·23	15·0	119	·060	·221

HCl Solutions TABLE XI

Photograph No.	Resistance $\times 10^4$ ohms	Conc. Calculated $\times 10^{-5}$N	Conc. - "end correction" $\times 10^{-5}$ N	Voltage Applied	Tan θ	Charge $q = \frac{n'g \tan\theta}{E}$ in e.s.u.
418	2·3	0·832	·01	121	·0215	·0794
419	1·35	1·418	·586	121	·0204	·0753
420				238	·040	
421	0·71	2·695	1·863	120	·0193	·0712
422				234	·038	
423	0·52	3·68	2·848	120	·017	·0628
424				233	·033	
425	0·28	6·84	6·008	120	·0147	·0542
426				230	·0275	
427	0·179	10·7	9·868	119	·0125	·0461
428				226	·024	
429	0·125	15·3	14·468	118	·0096	·0355
430	0·10	19·15	18·318	118	·0085	·0314
431	0·085	22·5	21·668	115	·00794	·0293
432	0·055	34·8	33·968	110	·00568	·0210

Graph 13 shows the drop charge - hydroxyl ion concentration curve for the NaOH solutions. As with the NH_4OH solutions, increasing the concentration of the OH^- ions caused an increase in negative charge acquired by the benzene drop, until the "saturation" charge was reached there being little increase in charge for concentrations above 7×10^{-5}N.

Graph 14 was drawn for the results listed in table X| and shows that there is again a steady decrease in charge as the solution is made acid, this time by adding HCl.

Graph 15 shows the drop charge acquired over the range of acid and alkaline solutions used and graph 16 relates drop charge with pH value for the NaOH and HCl solutions. These curves are identical in shape with those obtained for NH_4OH and H_2SO_4 solutions.

Similar results were again obtained with KOH and HNO_3 solutions, the drop charge, pH curve being shown in graph 17. The experiments using these solutions were designed to check the points of the charge / pH curve between the pH values 8·5 and 5·5, samples of each solution used being tested with a Marconi pH meter. There was good agreement between the results obtained in this manner and the previous results obtained for NaOH, NH_4OH, HCl and H_2SO_4. The pH value of the distilled water used was found to be 5·8 whereas it had been assumed to be 7 in the results calculated. The pH value of a solution, however, very rapidly alters with concentration of OH^- ions near the neutral value pH 7, so that this slight discrepancy was of little importance and all the results can be regarded as showing good agreement. The assumption made during the calculation of ionic concentrations that the distilled water was neutral was also shown to be reasonable by the fact that the pH value of this water, determined by pH meter, was 5·8.

The charges acquired by benzene drops of 1·65 m.m. diameter in sodium chloride, ammonium sulphate and potassium nitrate solutions were next measured. The results obtained are shown in table XII below.

TABLE XII

Photograph No.	Solution in use	Resistance x10^4 ohms	Conc. - "end Correction" x10^{-5} N	Voltage Applied	Tan θ	Charge $q = \frac{m'g \tan \theta}{E}$ in e.s.u.
448	Distilled Water	2·7	0	122	·0175	·0512
449	NaCl	1·3	2·68	121	·0175	·0512
450	NaCl	0·88	5·16	121	·0204	·0596
451	NaCl	0·67	7·55	121	·0181	·0529
452	NaCl	0·39	14·75	120	·0181	·0529
453	NaCl	0·245	25·0	119	·0170	·0497
454	NaCl	0·15	42·4	119	·0170	·0497
455	NaCl	0·075	87·3	119	·0181	·0529
511	Distilled Water and $(NH_4)_2SO_4$	1·75 & 0·1	0 and 52·42	120 118	·0181 ·0181	·0529 ·0529
512	Dist. Water & KNO_3	1·66 & 0·095	0 and 69·6	120 118	·0175 ·0181	·0512 ·0529

As can be seen from this table, addition of NaCl i.e. of Na^+ and Cl^- ions, had negligible effect on the charge acquired by the benzene drop, the charge remaining constant over the whole range of concentrations used. The same was also found to be true when $(NH_4)_2SO_4$ or KNO_3 were used.

The conclusion drawn from the above experiments was that the negative charge on the benzene drops, moving up through aqueous solutions, was due to selective adsorption of OH^- ions. A summary of the evidence leading to this conclusion is as follows.

Benzene drops have the same charge in distilled water and in water purified to a much greater extent. Remov ing the impurities to such an extent that the specific resistance is more than three times greater than that for distilled water, does not affect the magnitude of the negative charge acquired. The only difference is that the drops in the purer water more readily lose their charge in electric fields and this is thought to be due to the fact that the benzene drops in the less pure water are "screened" by ionic impurities.

Adding NaOH, NH_4OH or KOH increases the negative charge acquired by the drops until "saturation" charge is reached at hydroxyl ion concentrations greater than 7×10^{-5} N.

Adding HCl, HNO_3 or H_2SO_4 causes a decrease in the charge on the drops. A decrease in hydroxyl ion concentration must occur in these acid solutions because the relationship

$$[OH^-] [H^+] = 0{\cdot}6 \times 10^{-14} N \text{ at } 18^{\circ}C$$

must be maintained.

Adding NaCl, $(NH_4)_2 SO_4$ or KNo_3 has no effect on the charge acquired by the benzene drops. Thus, in the above acid and alkaline solutions the Na^+, NH_4^+, K^+, Cl^-, SO_4^{--} and NO_3^- ions have no effect on the charge. It is therefore obvious that it is the increase in hydroxyl ion concentration, when the solutions are made alkaline, which is effective in increasing the charge, and conversely the decrease in hydroxyl ion concentration when the solutions are acidified is effective in reducing the charge.

The negative charge on the drops must therefore be due to adsorption of the negatively charged hydroxyl ions at the benzene water interface. The straight line paths photographed in every case indicates that the equilibrium charge is reached before the drops enter the field, so that the maximum hydroxyl ion adsorption possible in each solution must occur while the drop is forming at the capillary tip and while it is moving up through the 8 cms. of solution between the tip and the deflecting plates. Any charging up time required by the drop must therefore be less than the time taken for the drop to form and reach the electric field, this usually being of the order of two seconds to one minute, the drops in the former case leaving the dropper after a very rapid rate of formation, and being forced out under pressure.

The origin of the negative charge being known, the next object was to see if the charge on the benzene drops in distilled water could be increased by the addition of negative ions other than hydroxyl ions. The ions Cl^-, SO_4^{--} and NO_3^- were found to have little, if any, effect on the charge, and it was therefore decided to try a more heavily charged multivalent ion . Potassium ferrocyanide, giving the tetravalent negative ion $Fe(CN)_6^{----}$, was used in solution and the results obtained are given in table XIII below, the drop diameter being 2m.m.

Potassium Ferrocyanide Solutions TABLE XIII

Photograph Number	Resistance x10^4ohms	Voltage Applied	Tan θ	Charge q e.s.u. $= \frac{m'g \tan\theta}{E}$
465	1·85	121	·0187	·069
466	0·64	120	·0198	·073
467	0·27	119	·0187	·069
468	0·12	115	·0198	·073

It is clear from these results that there was no increase in the negative charge on the benzene drops on the addition of $Fe(CN)_6^{----}$ ions. It therefore appears that negative ion adsorption at the benzene water interface is confined to hydroxyl ions, no other negative ion producing similar increases in negative drop charge.

The forces bringing about such adsorptionmust not, therefore, be purely electrostatic in nature, otherwise one would expect any negative ion in solution to be attracted to the interface, the more heavily charged the ion, the greater being the force of attraction. That the process of adsorption is not a simple electostatic phenomena has already been suggested by other workers notably Mukherjee[21], Stern[22] and Schofield[23]. Mukherjee pictured the electrification as taking place in two distinct processes (a) the formation of a "condensed" layer of ions close to the surface, and (b) the electrical attraction of oppositely charged ions to form a diffuse layer in the immediate volume of liquid surrounding the interface. The forces bringing about this second process were considered to be purely electrostatic but the "condensation" of ions was attributed to "chemical" or "quasi-chemical" forces. Schofield pointed out that there is evidence that forces non electrical in nature come into play in the condensed layer, as some electrocapillary curves, such as those for potassium iodide, show that iodide ions form a condensed layer on a mercury surface when the electrical forces at the interface are such as to repell rather than attract negative ions. This is evidently selective ionic adsorption in which the ion is held to the surface by a chemical force and it indicates how a complex ionic layer may be built up on a non conductor.

As explained in the introduction to this thesis molecular orientation may also play an important part in electrostatic attraction of ions to an interface. Indeed, Alty[12] explained the charges on air bubbles in water as due to orientation of the water molecules in the interface, such that negative ions of impurities present in solution are attracted to the surface. He discounted the effect of hydroxyl ion adsorption because of process (b) above, suggesting that the binding forces between OH^- and H^+ ions are so great that an OH^- ion adsorbed would be almost immediately "covered" by an H^+ ion, the net charge then becoming zero. It is clear that although molecular orientation may contribute towards the electrostatic attraction of ions to the benzene / water interface and to the formation of a diffuse double layer of the type suggested by Gouy[24], it cannot fully explain the preferential adsorption of OH^- ions. To do this, one must resort to the rather ambiguous quasi chemical forces of Mukherjee.

Mukherjee in his paper on the neutralization of charge on a colloidal particle, made no attempt to investigate quantitatively the chemical adsorption process but confined his treatise to consideratious of the secondary process of electrostatic attraction of "covering" ions. An attempt was therefore made, using the results obtained with benzene drops in the above solutions, to relate the hydroxyl ion concentration with the number of ions adsorbed in the condensed layer, in a manner similar to that adopted by Mukherjee for neutralization of drop charge with ionic concentration.

As the formation of a condensed layer of charge on a drop in a stationary liquid must almost immediately produce a diffuse distribution of charge due to electrostatic attraction of oppositely charged ions, the separation of one effect from the other under such circumstances is most difficult. In the above experiments, however, the drops were moving through the solution at their terminal velocities, and these velocities were in excess of the maximum for which streamline flow takes place. It was found that a resistance law of the type

$$R \propto (av)^{3/2}$$

was in force for the drops of benzene in use. As suggested in Chapter 2 such conditions will not be favourable for the formation of a diffuse atmosphere of charge owing to disturbances in the liquid round the drop, and consequently it is reasonable to assume that the charge q as derived from the relationship

$$F = E.q$$

will represent the primary or condensed charge on the drop, the covering action due to the diffuse charge being negligible. The charges measured in this manner will thus give a direct indication of the number of ions adsorbed in the condensed layer and the effect of concentration on such a layer can be determined from the above results. If the liquid motion round the drops moving with these velocities is not sufficiently disturbed to completely prevent the formation of the diffuse layer of charge i.e. if some covering ions are still able to follow the drop through the liquid, one must make the additional assumption that the percentage of ions covered for drops of the same size, moving with the same velocity through the liquid, will be of the same order over the range of concentrations used. The charge q will then represent a constant percentage of the condensed charge.

From the curves relating drop charge with hydroxyl ion concentration it is obvious that there is a maximum possible charge, which the benzene drop can attain, it then being "saturated" with hydroxyl ions. If there are "no""places" available on a drop of radius "a" at which hydroxyl ions can be adsorbed, and if "n" of these places are still available when the hydroxyl ion concentration is C gram equivalents per litre, then (no-n) ions must be adsorbed. The charge on the drop will therefore be (no-n)e where e is the electronic charge in e.s.u.

If α is the fraction of the maximum charge acquired by the drop at concentration C then

$$\alpha = \frac{n_0 - n}{n_0}$$

$$1 - \alpha = \frac{n}{n_0}$$

$$\frac{\alpha}{1-\alpha} = \frac{1 - \frac{n}{n_0}}{\frac{n}{n_0}}$$

If at this concentration C, there is an infinitesimal increase in concentration dC there will be additional adsorption anda corresponding decrease dn in n. The magnitude of dn will depend upon (i) the magnitude of dC. There may be a linear relationship i.e. $dn \propto dC$, or it may be more complicated.

(ii) n, the number of places available. Obviously when n=o i.e. at saturation charge, dn will also be 0 no matter how big dC is made.

As a first approximation we may therefore say

$$dn = -K.n.\,dC \qquad \text{———— } 32$$

where K is a constant.

$$\frac{dn}{n} = -Kdc$$

$$\log_e n = -KC + \text{constant}$$

$$n = Be^{-KC}$$

When C = 0, n = no and the constant B must equal no

$$\therefore n = no.e^{-KC}$$

$$\frac{n}{no} = e^{-KC} \qquad \text{———— } 33$$

Substituting this in equation (31) above we have

$$\frac{\alpha}{1-\alpha} = e^{KC} - 1 \qquad \text{———— } 34$$

If KC is large $e^{KC} \gg 1$ and

$$\frac{\alpha}{1-\alpha} = e^{Kc}$$

The function $\frac{\alpha}{1-\alpha}$ was calculated for contentrations of OH-ions between 10^{-5}N and 6×10^{-5} for each of the curves shown in graphs 9 and 13. $\text{Log}_{10} \frac{\alpha}{1-\alpha}$ was plotted against C over this range of concentrations and the straight line curves obtained are shown in graphs 18 and 19. These are in excellent agreement with equation (35) above and indicate that over this range of concentrations $e^{KC} \gg 1$.

The relationship between $\log_{10} \frac{\alpha}{1-\alpha}$ and C was plotted for concentrations below 10^{-5} N i.e. for acid solutions, from the results obtained for HCl solutions and shown in graph 14. The curve obtained is given in graph 20 and it shows that the straight line curves of graphs 18 and 19 become asymptotic to the $\log_{10} \frac{\alpha}{1-\alpha}$ axis as $C \longrightarrow 0$. From graphs 18, 19 and 20, it is therefore evident that the relationship

$$\frac{\alpha}{1-\alpha} = e^{KC} - 1$$

is in good agreement with the results obtained experimentally, showing that the assumptious upon which equation (32) is based are reasonable. The value of K derived from the slopes of the graphs 18 and 19 are respectively

$7{\cdot}74 \times 10^{-4}$ N^{-1} for the NH_4OH results and
$7{\cdot}25 \times 10^{-4}$ N^{-1} for the NaOH results.

The fundamental assumptions underlying equation (32) are as follows:

(a) the work necessary to adsorb an hydroxyl ion at the water / benzene interface is constant over the range of concentrations used. This implies that any variation with concentration, in the ionic atmosphere of positive ions surrounding an OH^- ion, over the range of concentration $10^{-10}N$ to $10^{-3}N$, has a negligible effect, it being as easy for an OH^- ion to be adsorbed from an acid solution containing many H^+ ions as from an alkaline solution.

(b) The OH^- ions already adsorbed in the surface exert no repelling force on other OH^- ions which are in the process of being adsorbed. If this were not so, the power of n in equation (32) would not be unity. This really means that the "places" at which OH^- ions can be adsorbed at the surface are sufficiently separated for an OH^- ion in one "place" to exert negligible repulsive force on an OH^- ion in the adjacent "place".

(c) The percentage of OH^- ions adsorbed at the surface of the drop, moving through the fluid at its terminal velocity of 7cms / sec, which are covered by positive ions in solution is either zero or constant over the range of concentrations covered.

Though these three assumptions are shown to be correct by the good agreement obtained, with the experimental results, the nature of the chemical forces causing hydroxyl ion adsorption is still uncertain.

In all the above experiments, only monovalent positive ions were present in solution with the hydroxyl ions, and as we have seen, "covering" of the negative charge by these ions could be neglected. It was therefore decided to try solutions containing divalent and trivalent positive ions, in order to see if the electrostatic covering effects outlined by Mukherjee would occur with these more heavily charged ions.

Lanthanum nitrate and barium nitrate were the electrolytes used and the results obtained are given in tables XIV and XV below, the drop diameters being 1·6 m.m.

TABLE XIV

Lanthanum nitrate Solutions $La(NO_3)_3$

Photograph No.	Resistance $\times 10^4$ ohms	Calculated Concentration $\times 10^{-5}$N	Conc. -"End Correction" $\times 10^{-5}$N	Voltage Applied	Tan θ	Charge $q = \frac{m'g\tan\theta}{E}$ in e.s.
470	4·7	1·295	0	121	·01588	·0301
471	3·6	1·69	0·395	121	·01418	·0269
472	1·33	4·575	3·38	120	·00738	·01985
473	0·83	7·33	6·035	120	·00624	·0168
474	0·64	9·5	8·205	120	·00567	·01525
475	0·44	13·8	12·505	119	·00567	·01525
476	0·315	19·3	18·005	118	·0051	·0137
477	0·219	27·8	26·505	116	·0051	·0137
478	0·148	41·1	39·805	115	·00425	·01143
479	0·09	67·6	66·305	112	·0034	·00914
480	0·051	119·25	117·955	110	·00283	·0076
481	0·018	338·0	336·705	96	·00227	·0061

TABLE XV

Barium Nitrate Solutions $Ba(NO_3)_2$

Photo-graph No.	Resistance $x10^4$ ohms	Calculated Conc.$X10^{-5}N$	Conc. -"End Correction" $x10^{-5}N$	Voltage Applied	Tan θ	Charge $q=\frac{m'g\tan\theta}{E}$ in e.s.u
482	2·4	2·66	0	120	·0153	·0290
483	1·5	4·26	1·6	120	·01416	·02685
484	0·95	6·73	4·07	120	·01416	·02685
485	0·67	9·55	6·89	120	·0136	·0258
486	0·455	14·05	11·39	119	·01332	·02525
487	0·25	25·6	22·94	117	·0130	·02465
488	0·145	44·1	41·44	114	·01076	·0215
489	0·075	85·3	82·64	111	·00963	·01976
490	0·024	266·5	263·84	98	·00794	·0180

The drop charge related to La^{+++} ion concentration is shown in graph 21 and the curve relating charge with Ba^{++} ion concentration is shown in Graph 22. As can be seen La^{+++} and Ba^{++} ions, especially the former, are effective in reducing the drop charge, this indicating that some electrostatic "covering" is possible with the more heavily charged positive ions, even when the drops are moving through the fluid with a velocity greater than the maximum for which streamline flow occurs.

Mukherjee derived a mathematical formula for this "covering" effect relating fractional loss of charge θ,, with concentration of neutralizing electrolyte C, and the formula he obtained was

$$\theta_1 = \frac{k_4}{k_1} . u . e^{-W/kT} \frac{n_2^2}{n_1} . C \left(1 - \frac{n_1}{n_2}\theta_1\right)\left(1 - \theta_1\right)$$

where u = mobility of the "covering" ion

n_2 = valency of the "covering" ion

n_1 = valency of the adsorbed primary ion

W = energy necessary to separate the neutralizing ion from the adsorbed ion.

k = Boltzmann's constant

T = absolute temperature

and

$\frac{k_4}{k_1}$ can be regarded as a constant depending, among other things upon the size of the colloidal particle or charged drop.

The assumptions used in the derivation of this formula are

(i) the surface does no exert any chemical affinity on the "covering" ions, their attraction being purely electrostatic in nature.

(ii) maximum "covering" occurs for neutralization of charge.

(iii) the places at which primary ions are chemically adsorbed are widely separated compared with molecular dimensions, so that interaction between ions at adjacent "places" can be neglected.

An attempt was made to see if the neutralization of charge on the benzene drops by La^{+++} ions followed along the lines indicated by Mukherjee's equation.

For these results, as there are only La^{+++} ions in solution covering the chemically adsorbed OH^- ions

u is constant and equal to 57 at 18°C.

n_2 is 3, the valency of the La^{+++}

n_1 is 1 for the OH^- ions

W is constant and equal to $\frac{3e^2}{Dx}$ where D is the dielectric constant for water, e is the electronic charge and x is the distance between the centres of the adsorbed OH^- ion and the La^{+++} covering ion.

For the $La(NO_3)_3$ solutions we can therefore say

$$\theta_1 = A\left(1-\frac{\theta_1}{3}\right)\left(1-\theta_1\right).C$$

where A is a constant and equal to $9\frac{k_4}{k_1}.u.e^{-W/kT}$

The function $\frac{\theta_1}{\left(1-\frac{\theta_1}{3}\right)\left(1-\theta_1\right)}$ was calculated for the concentrations indicated in table XVI below

TABLE XVI

Concentration of La+++ ions $\times 10^{-5}$ N	θ_1	$\frac{\theta_1}{(1-\theta_1)(1-\frac{\theta_1}{3})}$	$\log_{10}(C \times 10^5)$	$\log_{10}\left\{\frac{\theta_1}{(1-\theta_1)(1-\frac{\theta_1}{3})}\right\}$
1	0·358	0·632	0	-0·1993
1·5	0·443	0·933	0·1761	-0·0301
2	0·475	1·075	0·3010	0·0315
3	0·521	1·315	0·4771	0·1189
4	0·557	1·545	0·6021	0·1889
5	0·579	1·705	0·6990	0·2316
6	0·593	1·814	0·7782	0·2586
7	0·6065	1·932	0·8451	0·2860
8	0·616	2·017	0·9031	0·3047
9	0·625	2·105	0·9542	0·3232
10	0·634	2·192	1·0000	0·3408
15	0·664	2·532	1·1761	0·4034
20	0·6865	2·84	1·3010	0·4533
25	0·7015	3·065	1·3979	0·4864
30	0·716	3·315	1·4771	0·5204
40	0·735	3·69	1·6021	0·5670

It is obvious from this table that there is no linear relationship between the function $\frac{\theta_1}{(1-\theta_1)(1-\theta_1/3)}$ and the concentration C as suggested by Mukherjee's equation.

Graph 23 was therefore plotted using $\log_{10} \frac{\theta_1}{(1-\theta_1)(1-\frac{\theta_1}{3})}$ against $\log_{10}C$, this being done in order to see if $\frac{\theta_1}{(1-\theta_1)(1-\theta_{1/3})}$ was proportional to any power of C over the range covered. This curve approaches a straight line curve for the higher concentrations of La^{+++} ions, the slope of this line being

$$\frac{\log_{10} \frac{\theta_1}{(1-\theta_1)(1-\theta_{1/3})}}{\log_{10} C} = \frac{1}{3}$$

indicating that over this range of concentrations i.e. between 4×10^{-5}N and 4×10^{-4}N. the power law $\frac{\theta_1}{(1-\theta_1)(1-\theta_{1/3})} \propto C^{1/3}$ is more correct. It can be seen however that at very low concentrations approaching infinite dilution i.e. below 2×10^{-5}N, the slope of the curve, $\frac{\log_{10} \frac{\theta_1}{(1-\theta_1)(1-\frac{\theta_1}{3})}}{\log_{10} C}$ does approach unity. Thus at these extreme dilutions $\frac{\theta_1}{(1-\theta_1)(1-\theta_{1/3})}$ is directly proportional to C as indicated by Mukherjee's equation. It therefore appears that though the assumptions, upon which the equation was based, hold good in very weak solutions, they become incorrect as the concentration of the La^{+++} ions increases above 2×10^{-5}N.

The assumption that the covering ions are so widely separated as to exert no electrostatic repulsion on each other is definitly open to criticism at the higher concentrations, especially as Mukherjee based it upon the results of M^{c}Taggart[11] who measured charges on air bubbles in water. Mukherjee distributed the charge measured, evenly over the surface and thus estimated the approximate distance between ions on the surface. The charges on the bubbles as measured by $M^cTaggart$, however, may well have been only the excess of charge due to the few adsorbed ions remaining uncovered. Miss Newton[14] has also shown that $M^cTaggart$'s results are not reliable as they must have been complicated by electroendosmotic flow in the tube along which the bubbles moved.

Although in the treatment on the chemical adsorption of hydroxyl ions, it was stated that, as equation (32) was found to be experimentally correct, the forces of repulsion between adjacent OH^- ions in the condensed layer must be small, it must be remembered that during such adsorption the quasi chemical forces may be very large compared with the electrostatic forces between the adjacent ions, so that the latter may be neglected. As the forces bringing about "covering," however, are purely electrostatic in nature, the repulsion between adjacent covering ion will become comparable with the forces of attraction exerted by the condensed layer. This will be especially so at the higher concentrations when there is a high percentage of primary ions on the condensed layer covered, and therefore neutralized.

The fractional decrease in charge obtained with Ba^{++} ions, over the range of concentrations covered, is too small to enable them to be used in the above manner as an empirical check on Mukherjee's equation. There is agreement, however, in the fact that the divalent Ba^{++} ions are less effective in reducing drop charge than the trivalent, and equally mobile, La^{+++} ions.

In the experiments described so far in this chapter drops of the order of 2m.m. diameter were used. Attempts were therefore made to obtain benzene drops of different sizes in order to investigate variation of drop charge with radius. These were not very successful, however, the difficulty lying mainly in the fact that very fine thin walled capillaries were needed to produce sufficiently small drops and these capillaries were inconsistent in behaviour. Drops with diameter much greater than 3m.m. could not be used for this investigation, as their drop paths were erratic, the motion being zig zag even when the drops were rising under the influence of gravity in the absence of an electric field. Discussion of these erratic drop paths is left until a little later in the chapter.

A set of results was obtained witha capillary producing drops of diameter 2·9 m.m. and the charge on these in distilled water and NaOH solutions was measured. These results are given in table XVII below.

TABLE XVII

Photograph No.	Resistance $\times 10^4$ ohms.	Conc. Calculated $\times 10^{-5}$N	Conc.-"End Correction" $\times 10^{-5}$N	Voltage Applied	Tan θ	Charge $q = \frac{m'g\tan\theta}{E}$ in e.s.u.
521	1·95	1·74	·01	120	·0255	0·2875
522	1·39	2·44	0·7	120	·0351	0·396
523	0·96	3·74	2·0	119	·0487	0·55
525	0·56	6·70	6·7	118	·0566	0·638
526	0·22	15·4	13·66	105	·0498	0·642

The curve relating drop charge and hydroxyl ion concentration was plotted and is shown in graph 24. It is of very similar form to that obtained for the smaller drops. Using this curve, $\log_{10} \frac{\alpha}{1-\alpha}$ was plotted against C and a good straight line relationship again obtained. The value of K, the constant in equation (32), obtained from the slope of this line was $8{\cdot}06 \times 10^4$ N^{-1}, this being in good agreement with the value of K obtained for the smaller drops.

Further investigations on the variation of drop charge with radius were postponed until other liquid drops had been tried in aqueous solutions, in order to see if a more satisfactory liquid than benzene could be found. It was decided that a liquid heavier than water would be more convenient to use for these experiments, as then a number of droppers producing drops of different radii could be prepared simultaneously and each one positioned above the cell when required, this removing the difficulty of sealing each dropper into the base of the cell.

Drops of other Orgainic Liquids in Aqueous Solutions

Liquids which were still less dense thanwater were first used, and as a clean dropper and reservoir was needed for each liquid to avoid contamination of one liquid with another, the cell was modified to enable the capillary dropper to be more conveniently changed. For this purpose the tube cemented over the hole in the centre of the base of the cell was replaced by a wider tube and ground glass joint as shown in fig. 19. The narrow tube drawn off into a capillary was cemented into the other half of the ground glass joint, this arrangement enabling the capillary and reservoir to be removed quickly and conveniently from the cell.

Drops of the simpler paraffins hexane, n. heptane and iso. octane and the compounds tolune and xylene were used in water and solutions of NaOH. The simpler paraffins are insoluble in water, and xylene and toluene have slight solubilities of the same order as benzene. Drops of these compounds behaved in a very similar manner to benzene drops, all attaining a negative charge in distilled water, this charge increasing to a maximum, saturation charge as the concentration of the hydroxylions increased. Details of the results obtained are shown in tables XVIII to XXII below, and the drop charge - hydroxyl ion concentration curves are plotted in graphs 25 to 29.

TABLE XVIII

Hexane Drop diameter 1·84m.m. Density at 20°C=0·658

Photograph Number	Calculated Conc. of OH^- ions x10^{-5}N	Voltage Applied	Tan θ	Charge $q=\frac{m'g \tan\theta}{E}$ in e.s.u.
557	0	120	·002269	·01864
560	1·305	116	·00680	·0559
561	3·445	120	·01360	·1117
562	6·345	119	·0170	·1396
563	12·695	116	·01758	·1444

TABLE XIX

n. Heptane Drop diameter 1·69m.m. Density$_{20^\circ C}$=0·683

Photograph Number	Concentration of OH^- ions x10^{-5}N	Voltage Applied	Tan θ	Charge $q=\frac{m'g \tan\theta}{E}$ in e.s.u.
547	0	120	·01305	0·0772
550	1·18	120	·01815	0·1074
540	2·47	119	·02155	0·1274
541	4·9	119	·0244	0·1443
542	7·04	118	·0244	0·1443
543	12·82	117	·0244	0·1443

TABLE XX

iso Octane Drop diameter 1·56 m.m. Density$_{20^\circ C}$=0·702

Photograph Number	Concentration of OH^- ions $\times 10^{-5}$N	Voltage Applied	Tan θ	Charge $q=\frac{m'g\tan\theta}{E}$ in e.s.u.
552	0	120	·001134	·00494
553	2·56	119	·00456	·02251
554	5·54	118·	·00964	·0476
555	11·42	116	·00964	·0476
556	21·22	113	·00964	·0476

TABLE XXI

Toluene Drop diameter 2·2 m.m. Density$_{20^\circ C}$= 0·88

Photograph Number	Concentration of OH^- ions $\times 10^{-5}$N	Voltage Applied	Tan θ	Charge $q=\frac{m'g\tan\theta}{E}$ e.s.u.
567	0	120	·00794	·0390
568	0·8	120	·01134	·0557
569	1·7	120	·01475	·0815
570	3·3	120	·01985	·0976
571	5·5	119	·0227	·1116
572	8·1	118	·0227	·1116
573	12·5	116	·0226	·1116

TABLE XXII

Xylene Drop diameter 2·45 m.m. Density$_{20^\circ C}$ = 0·88

Photograph Number	Concentration of OH^- ions $\times 10^{-5}$N	Voltage Applied	Tan θ	Charge $q = \frac{m'g \tan\theta}{E}$ in e.s.u.
576	0	120	·00623	0·0426
577	0·93	120	·00907	0·0617
578	3·29	119	·01474	0·100
579	7·91	117	·01700	0·1156
580	18·09	115	·01700	0·1156

It has been shown that the increase in charge on the benzene drops as the hydroxyl ion concentration increased followed the simple equation

$$dn = -Kn.dC$$

and the value of the constant K was found to be

$7 \cdot 74 \times 10^4\ N^{-1}$ in NH_4OH solutions
$7 \cdot 25 \times 10^4\ N^{-1}$ in NaOH solutions

for drops of 1·5 and 2 m.m. diameter and

$8 \cdot 06 \times 10^4\ N^{-1}$ in NaOH solutions

for 2·9 m.m. diameter drops. From the results tabulated above the following valves of K for the other non conducting liquids were determined from the slope of the $\log_{10} \frac{\alpha}{1-\alpha}$ concentration curves

	Hexane	$7 \cdot 83 \times 10^4\ N^{-1}$
n	Heptane	$7 \cdot 86 \times 10^4\ N^{-1}$
iso	Octane	$8 \cdot 12 \times 10^4\ N^{-1}$
	Toluene	$7 \cdot 68 \times 10^4\ N^{-1}$
	Xylene	$8 \cdot 18 \times 10^4\ N^{-1}$

All these values of K are in close agreement with the values obtained for the benzene drops.

The factors with which the constant Kof equation (32) would be expected to vary are

(i) the age of the drop surface
(ii) the curvature of the drop surface i.e. the drop radius.
(iii) the material forming the drop.

With respect to (i), no difference in charge was observed in any of the above experiments between a drop formed quickly at the dropper i.e. with a rate of formation of one drop per second, and one formed slowly with the rate of formation one drop every two or three minutes. The "age" of the surface, however, may have to be reckoned in terms of a much shorter interval of time than the second. Alty[12] found that equilibrium charge on an air bubble in water was very quickly reached except in water of extreme purity $\ll 2 \times 10^{-6}$ ohm^{-1} cm^{-1}. In this pure water there was a "charging up" effect in which equilibrium charge was not reached until the surface was a few minutes old.

The value of K calculated from the results obtained with the benzene drops of diameter 1·95 m.m. and 2·9 m.m. also show very close agreement, pointing to the fact that K is independent of drop radius and ruling out factor (ii) above.

As the value of K obtained for the simpler paraffins, benzene, toluene and xylene are all in close agreement it is also evident that K is independent of the non conducting materials used. The actual magnitude of the saturation negative charge does vary a little from material to material, but the process by which this charge is acquired must be very similar for each of the materials used i.e. the same type of quasi chemical forces must bring about the hydroxyl ion adsorption at the interface in each case.

Variation of drop charge with drop radius.

Carbon disulphide and carbon tetrachloride were the next non conducting liquids used. Their respective densities at 20°C are 1·263 and 1·594, so that drops of them in water move downwards under the influence of gravity. The top of the cell was modified for use with these drops, a 15cm. long vertical tube being cemented in, vertically above and midway between the deflecting plates. The droppers used were separate units from the cell and were placed in position when required, the drops forming in the liquid in the 15cm tube as shown in fig. 20. Any oscillations in the drops on leaving the dropper were damped in the tube before they entered the electric field. The glass capillary droppers were cleaned with chromic acid and distilled water, and thoroughly dried before use.

The diameter of the drops forming in water at the end of these droppers was measured, as before with a microscope fitted with a scale in the eye-piece. The terminal velocity as measured from the photographic plates was also used as a measure of drop radius, the resistance law

$$R \propto (v_x a)^{3/2}$$

being in force over most of the range covered and consequently

terminal velocity, v_x $\propto$ drop radius, a

The results obtained with carbon disulphide drops were not very satisfactory, again owing to the inconsistent behaviour of the thin walled capillaries. Those that were obtained, however, showed that in solutions of the same hydroxyl ion concentration, the deflection in an electric field, and consequently tan θ, was independent of drop radius for drops between 0·8 and 1·8 m.m. diameter. This indicates that the drop charge acquired under the experimental conditions was proportional to the cube of the drop radius. That this is so was proved by the more satisfactory results obtained with carbon tetrachloride drops of diameters between 0·25 m.m. and 1·8m.m., in distilled water and NaOH solutions.

Drops of diameter greater than 1·8 m.m. were very erratic in motion, not even falling vertically under gravity in the absence of an electric field, but tending to have a zig zag type of path. This phenomenon is similar to the one mentioned earlier, in which drops of benzene with diameter greater than 3m.m. were observed to have an erratic drop path. Drops of carbon disulphide of diameter greater than 2·4 m.m. also behaved in this manner. This inconsistency is probably due to the fact that the drops with diameter greater than these limits, have high terminal velocities and turbulent conditions will consequently exist in the liquid surrounding the drops in motion. Measurements on the terminal velocities of the carbon tetrachloride drops show that until the diameter 1·8 m.m. is reached, the terminal velocity v_x is proportional to drop radius a and consequently the liquid resistance R is proportional to $(v_x a)^{3/2}$. With carbon tetrachloride drops of diameter greater than 1·8 m.m., the terminal velocity measurements show that the resistance law changes from a $3/2$ power to a square law and R becomes proportional to $(v_x a)^{3/2}$

Unstability is therefore to be expected above this diameter especially as any turbulence or eddy formation around such a fluid sphere will almost certainly cause distortion of the sphere and motion of the fluid in it. With the smaller spheres, when the 3/2 power law is in force, there will be less disturbance in the liquid round the drops, enabling them to follow a smoother drop path.

The results obtained with carbon tetrachloride spheres are given in table XXIII below.

TABLE XXIII

Carbon Tetrachloride drops in NaOH Solutions

Photograph Number	Hydroxylion concentration $\times 10^{-5}$N	Drop diameter in scale divs. 10sc. divs. = 2·335 mm.	Terminal Velocity Length of ten dashes in cms.	Voltage Applied	Tan θ
605	10^{-2}	6	6·8 & 7·1	234	·01134
606		6	7·05	234	·01020
607		7	8·0	234	·01020
608		3·5	3·85 & 4·85	234	·01134
609		2 to 3	3·15	234	·00793
610	7·33	2 to 3	2·6	222	·01586
611		3·5	4·75	222	·02270
612		6	7·8	222	·02270
613		7 to 8	8·8	222	·03285
614	15·83	8 to 9	9·3	116	·02150
615		6	7·55	116	·01134
616		3·5	4·6	116	·01134
617		3	3·85	116	·01020

As the terminal velocity is proportional to drop radius over most of the range covered it was decided to plot $\frac{\text{drop charge}}{a^3}$ directly against terminal velocity instead of a.

$$\text{Now } \tan\theta = \frac{F}{mg}$$

so that tan Θ was plotted against V_x. Graphs 30, 31, and 32 are the tan Θ, V_x curves for the distilled water and NaOH solutions used. These graphs show that in all the solutions used, $\frac{\text{charge}}{a^3}$ is constant over most of the range of radii covered. There is a slight decrease in $\frac{\text{charge}}{a^3}$ for the smallest values of a, and in the two NaOH solutions used there is a sharp increase in $\frac{\text{drop charge}}{a^3}$ for the highest valves of a used, this increase occurring with drops of diameter very near the limit at which the erratic paths are observed. This sudden increase in $\frac{\text{Drop charge}}{a^3}$ is evident in graphs 31 and 32. That this phenomenon was not observed in distilled water is due to the fact that sufficiently large drops were not used, the increase taking place above a sharp upper limit. The sudden increase in $\frac{\text{charge}}{a^3}$ at the higher values of a is probably intimately connected with the suddenchanges in fluid flow round the drops which occurs for the larger values of a, the fluid resitance then becoming proportional to $(V_x a)^2$. The increase in the disturbances in the fluid round these larger, and quickly moving, drops may be sufficient to reduce even further, the amount of covering by positive ions in solution which was possible when the R $\propto (V_x a)^{3/2}$ law was in force. This decrease in covering will leave the adsorbed negative charge almost completely exposed and give rise to a sudden increase in $\frac{\text{charge}}{a^3}$. This explanation is borne out by the fact that there is a corresponding decrease in $\frac{\text{charge}}{a^3}$ for the smallest drops used. For such small drops motion of the fluid round the drop, when terminal velocity is reached, must be approaching streamline flow, and under such conditions the maximum amount of covering due to electrostatic attraction of positive ions will be possible, this causing a decrease in the negative charge exposed to the electric field.

The fact that $\frac{\text{charge}}{a^3}$ is constant over the greater part of the range of radii used is a more difficult phenomenon to explain. One would expect the adsorption of the hydroxyl ions at the interface to be a pure surface effect, in which case the charge should be proportional to a^2. Wagstaff[16] and later Curry found a similar law to exist for the positive charges acquired by mercury drops in sulphuric acid solutions, the charge in all cases being proportional to the cube of the drop radius.

A more exact knowledge of the quasi chemical forces causing such ionic adsorption is essential before a satisfactory explanation of this cubic law can be made.

In conclusion, it should be noted that although no curves relating drop charge and hydroxyl ion concentration are shown for the carbon tetrachloride drops, the experiments being performed to investigate the relationship between drop charge and drop radius, the results obtained with the solutions used, show that the drop charge increases to a maximum, saturation charge in a very similar manner to that observed for the other non conducting drops. It is therefore reasonable to assume that the conclusions arrived at from the resultsobtained with the carbon tetrachloride drops will apply to drops of the other non conducting liquids used.

CHAPTER VI

Measurements of charge on mercury drops in aqueous solutions.

Curry, in his work on mercury drops in aqueous solutions, used an experimental technique very similar to that described in this thesis. He measured the positive charges acquired by mercury drops in acid solutions and attributed the charge to hydrogen ion adsorption. As there was also an increase in positive charge on mercury drops in solutions other than acid solution, a wider explanation of the phenomena is that the positive charge is due to adsorption of positive ions present in the aqueous solutions. It is obvious from the measurement of charge acquired by mercury drops in various solutions of equal concentration, (Ph. D thesis p. 68) that the amount of adsorption possible varies with the positive ion in solution, and in order to gain more information on this aspect of the problem, the following series of experiments were performed.

The mercury in use was purified by bubbling air through a mixture of it and concentrated sulphuric acid for a number of hours, and then twice redistilling under reduced pressure. The dropper was constructed from thick walled capillary tubing, the drops forming at the rate of one every four or five seconds. Photographs 622 - 635, as listed below, were taken using drops of radius 0·695 m.m. in distilled water and NaOH solutions, the distance between the platinum deflecting plates being 3·05 cms.

TABLE XXIV

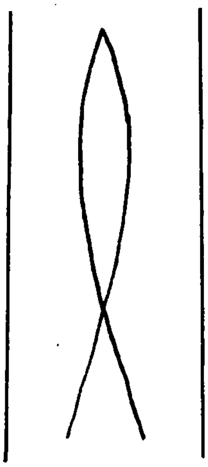
Photograph Number	Resistance Between plates $\times 10^4$ ohms.	Voltage Applied	Calculated NaOH Concentration $\times 10^{-5}$N	NaOH Conc. - "End Correction $\times 10^{-5}$N	Drop Sign
622	2·9	230	1·17	0	+
623	0·82	225	4·15	2·98	+
624	0·42	222	8·07	6·9	+
625	0·24	219	14·15	12·98	+
626	0·1	110	33·9	32·73	+
627	0·048	54, 105	70·5	69·33	+
628	0·014	85	242·0	240·83	+ve & then -ve
629	0·014	47	242·0	240·83	+
630	0·014	85	242·0	240·83	+ve & then -ve
631	0·0033	34, 10	1028	1026·83	+
632	0·0033	6·4	1028	1026·83	+
633	0·0015	6·4, 9·8	2260	2255·83	+
634	0·0007	6·4	4840	4838·83	+
635	1·3	740, 231	2·6	1·43	+

As was stated in Chapter 2, the magnitude of the charge cannot be determined accurately from the curved tracks photographed on the above plates, unless a tedious numerical approximation method is used. An indication of the magnitude was, however, obtained from the width of the deflection and the value of tan θ at the extremity of the paths. The construction of a larger cell would have enabled greater accuracy to be obtained but there was not sufficient time left in the research period for this to be done. The following conclusions could, however, be drawn from the above photographs:

(i) The deflection of the mercury drops in distilled water is towards the negative plate, indicating a positive drop charge, and this deflection increases with voltage gradient up to 246 volts / cm.

This positive charge can be attributed to adsorption of hydrogen ions, formed by the partial dissociation of the water, and also of positive ions of impurities in solution. The increase of this positive charge, in the lower voltage gradients, as NaOH is added to the water, suggests that there is also adsorption of Na^+ ions inthese NaOH solutions. In this case, as the solution becomes more alkaline, there will be less H^+ ions available for adsoption and the positive charge will be derived more and more from the comparatively large numbers of Na^+ ions available.

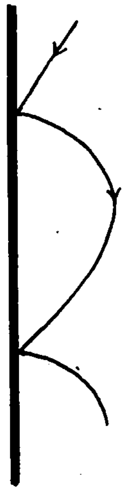
(ii) In the NaOH solutions, as the concentration of the Na^+ and OH^- ions increases, the positive charge in the lower voltage gradients increases, but it soon becomes evident that this positive charge is affected by the voltage gradient. This dependence on electric intensity becomes very obvious in the photggraphs 628, 629, 630 for the solution of concentration $2 \cdot 41 \times 10^{-3}$N. Photograph 629 shows that for a voltage gradient of 47 volts / 3 cms., the drop is decidely positive, being attracted to the negative plate. For the same solution, whenthe voltage gradient is increased to 85 volts / 3 cms., the drop when entering the field is positive but it quickly loses this positive charge and acquired a negative charge, becoming attracted to the positive plate. The drop paths on either side of the vertical thus form a loop as shown in the diagram below and in figs. 36 and 37, these being prints from photographs 628 and 630



It therefore appears that the charge ona mercury drop in a field free solution of this concentration is decidely positive, but voltage gradients of a sufficiently high order quickly remove the charge from the drop and enable it to acquire a negative charge.

This "reversal effect" is not present in the photographs taken using solutions of greater concentration than $2{\cdot}41 \times 10^{-3}$N, probably owing to the fact that sufficiently high voltage gradients were not possible due to the very large currents and heavy "gassing" which occur at these higher voltages.

(iii) In distilled water and in each of the NaOH solutions used, the drops very rapidly acquire an equilibrium charge. This is evident from the looped paths mentioned above and also fromthe drop paths after collision with the negative electrode. The positively charged drops after collision become negatively charged and are attracted towards the positive electrode, but once clear of the negative plate the drop rapidly loses its negative charge and reacquires a positive charge, becoming reattracted to the negative plate. The result is a series of "hops" down the negative plate as shown in the diagram below and in the photographs of figs. 38 and 45.



This hopping is similar to that noticed with water drops in benzene, under the influence of large potential gradients.

Although Curry did not observe the reversal effect mentioned above with pure mercury drops, he noticed a similar effect with higher voltage gradients using drops of cadmium and zinc amalgams in sulphuric acid solutions. Thus to remove any doubt about the purity of the mercury in use it was again redistilled and thoroughly washed with concentrated sulphuric acid followed by distilled water. A second dropper was also constructed and cleaned with chromic acid followed by distilled water. Photographs 636 - 651, tabulated below, were taken using drops of this repurified mercury, in distilled water and solutions of NaOH. The radius of the drops used was 0·66m.m.

TABLE XXV

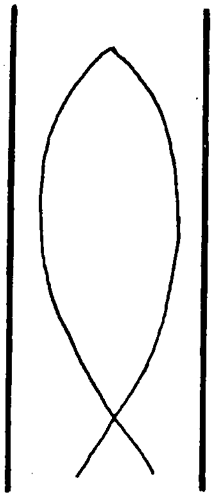
Photograph Number	Resistance between plates $x10^4$ ohms.	Calsulated NaOH Concentration $x10^{-5}N$	Conc. - "End Correction $x10^{-5}N$	Voltage Applied	Drop Sign
636	1·625	2·08	0	116	+
637	"			58	+
638	"			231	+
639	"			750	+
640	0·24	14·1	12·02	112	+
641	0·555	6·1	4·02	113	+
642	0·08	42·3	40·22	106	+
643	0·078	43·4	41·32	246	+ve and then -ve
644	0·0148	229·0	226·92	156	-ve
645	"			114	Mainly -ve
646	"			85	+ve then -ve
647	"			85	+ve then -ve
648	"			58	+ve then -ve
649	"			38	+
650	"			4	+
651	"			20·5	+

These results are in exact agreement with the previous results, so that the effects cannot be attributed to contamination of the mercury. Photographs 636 to 639 were taken using distilled water, for voltage gradients between 116 volts/3cms. and 750 volts / 3cms., and show that the deflections increase with voltage gradient up to the highest gradients available. There is no indication of reversal of drop sign in distilled water.

Photographs 640 to 642 again show the increase in positive charge, in the lower voltage gradients, on adding NaOH, the voltage gradients in each case being of the order 116 volts / 3 cms. Photograph 643, however, shows that if the voltage gradient is increased to 246 volts / 3 cms. for the solution used in photograph 642 i.e. at NaOH concentration 40×10^{-5}N, there is again a reversal in drop sign, the drop being originally positive and becoming negative in the electric field. Photograph 643 is shown in fig. 39.

Photographs 644 to 651 were exposed using an NaOH solution of the same concentration as that in which the reversal effect was first observed i.e. 200×10^{-5}N. For the highest gradient used, 156 volts / 3 cms., the mercury drops were immediately deflected to the positive plate, showing very little indication of the original positive charge. As the voltage gradient was decreased there was more and more evidence of the positive charge which the drop acquired in the field free solution until in voltage gradients below 36 volts / 3 cms. the drop was wholly positive in the field. Photograph 648 is of interest, the gradient in this case being 55 volts / 3 cms.

The loop under these conditions filled the whole of the electric field as shown in the diagram below. Fig. 40 is a print from the actual photograph, gas bubbles evolved at the electrodes tending to obscure the drop path.



As the reversal effect was observed in a solution of 220 x 10^{-5}N NaOH with voltage gradients as low as 55 volts / 3 cms., whereas in the less concentrated 40 x 10^{-5} NaOH, voltage gradients as high as 246 volts / 3 cms. were necessary, it is obvious that as the concentration of the NaOH increases, the voltage gradient necessary to produce reversal of drop sign decreases.

For all concentrations of NaOH used, the "natural" charge on the mercury drop in a field free solution was positive, the magnitude of the positive charge increasing as the Na^+ ion concentration increased. The reversal effect was obviously due to the presence of NaOH in solution and an explanation of the phenomenon may be as follows:

As previously stated, the mercury / water interface is of such a nature as to exert an attraction on all positive ions. The positive charge on the mercury drop in distilled water is thus due to adsorption of H^+ ions, and positive ions of impurities, at the interface. The H^+ ions are so firmly bound at the surface, that even at the highest voltage gradients in use they remain fixed. As NaOH is added, the number of H^+ ions in solution decreases and Na^+ ions replace H^+ ions at the interface, the number of Na^+ ions available for adsorption increasing as the concentration of the NaOH increases. It also appears that Na^+ ions are less firmly "bound" than H^+ ions to the interface and consequently more easily removed by an electric field. Thus in the NaOH solutions, application of a sufficiently strong electric field deprives the surface of the Na^+ ions and the drop of its positive charge. Consequently it will then be possible for mercurous ions, Hg^+, to leave the mercury surface, the phase boundary acting as a membrane permeable to positive ions only, the "atmosphere" of positive ions tending to keep the Hg^+ ions in the drop having been removed by the electric field. Loss of Hg^+ ions into the solution will leave the drop with a negative charge.

The reversal effect is therefore possible because (a) there are very few H^+ ions available for adsorption in the NaOH solutions, and (b) Na^+ ions are more easily removed than H^+ ions, from the surface of the drop, by an electric field. In order to verify this general theory it was decided to observe the effect of electric fields upon the positive charge acquired by mercury drops in neutral solutions of sodium chloride.

If the above theory is correct, on would expect a mercury drop in a solution of NaCl to collect a positive charge by adsorption of Na^+ and H^+ ions, the charge increasing as the concentration of the NaCl increases, and the proportion of Na^+ ions to H^+ ions adsorbed depending upon their relative concentrations. If the drop enters a sufficiently large electric field, the less firmly bound Na^+ ions should be removed from the surface leaving the more securely fixed H^+ ions still in place. The final equilibrium charge attained should still be positive and of the same value as that attained in distilled water, as the number of H^+ ions per c.c. in NaCl solution is the same as in distilled water. There may be a slight time lag between some of the "places" vacated by the Na^+ ions in the electric field being taken over by H^+ ions still in solution, but the final positive charge acquired should be the same as that for distilled water, providing that all the Na^+ ions are removed by the field.

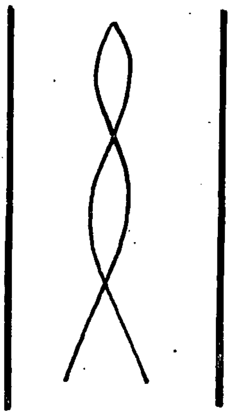
Photographs 659 to 663 tabulated below, were exposed using 0·66 m.m. radius drops in analar NaCl solutions.

TABLE XXVI

Photograph Number	Resistance between the plates $\times 10^{4}$ ohms.	Calculated NaCl concentration $\times 10^{-5}$N	Voltage Applied	Drop Sign
659	0·65	10·35	225	+
660	0·17	39·6	211	+
661	0·05	134·5	180	+
662	0·05	134·5	240	+, then- then +
663	0·014	480·0	120	+, then- then +

Plates 659 to 661 show increasing deflections of the mercury drops towards the negative plate proving that the addition of NaCl does increase the positive charge acquired by the mercury drops. This again bears out the suggestion that the positive charge is due to positive ion adsorption.

Plates 662 and 663 show an entirely different type of drop path to any so far observed, a curious double loop occurring at the beginning as shown in the diagram below and in fig. 41, this being a print from photograph 662.



These drop paths indicate that the drop on entering the electric field is initially positive, but that it quickly loses this charge and acquires a negative charge, losing this in turn and becoming positive. This final positive charge remains on the drop and is of the same order as that acquired by the drop in distilled water. It is to be noted that if similar concentrations of NaOH, instead of NaCl, had been used, there would have been a distinct reversal of charge, the drop ending up with a negative charge in the electric field.

At the concentrations of NaCl used for photographs 662 and 663, the number of Na^+ ions per c.c. is much greater than the number of H^+ ions per c.c., for photograph 662 the ratio being $1{\cdot}345 \times 10^4 : 1$. The positive charge on the drop in the field free NaCl solution must therefore be due almost entirely to adsorption of Na^+ ions. Upon entering the electric field the drop quickly loses these Na^+ ions and tends to gain a negative charge owing to loss of Hg^+ ions, but before this negative charge can become very large, the "places" vacated by Na^+ ions are filled, as far as possible, by the H^+ ions in solution. These ions being firmly bound, the drop rapidly attains an equilibrium positive charge of the same order as that acquired in distilled water. In effect this process causes the double loop observed, and the results therefore bear out the simple theory used to explain the reversal effect in NaOH solutions.

NH_4OH and $(NH_4)_2\ SO_4$ solutions were next used in order to see if the reversal effect could be observed with the NH_4^+ ion. in solution. The photographs listed below were exposed.

TABLE XXVII

NH_4OH

Photograph Number	Resistance between plates	Calculated NH_4OH concentration	Voltage Applied	Drop Sign
664	7×10^2 ohms.	31.0×10^{-5} N	105	+ then -
665 & 666			190	+ then -
667			140	+ then -
668			65	+

$(NH_4)_2\ SO_4$

Photograph Number	Resistance Between plates $\times 10^2$ ohms.	Calculated $(NH_4)_2\ SO_4$ conc. $\times 10^{-5}$ N	Voltage Applied	Drop Sign
669	1·2	446	130	+
670	1·2	446	130	+
671	5	111	246	+
672	5	111	246	+

Photographs 664 - 668 all show the same type of looped path, indicating reversal of sign of drop charge from positive to negative in the electric field, in a manner similar to that observed with the NaOH solutions. Figs. 42 and 43 are prints from photographs 664 and 667 showing the looped paths obtained with the NH_4OH solutions of concentration $31 \cdot 0 \times 10^{-5}$N.

The voltage gradients necessary to produce reversal of drop sign in the NH_4OH solutions were lower than when NaOH solutions of the same concentration were used, the loop being evident with voltage gradients as low as 35 volts / cm. This must mean that NH^{+}_4 ions are less firmly held at the surface than Na^+ ions.

With the $(NH_4)_2\ SO_4$ solutions used, although no double loop was observed as with NaCl, the drops in no case became negative as with NH_4OH solutions. The type of path obtained for these $(NH_4)_2\ SO_4$ solutions is shown in fig. 44 and it can be seen that the drop travelled about 3 cms. through the field before becoming suddenly deflected towards the negative plate. The path of a drop falling vertically is also shown as the zero line of reference. It is reasonable to suppose that this time delay before the drop acquired it s equilibrium positive charge is due to loss of NH_4^+ ions in the electric field, and gain of H^+ ions, the vertical portion of the drop path corresponding to the double loop observed with NaCl solutions.

Owing to the termination of the research period available, no further experiments were performed, but the few results obtained with the pure mercury drops described in this chapter open up new lines of thought on the mercury / water interface. The forces causing posiion adsorption at this interface appear to be purely electrostatic in nature, as all positive ions used appear to contribute to the drop charge. They differ in this respect from the forces causing OH^- ion adsorption at the non conductor / water interface.

It is also evident from these results that the force binding a positive ion to the mercury surface varies with the cation adsorbed, and it is possible that this binding force is intimately connected with the radius of the adsorbed positive ion. It is obvious that the radius of the ion, r, will control the nearness to which the ionic centre can approach the mercury surface, and the binding force, B, tending to hold the adsorbed ion in position may be related to r in the form

$$B \propto \frac{ne}{(r+a)^2}$$

where n is the ionic valency,

e is the electonic charge,

and a is a constant for the mercury / water interface.

APPENDIX

Measurements on the decrease in the mass of water drops, forming in air at the tip of a capillary, due to electrification of the drop.

It was observed in Chapter 3, that applying voltages between a dropper and a cylindrical copper screen surrounding the dropper caused a decrease in the mass of the water drops forming at the end of the capillary. The mass of the water drops formed at the tip of a glass capillary was measured when voltages between 0 and 1860 volts were applied between the dropper and a copper screen of diameter 2 cms. This was done for different heights of the water reservoir above the end of the dropper and the results are tabulated below. The mass of the drops was determined in each case by collecting and weighing 50 of them in a porcelain crucible.

TABLE XXVIII

Head of water causing drop formation = 25.8 cms.

Voltage between screen and dropper	Wt. of 50 drops in grams.	Time taken for 50 drops to form	Mass of water flowing per second X 10^{-3} grams.
0	0.360	83.1	4.314
198	0.3585	82.9	4.318
420	0.355	81.8	4.339
618	0.345	79.4	4.345
816	0.334	76.7	4.354
1047	0.319	73.55	4.337
1245	0.3025	68.9	4.390
1430	0.286	65.0	4.411
1615	0.262	59.6	4.396
1862	0.226	52.6	4.267

TABLE XXIX

Height of water causing drop formation = 36.5 cms.

Voltage between screen and dropper	Wt. of 50 drops in grams.	Time taken for 50 drops to form in seconds.	Mass of water flowing per second X 10 $^{-3}$ gms.
0	0.367	65	5.646
198	0.366	64.5	5.589
420	0.3605	64	5.632
618	0.352	62.5	5.631
816	0.342	60.75	5.628
1047	0.329	57.9	5.665
1245	0.306	54.4	5.645
1430	0.293	51	5.745
1615	0.267	47	5.680
1862	0.236	40.75	5.792

TABLE XXX

Height of water causing drop formation = 60.5 cms.

Voltage between screen and dropper	Wt. of 50 drops in grams.	Time in seconds for 50 drops to form	Mass of water flowing per second X 10^{-3} grams.
0	0.3715	41.3	8.995
198	0.368	40.8	9.018
420	0.363	40.35	8.997
618	0.355	39.45	8.999
816	0.345	38.25	9.018
1047	0.325	36.45	8.915
1245	0.3105	34.2	9.080
1430	0.295	32.325	9.126
1615	0.2695	29.7	9.074
1862	0.234	26	8.999

TABLE XXXI

Height of water causing drop formation = 77 cms.

Voltage between screen and dropper	Wt. of 50 drops in grams.	Time in seconds for 50 drops to form	Mass of water flowing per second X 10^{-2} grams.
0	0.375	32.35	1.159
198	0.370	32.0	1.156
420	0.365	31.45	1.161
618	0.3555	30.72	1.157
816	0.345	29.62	1.165
1047	0.326	28.4	1.150
1245	0.3115	26.8	1.162
1430	0.295	25.3	1.166
1615	0.2695	23.15	1.164
1862	0.234	20.2	1.164

TABLE XXXII

Height of water causing drop formation = 95 cms.

Voltage between screen and dropper	Wt. of 50 drops in grams	Time in seconds for 50 drops to form	Mass of water flowing per second X 10^{-2} grams.
0	0.371	26.1	1.422
198	0.364	25.8	1.411
420	0.359	25.6	1.403
618	0.353	24.95	1.415
816	0.342	24.1	1.420
1047	0.325	22.85	1.422
1245	0.307	21.82	1.407
1430	0.2895	20.28	1.424
1615	0.2655	18.55	1.431
1862	0.229	16	1.431

Graph 33 shows the relationship between the weight of 50 drops and the voltage between screen and dropper, for "h", the height of water causing drop formation, equal to 28.5 cms. Very similar curves to graph 33 were obtained for the other values of h.

From the above results the following conclusions were drawn:

(1) The volume of water flowing per second is independent of the voltage applied between the screen and dropper. This rate of flow is constant for any one value of h and is directly proportional to h as would be expected from Poiseuille's law. The linear relationship between h and Q the volume of water flowing per second is shown in graph 34.

(2) The mass of the drop is constant for any one voltage V between screen and dropper being independent of h within the limits of V and h used experimentally.

(3) The diminution in mass of the drop, when a certain voltage is applied, is the same whether the dropper is positive or negative with respect to the screen.

(4) The position of the end of the dropper in the screen is not critical providing that the drops do not coalesce with the sides of the screen.

Abbonnene[25] observed that a similar diminution in the weight of drops, forming at the end of a tube, occurred when the drops were charged, but he made no quantitative measurements. An attempt was therefore made to relate the results obtained experimentally with the results one would expect theoretically from a consideration of the forces resulting from the electrical charges on the surface of the drops.

If the mass of a drop "m" fallingfrom the end of a tip is independent of the shape of the drop but is only dependent on "r" the radius of the tip and "T" the surface tension then

$$m g = 2\pi r . T \quad \text{--------} \quad 36$$

This mass m is denoted by Harkins and Brown[20] as the mass of the ideal drop, as no account has been taken of the drop shape, and they modified the equation to account for drop shape by introducing a dimensionless function $f \frac{(r)}{(a)}$, where r is the tip [illegible] radius and a is dependent on the radius of the drop. The equation taking the drop shape into account thus became

$$m g = 2\pi r . T . f\left(\frac{r}{a}\right) \quad \text{-------} \quad 37$$

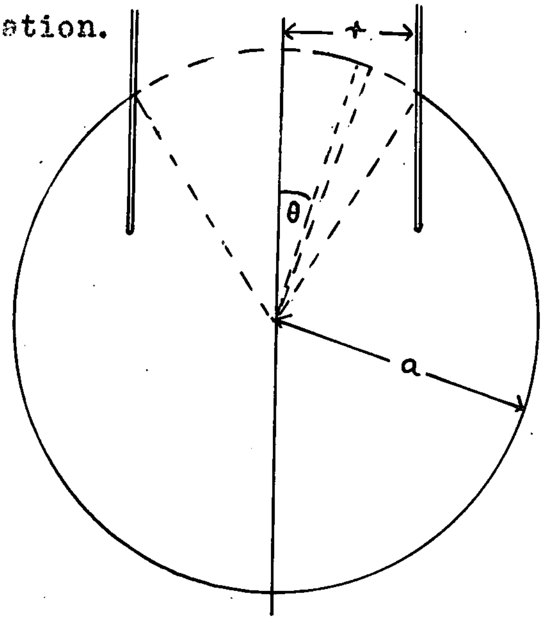
With the glass capillary droppers in use $f \frac{(r)}{(a)}$ was approximately unity as the surface tension of water calculated from the weight of the drop formed using equation (36) was found to be 77.5 dynes/cm at 20° C.

Consider, now, the effect of charging the drop as it is forming at the end of the capillary.

We shall initially assume that the drop when on the point of leaving the dropper is spherical and of radius a. If the voltage between screen and dropper is V then σ the surface density of charge will be given by the equation

$$4\pi a^2 \sigma = \frac{Va}{300}$$

assuming that the charge is evenly distributed over the surface. The force per unit area of drop due to electrification will therefore be $2\pi\sigma^2$, the dielectric constant of air being unity. This force acts perpendicular to the surface of the drop at every point. There is no force due to electrification over the area of the drop intercepted by the capillary and there is therefore a resultant downward force acting on the drop due to electrification.



Consider the circular element $2\pi a \sin\theta . a\, d\theta$ shown in the diagram.

The vertical force due to surface charge σ/cm^2 on this element would have been

$$2\pi a^2 \sin\theta . d\theta \; 2\pi\sigma^2 \cos\theta$$

The resultant downward force due to the capillary covering part of the drop is therefore

$$4\pi^2 a^2 \sigma^2 \int_{\sin^{-1} r/a}^{0} \sin\theta . \cos\theta \, d\theta$$

$$= 2\pi^2 r^2 \sigma^2$$

Instead of the ideal equation (36), we thus have, due to electrification

$$mg + 2\pi^2 r^2 \sigma^2 = 2\pi r T \quad ------ \quad 38$$

and on substituting for σ this becomes

$$mg + \frac{2r^2 V^2}{(1200)^2 a^2} = 2\pi r T$$

or

$$mg = A - B\left(\frac{V^2}{a^2}\right) \quad ---- \quad 39$$

where

$$A = 2\pi r . T$$

$$B = \frac{2r^2}{(1200)^2}$$

When V = 0, m = mo and we therefore have the relationship

$$(m_o - m) g = B\left(\frac{V^2}{a^2}\right) \quad ------ \quad 40$$

(mo-m) being the diminution in weight due to voltage V between screen and dropper.

No linear relationship was obtained between (mo-m) and $\frac{(V)^2}{(a)^2}$ using glass capillary droppers in which the drop of water wetted the outer walls of the capillary when forming. As the process of formation of a drop of water at the tip of such a dropper is by no means ideal for the above equations, a dropper for which this wetting effect did not occur was constructed. This was accomplished by covering the outer walls of the capillary with a thin layer of paraffin wax.

A series of observations were made using two such droppers, and the results are tabulated below.

TABLE XXXIII

Dropper A

Voltage between screen and dropper	Wt. of one drops in grams	$\frac{V^2}{a^2} \times 10^6$	$(mo - m) \times 10^{-5}$ grams
0	0.01485	0	0
198	0.0148	1.755	5
420	0.01472	7.91	13
816	0.0143	30.55	53
1047	0.0139	51.1	95
1245	0.01338	72.5	147
1430	0.0130	100.0	185
1615	0.01236	132,0	249
1862	0.0114	185.0	345

TABLE XXXIV

Dropper B

Voltage between screen and dropper	Wt. of one drop in grams	$\frac{V^2}{a^2}$ X 10^6	mo - m X 10^{-5} grams
0	0.00894	0	0
618	.00862	24.6	32
816	.00836	36.5	58
1047	.00798	74.0	96
1245	.00764	108.1	130
1430	.00716	148.0	178
1615	.00653	202.0	241
1862	.00572	294.0	322

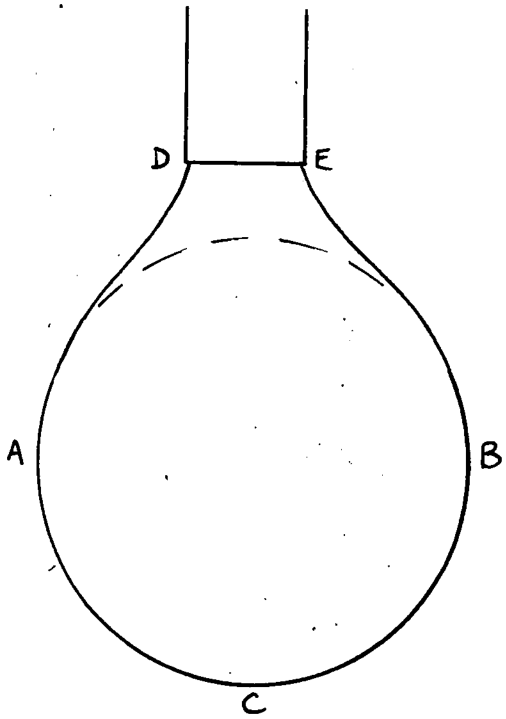
Graphs 35 and 36 were drawn, using these results and show the linear relationship existing between (mo-m) and $\frac{(v)^2}{(a)^2}$ for such droppers, in agreement with equation (40)

The slopes of these curves were measured and the radii of the capillaries calculated using the relationship

$$\frac{(m_o - m)\,g}{\left(\frac{V}{a}\right)^2} = B = \frac{2r^2}{(1200)^2}$$

The radii of droppers A and B were calculated to be 0.114 cms. and 0.0905 cm. respectively, these values being about ten times bigger than the values of r measured with a microscope. The electrical forces acting on the surface of the drop as outlined above thus do not account in full for the observed diminution in weight of the drop.

In the above equations we assumed that the drop was a perfect sphere when on the point of leaving the tip of the capillary, but for the sizes of drops used i.e. 2 to 3 m.m. diameter, there was a large deviation from this perfect spherical shape. The drops when on the point of leaving were of the shape illustrated below, the lower half being spherical but the upper half was elongated as shown.



The resultant vertical force due to electrification of the lower surface ACB will be $\pi a^2 \times 2\pi\sigma^2$ acting downwards, assuming this part of the surface to be spherical and of radius a.

Owing to the distortion, the vertical force due to charge density σ on the surface ADEB will be smaller than the

$$2\pi\sigma^2\left(\pi a^2 - \pi r^2\right)$$

indicated by the above theory. The actual magnitude of this force is

$$2\pi\sigma^2\left(\pi a^2 - \pi R^2\right)$$

where $R > r$ and πR^2 is the effective area of no electrification.

As the shape of the drop depends upon the ratio of a linear dimension of the tip such as r and a linear dimension of the drop such as a, the deviation of the shape of the drop from the perfect shape can be accounted for in equation (38) above by introducing the dimensionless function $f'\left(\frac{r}{a}\right)$. We then have

$$mg + 2\pi^2\sigma^2 r^2 f'\left(\frac{r}{a}\right) = 2\pi r T \text{ --- } 41$$

and

$$f'\left(\frac{r}{a}\right) = \frac{R^2}{r^2}$$

For the extremes of voltage used to obtained the results for droppers A and B, i.e. 0 and 1861 volts, the radius of the drop was respectively 0.1496 cm. and 0.1370 cms. Because r, the radius of the tip, was so much smaller than a there would therefore be little difference in the "shape" of the drop when on the point of leaving the tip over the range of voltage used. This means that $f'\left(\frac{r}{a}\right)$

is almost constant over this range. The values of $f'\left(\frac{r}{a}\right)$ for droppers A and B were calculated from the results obtained and found to be 14.85 for dropper A and 23.1 for dropper B.

As Harkins and Brown allowed for the shape of the drop in the ideal equation by introducing a similar dimensionless function $f\left(\frac{r}{a}\right)$, the equation completely corrected for shape will therefore be

$$mg + 2\pi^2\sigma^2 r^2 f'\left(\frac{r}{a}\right) = 2\pi r T . f\left(\frac{r}{a}\right)$$

$f\left(\frac{r}{a}\right)$ being approximately unity for the droppers used in the above experiments.

SUMMARY

The first part of the thesis is a description of attempts made to measure the natural charges acquired by water drops while falling through air. The method of measurement is by photographing the deviation from the vertical of drops falling through a horizontal electric field. These initial experiments being unsuccessful, a description is given of attempts made to improve the sensitivity of the method and a chapter is devoted to experiments in which it was hoped to measure the charge after the water drops fell from the air into the nonconducting liquid, benzene. It is shown that such drops acquire a characteristic negative charge in the electric field in the benzene, the charge being due to impurities in solution and proportional to field intensity and drop radius.

An account is then given of experiments performed using benzene drops in aqueous solutions, the object being to gain information on conditions existing at the benzene/water interface. The effect of hydroxyl ion concentration on drop charge, is determined both acid and alkaline solutions being used and the reasons for attributing the negative charges acquired by the benzene drops to hydroxyl ion absorption are given. The drops acquire a saturation negative charge in solution of hydroxyl ion concentration greater than 7×10^{-5} N and a mathematical interpretation of the charge - hydroxyl ion concentration curve is given.

The results obtained for other non conducting drops in aqueous solutions are listed, the simpler paraffins hexane, n. heptane and iso. octane and also toluene and xylene being used. The "chemical" absorption of hydroxyl ions is shown to be of very similar nature in each case. By means of carbon tetrachloride drops the effect of drop radius on drop charge is measured and a discussion of the results in terms of turbulence of liquid flow round the drop is given. Some results obtained with Lanthanum Nitrate solution are used as an empirical check on Mukherjee's equation for neutralization of charge on a colloidal particle.

Results obtained with pure mercury drops in aqueous solutions, and the influence of potential gradients on drop charge, are given. Reversal of drop sign from positive to negative is observed with high potential gradients in neutral and alkaline solutions and a possible explanation of the results is made.

A short appendix is devoted to the explanation of a phenomenon observed in the earlier experiments viz. the decrease in mass of drops falling from a capillary dropper, due to electrification of the drops at the capillary tip by an electric field.

I wish in conclusion to express my sincere thanks to Professor J. E. P. Wagstaff, M.A., D.Sc., for his continual help, advice and encouragement throughout the period of research and to all others who showed interest in the work.

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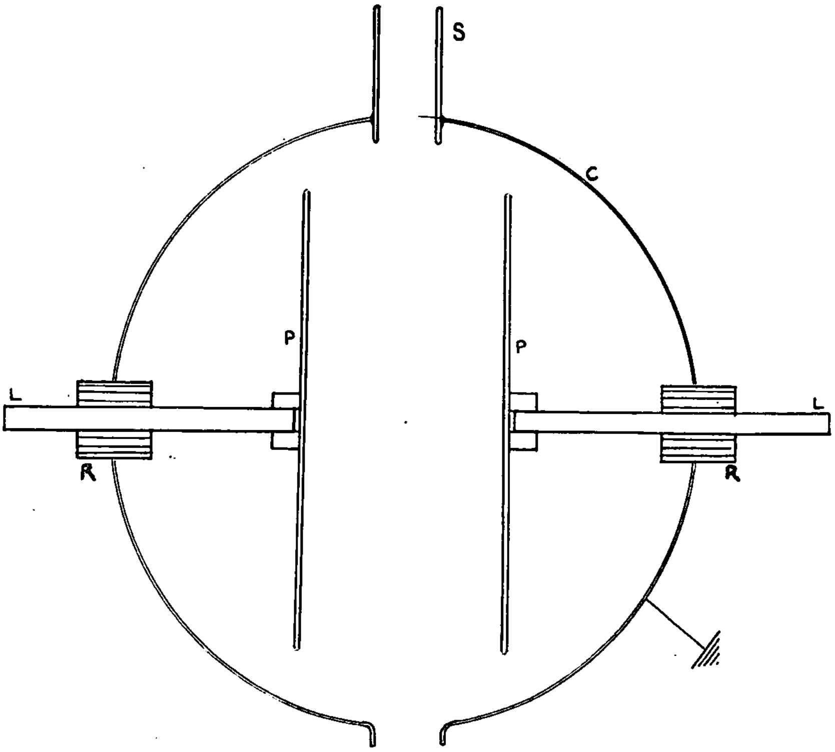

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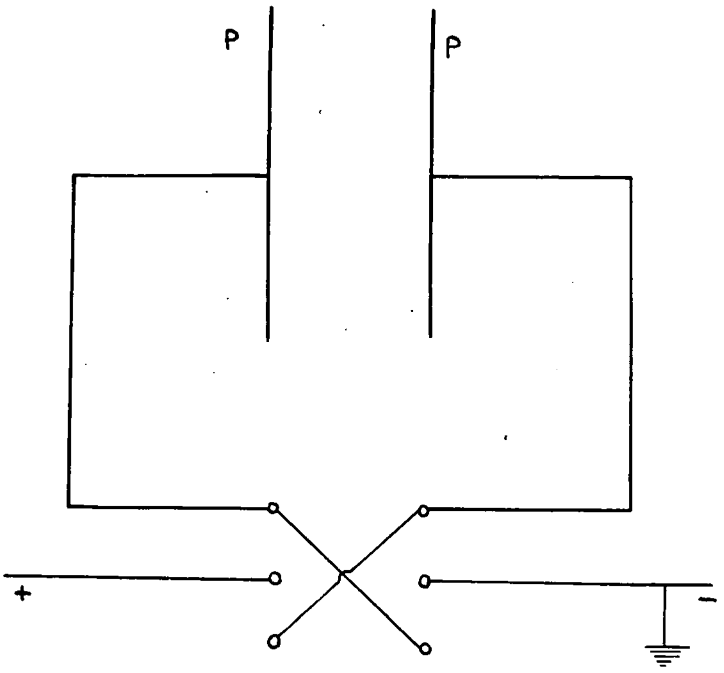


FIG. 2

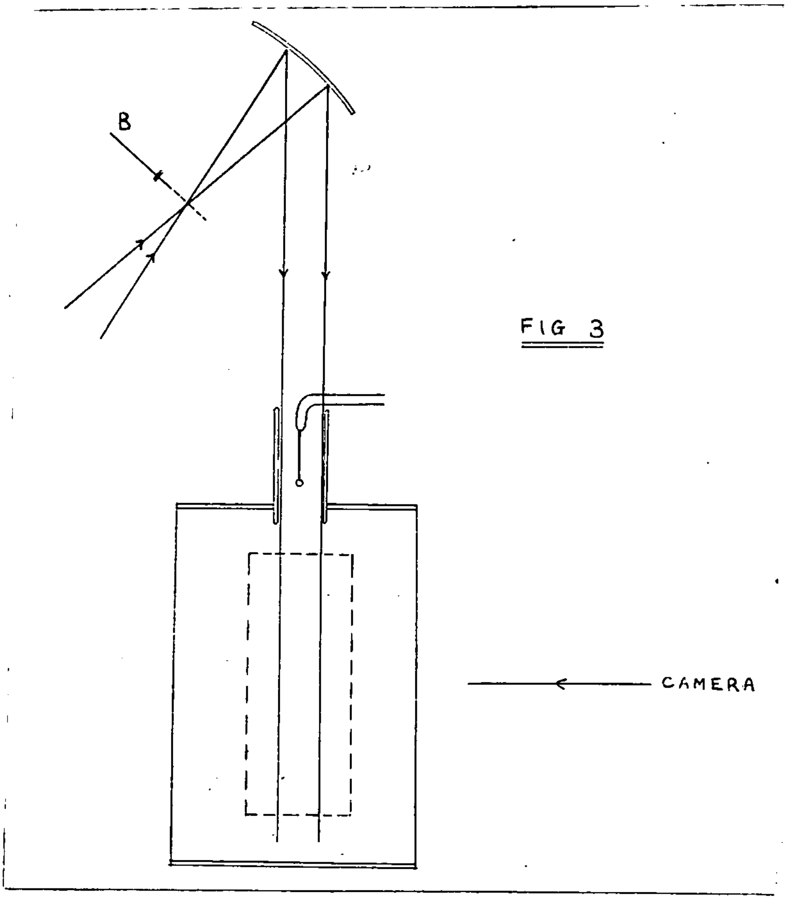
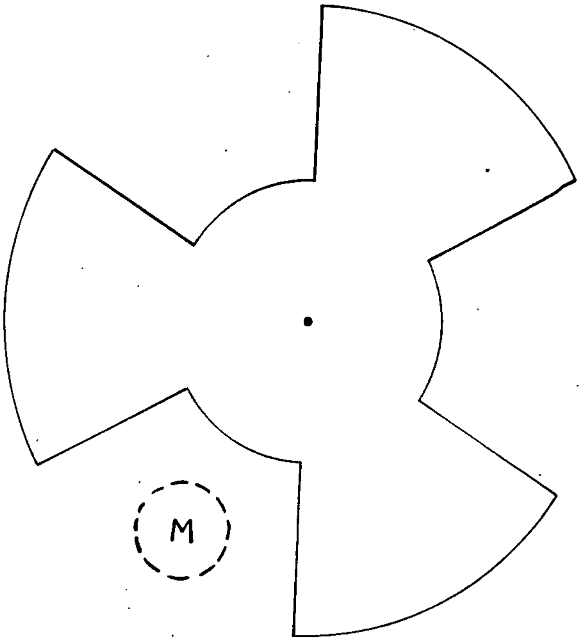


FIG 3



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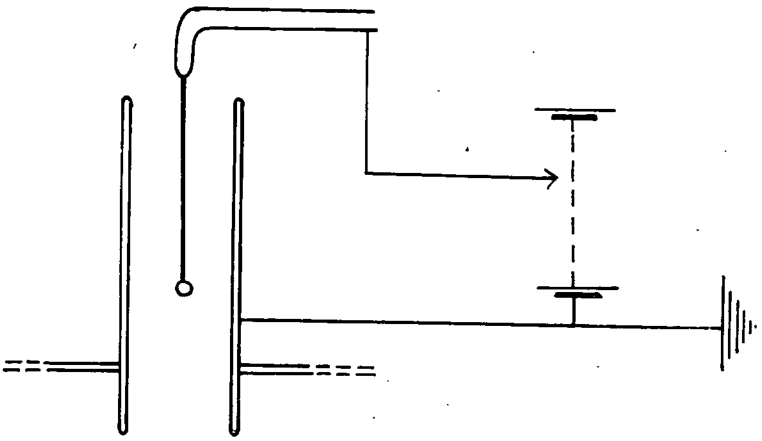

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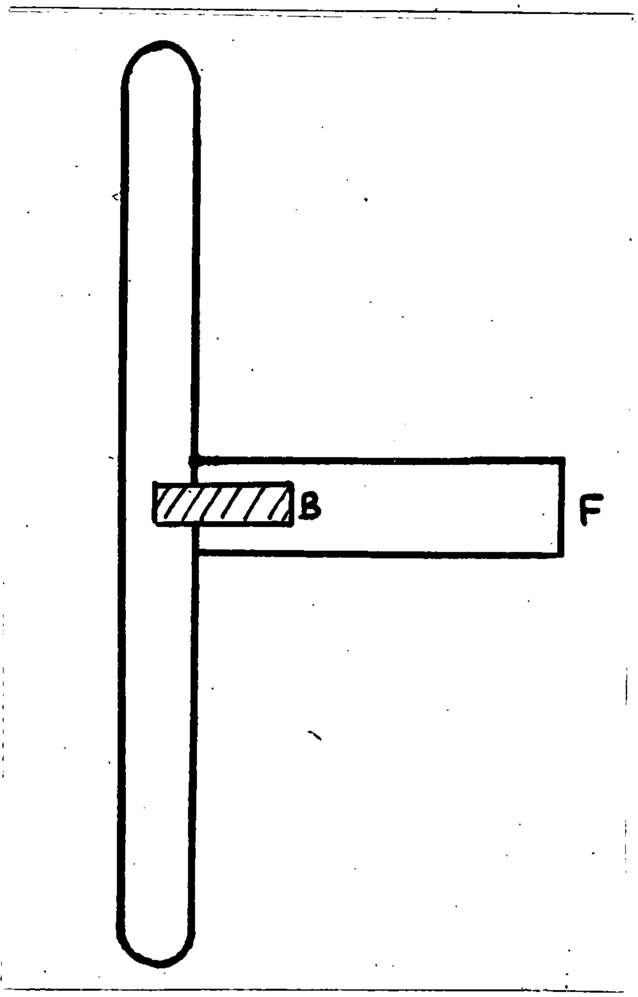

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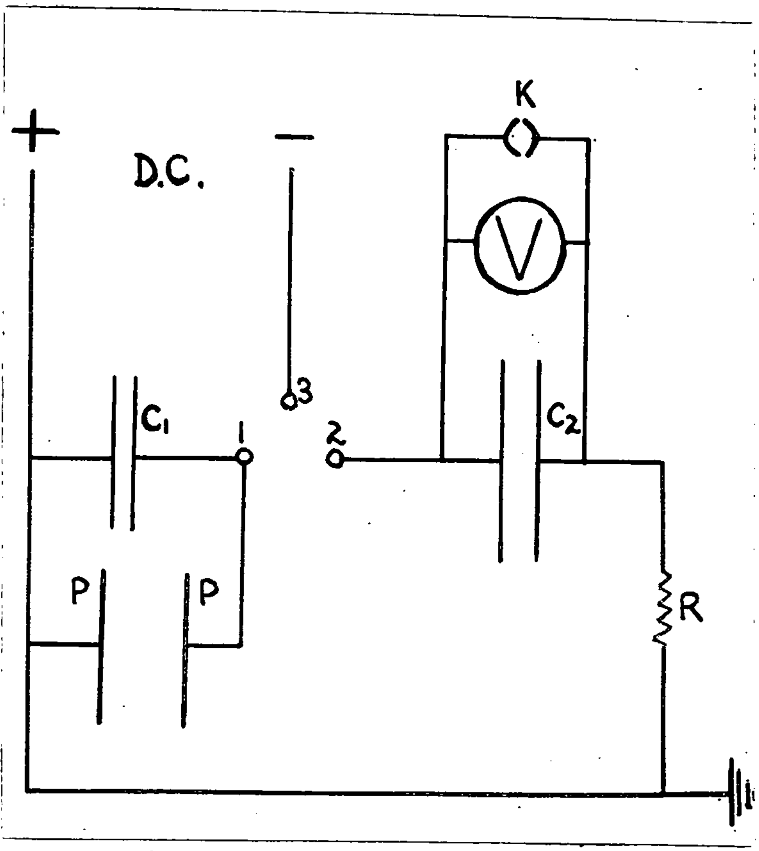
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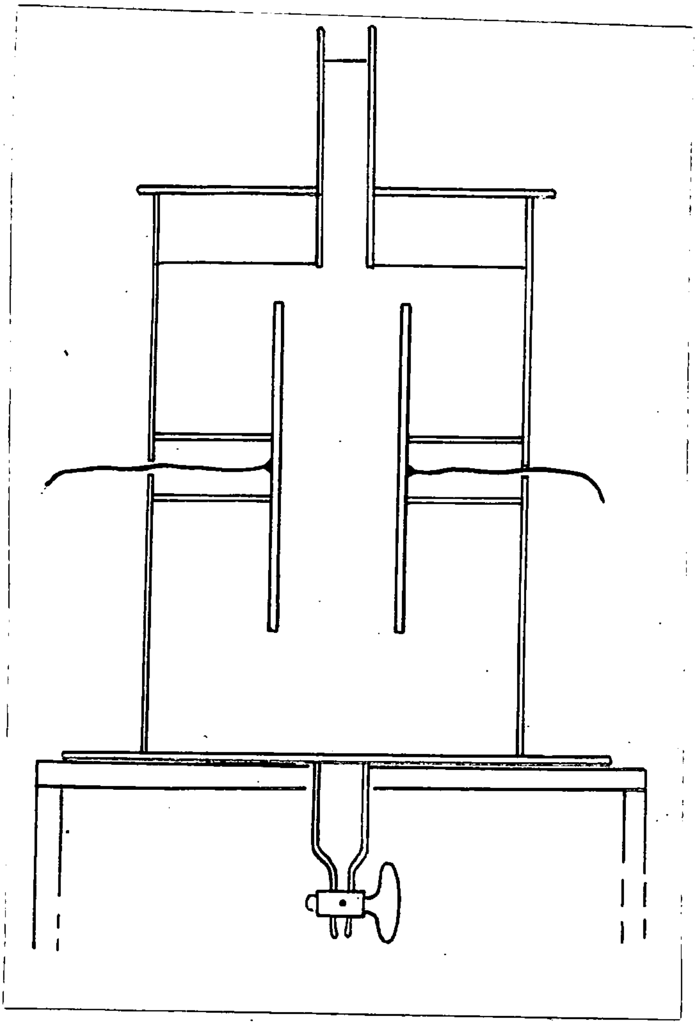
FIG. 7.



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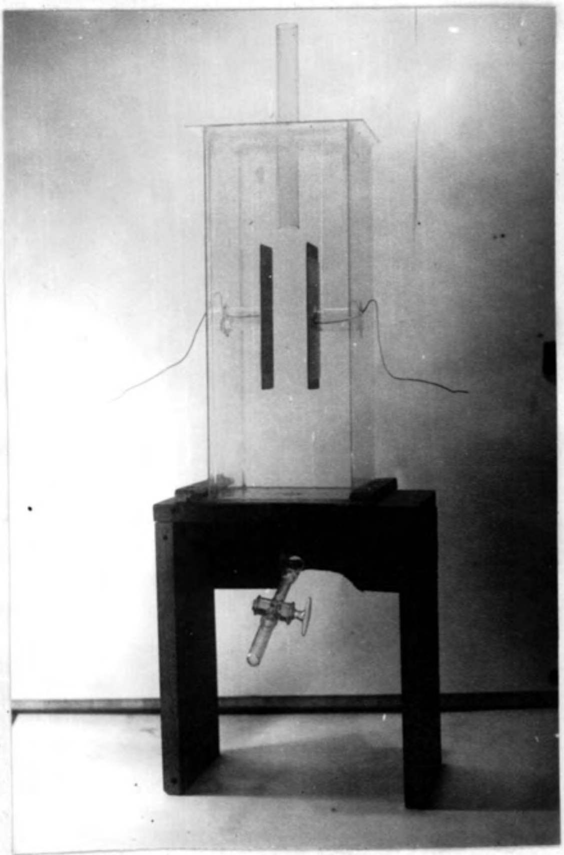

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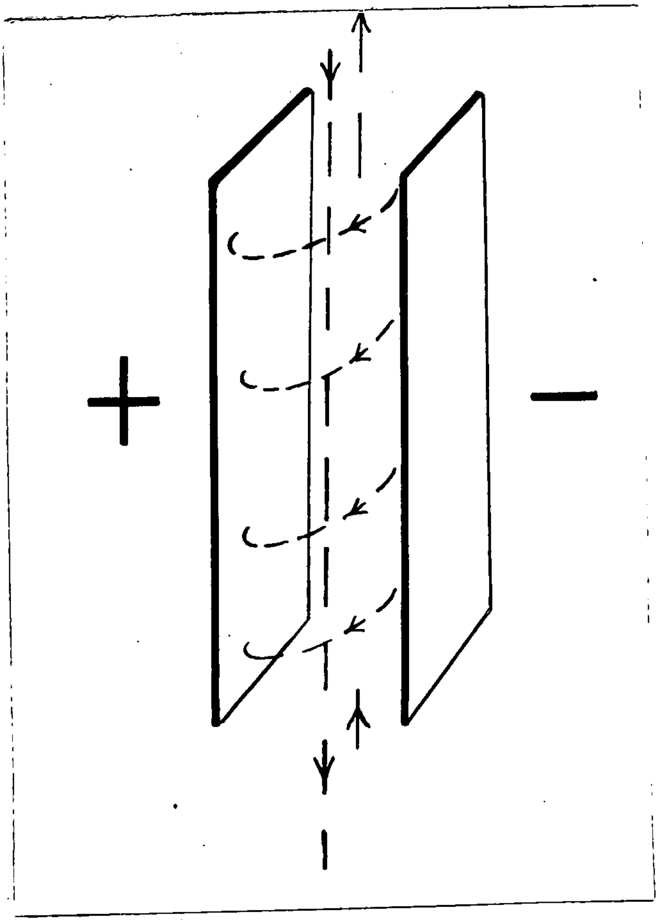

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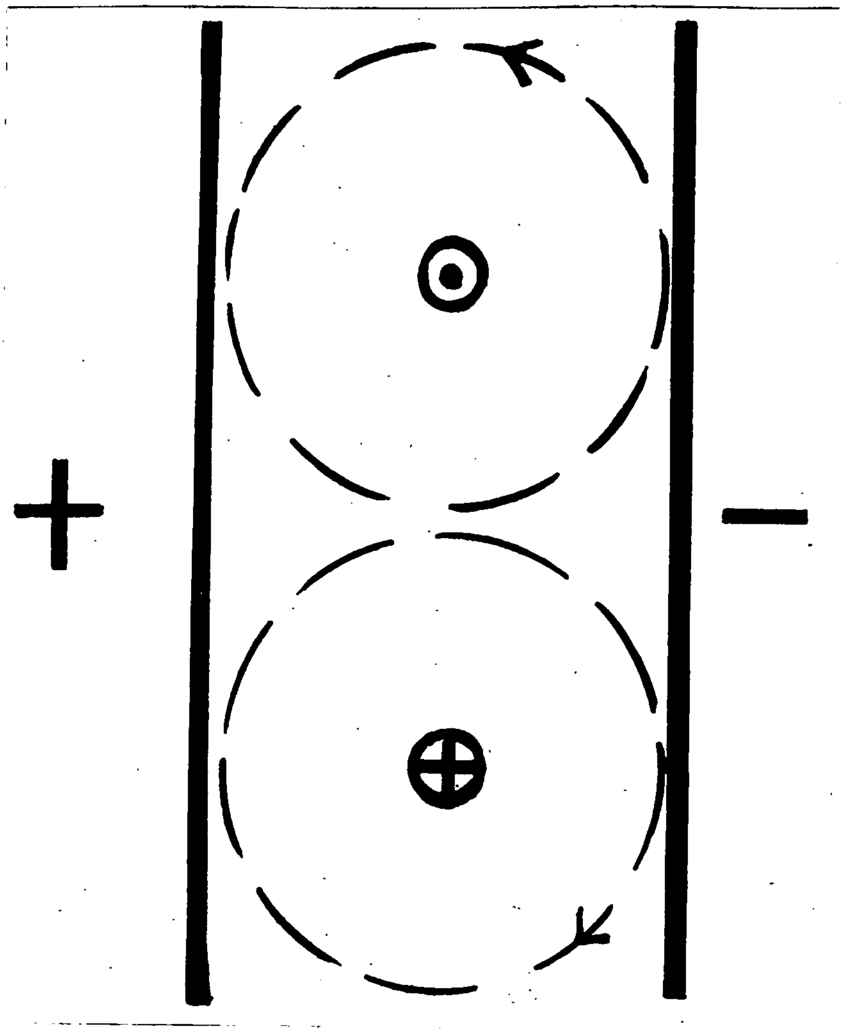

FIG. 11.

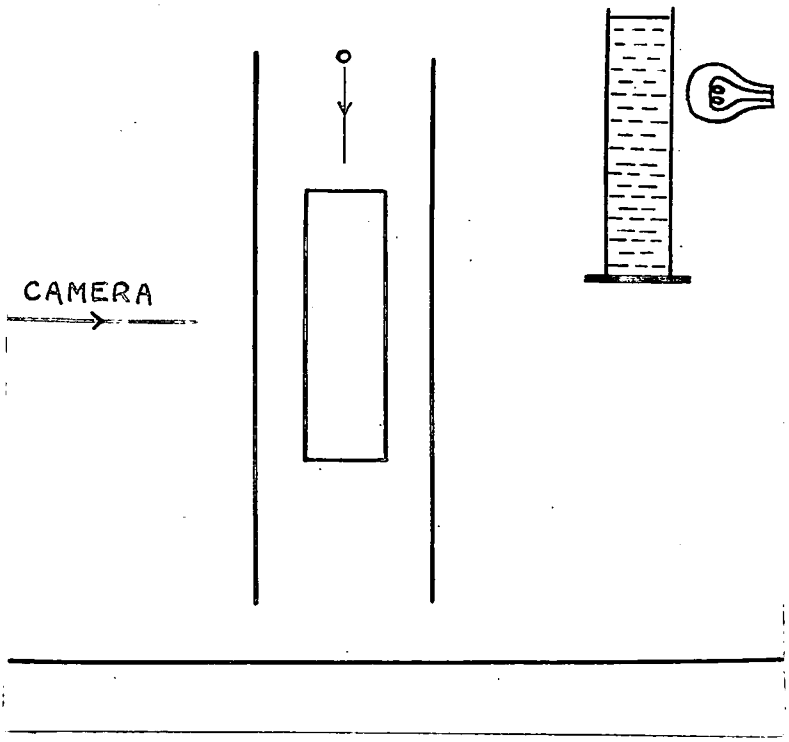

FIG.12.

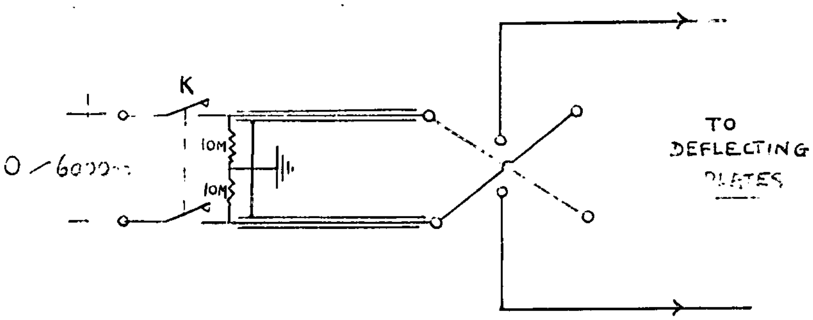

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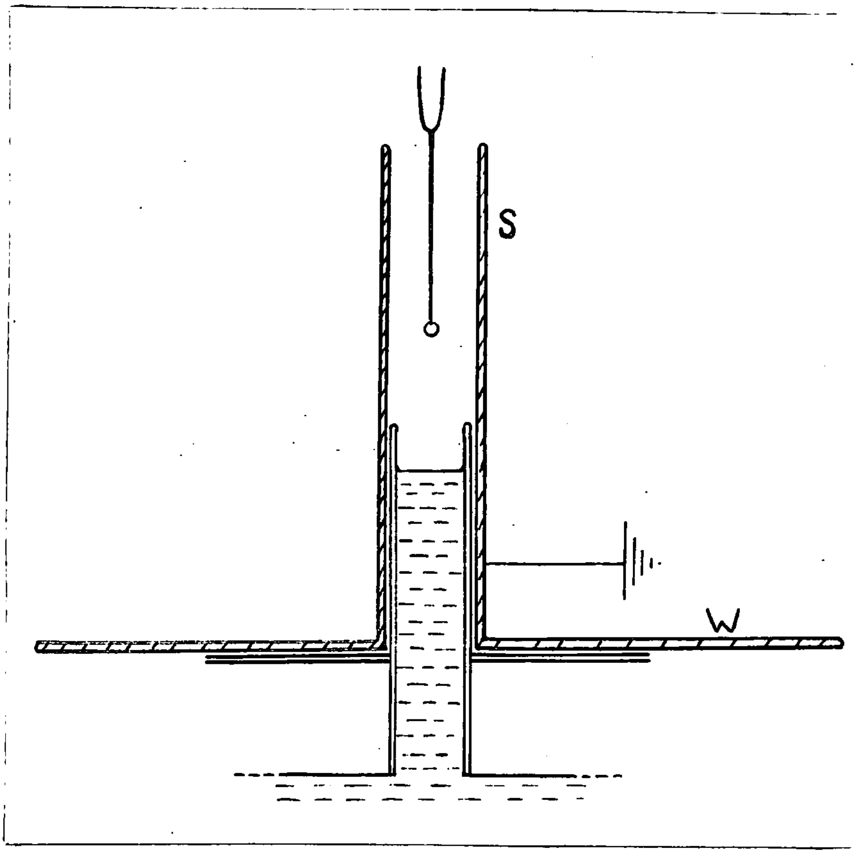
FIG. 13.



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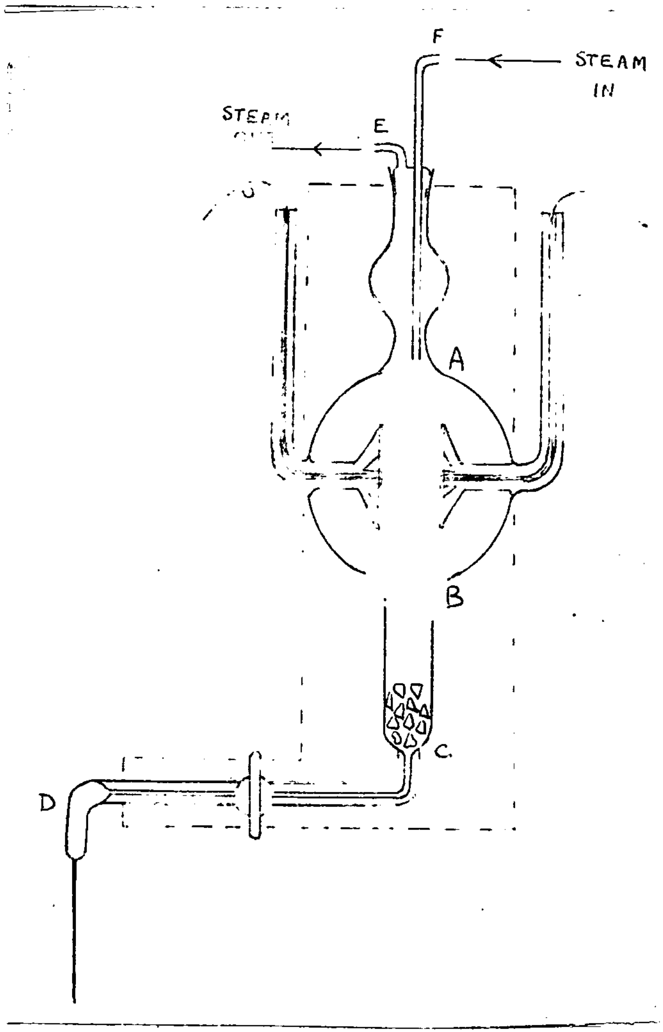
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STEAM IN
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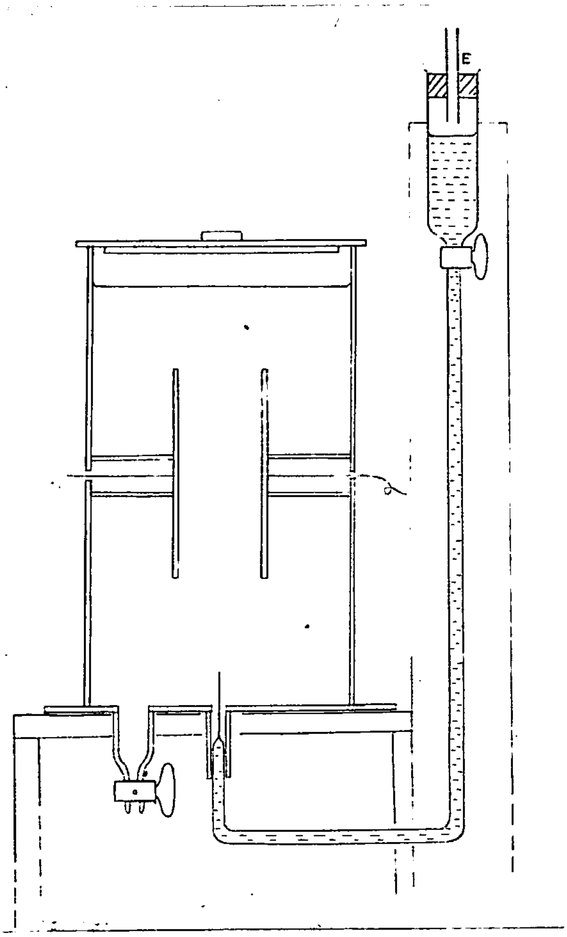
FIG. 15.



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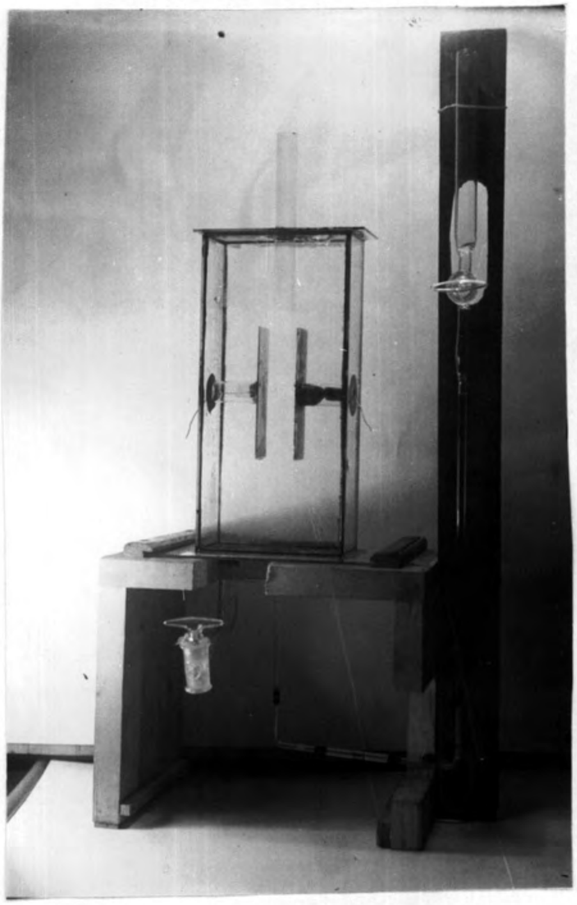

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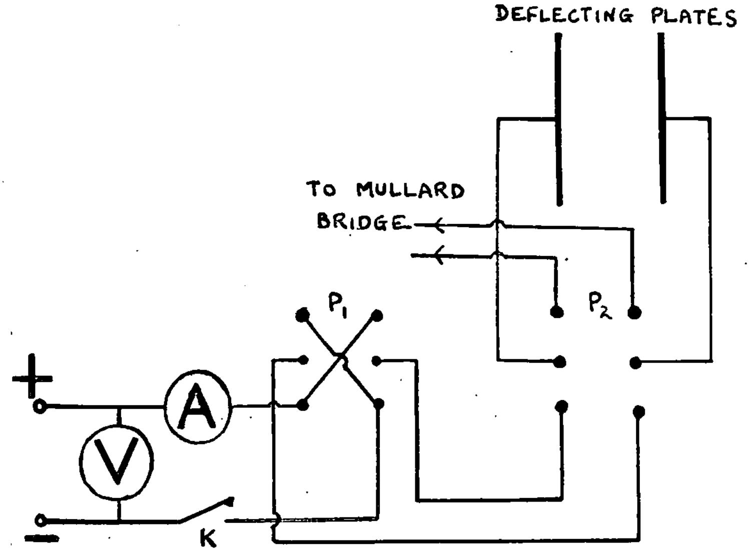
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P₁
P₂
+
A
V
−
K

FIG. 18.

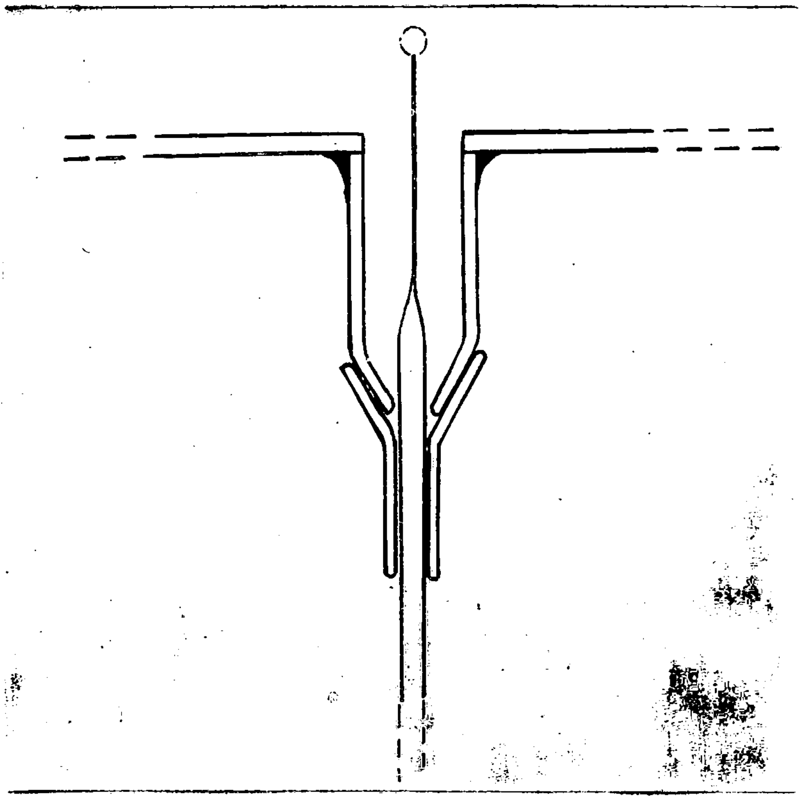


FIG. 19.

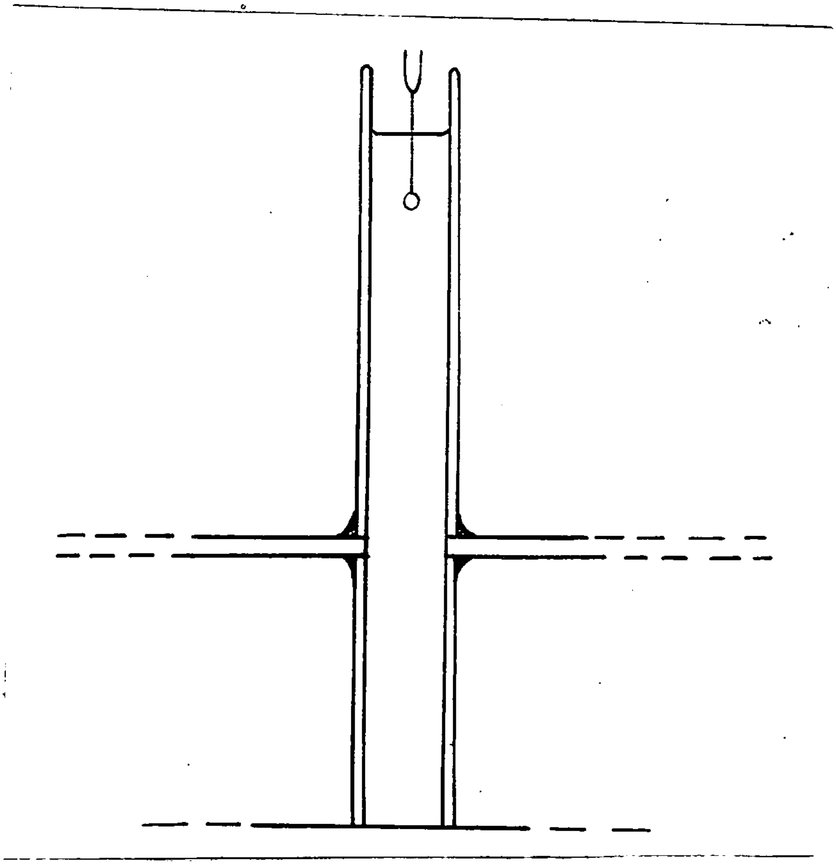


FIG. 20.

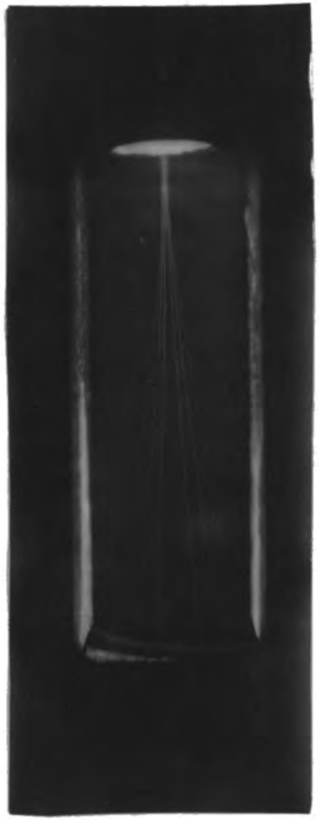


FIG. 21.

FIG. 22.

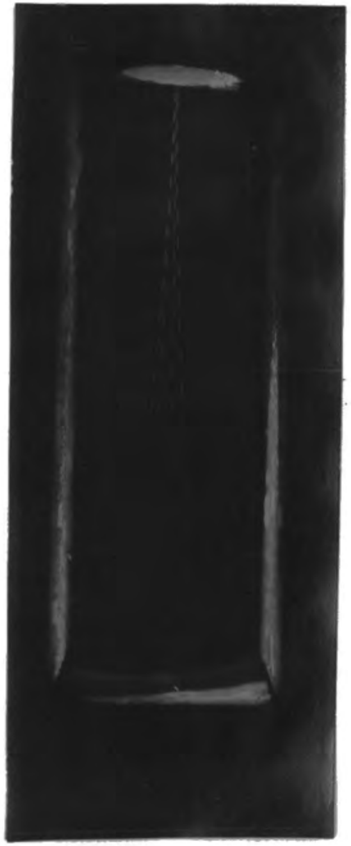


FIG. 23.

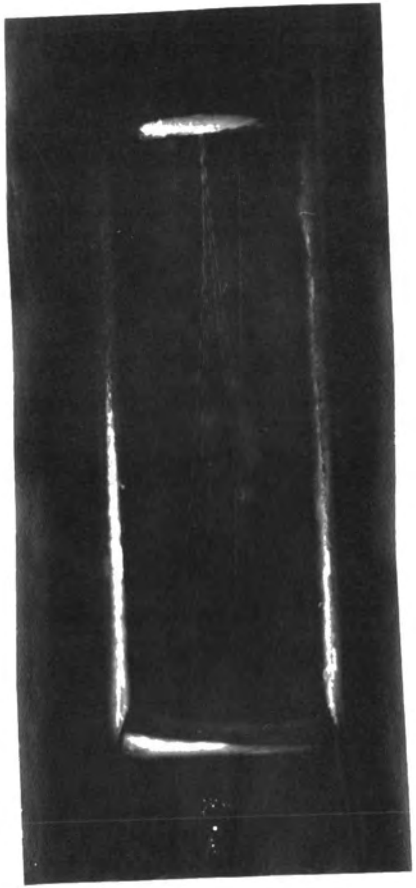


FIG. 24.

FIG. 25.

FIG. 26.

FIG. 27.

FIG. 28.

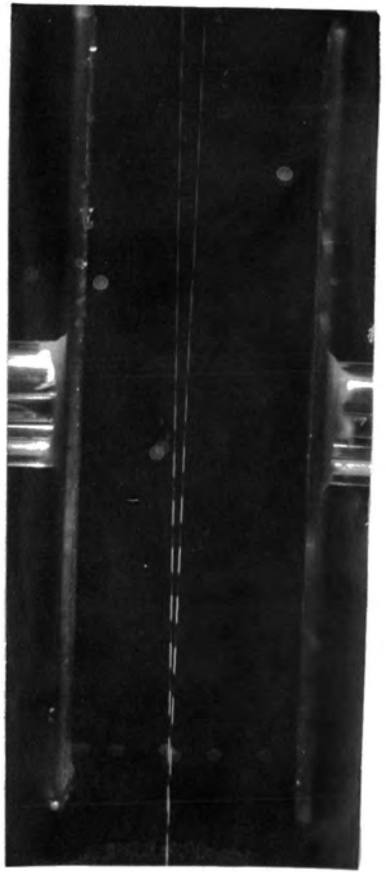


FIG. 29.

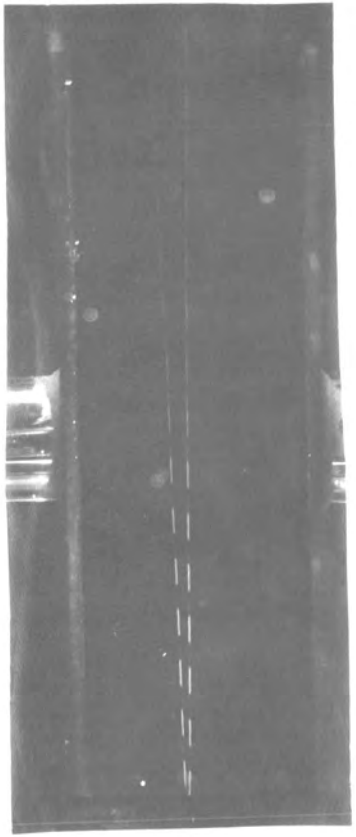


FIG. 30.

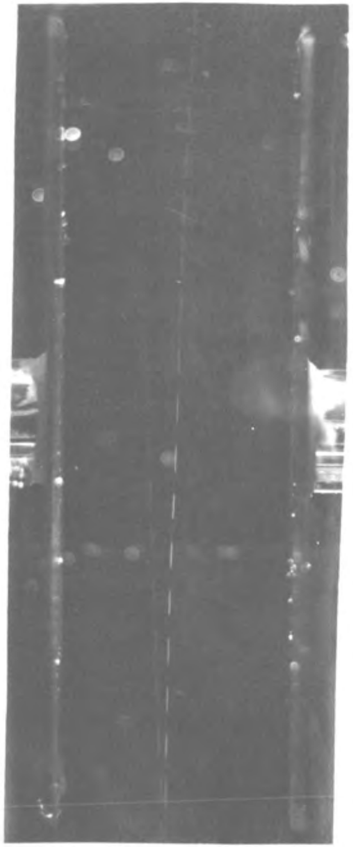


FIG. 31.

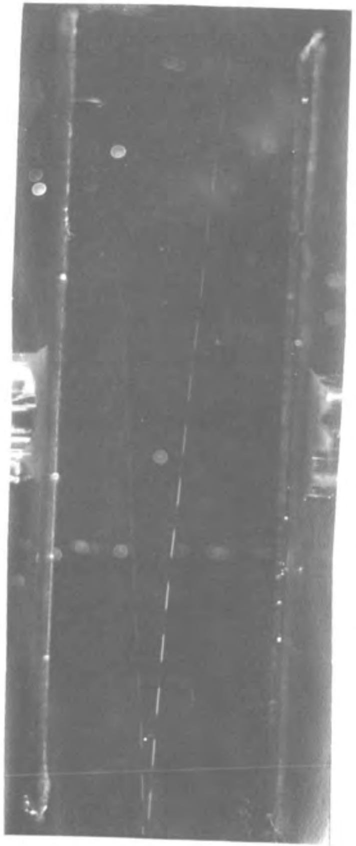


FIG. 32.

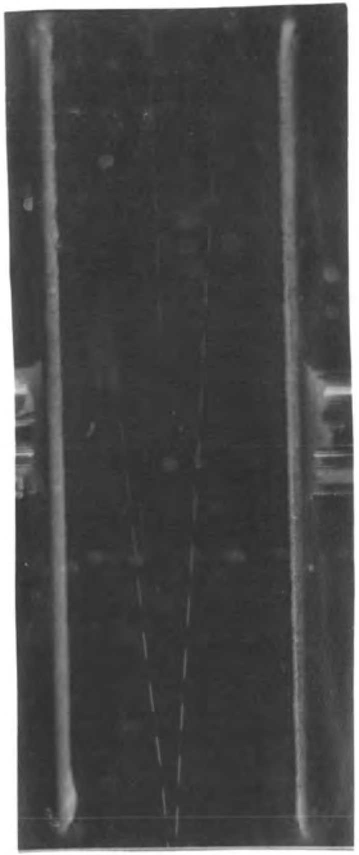


FIG. 33.

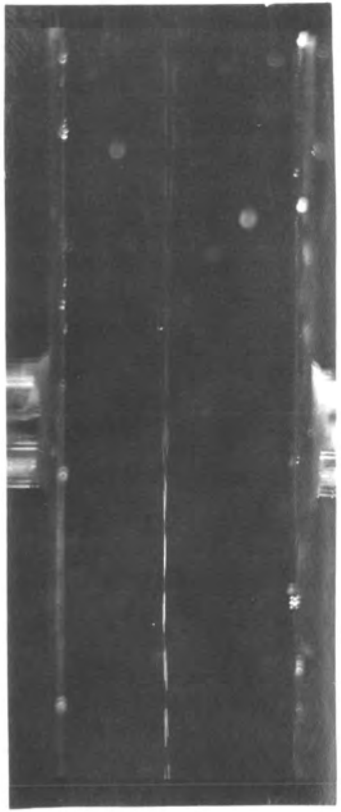


FIG. 34.

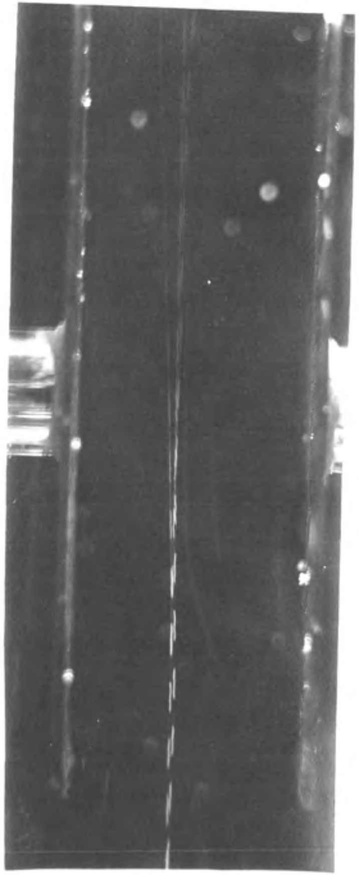


FIG. 35.

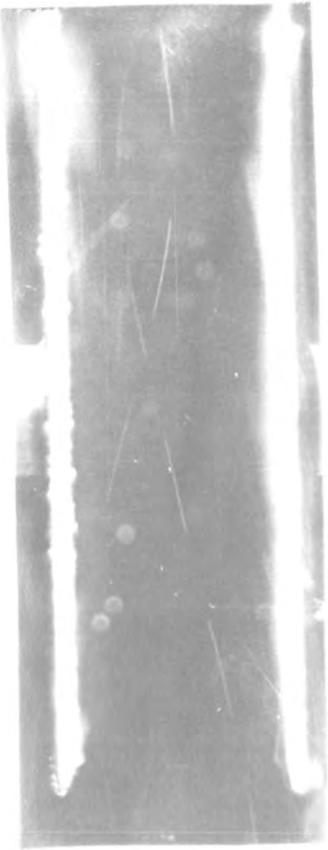


FIG.36.

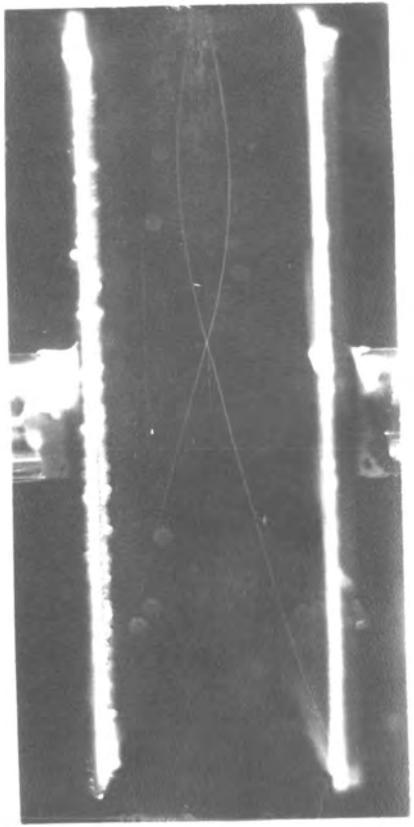


FIG. 37.

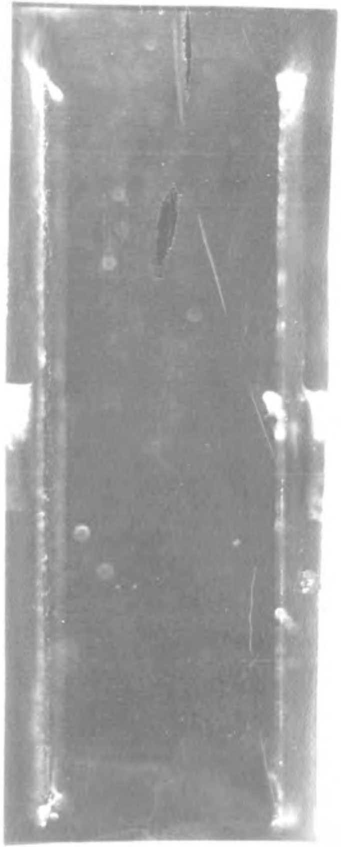


FIG. 38.

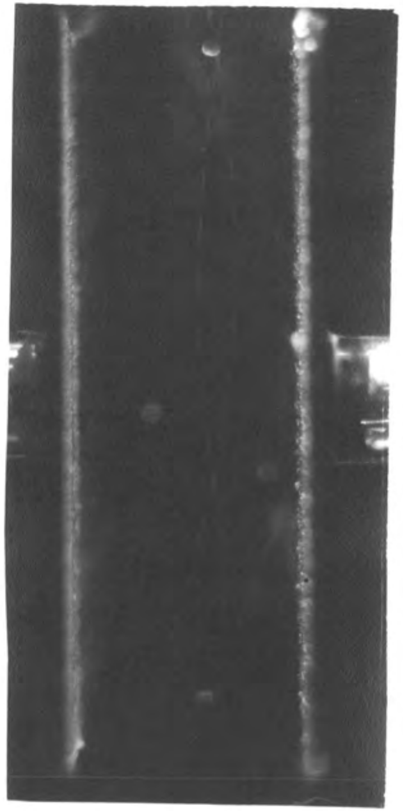


FIG. 39.

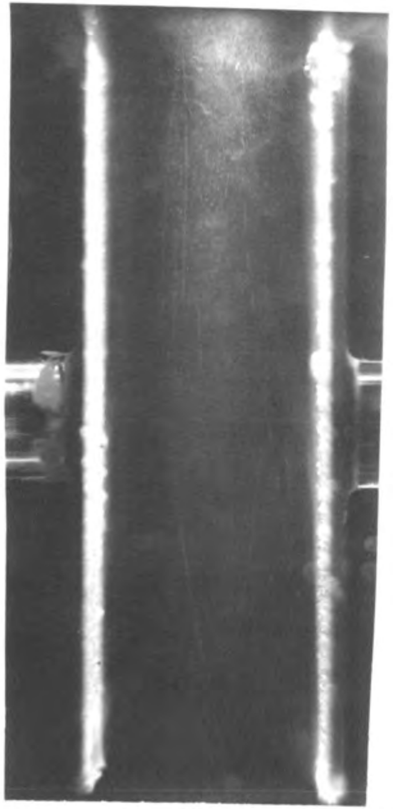


FIG. 40.

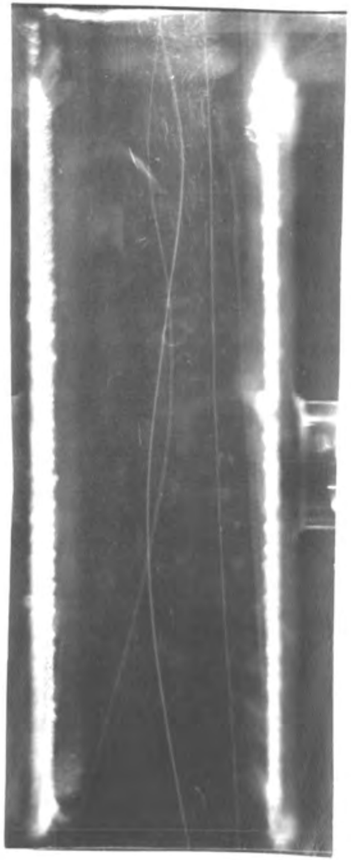


FIG. 41.

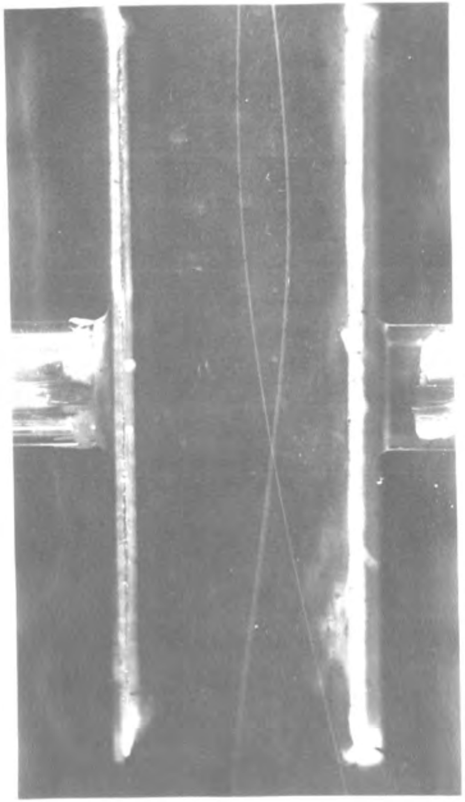


FIG. 42.

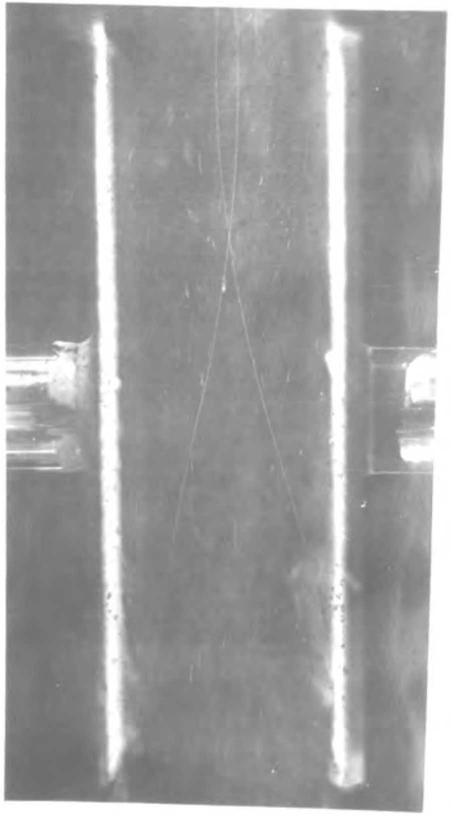


FIG. 43.

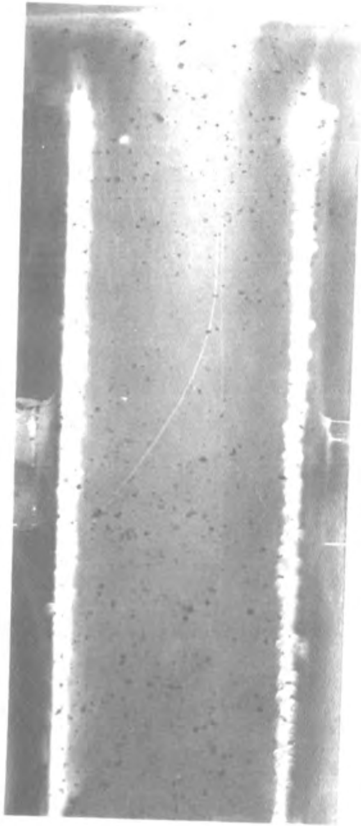


FIG. 44.

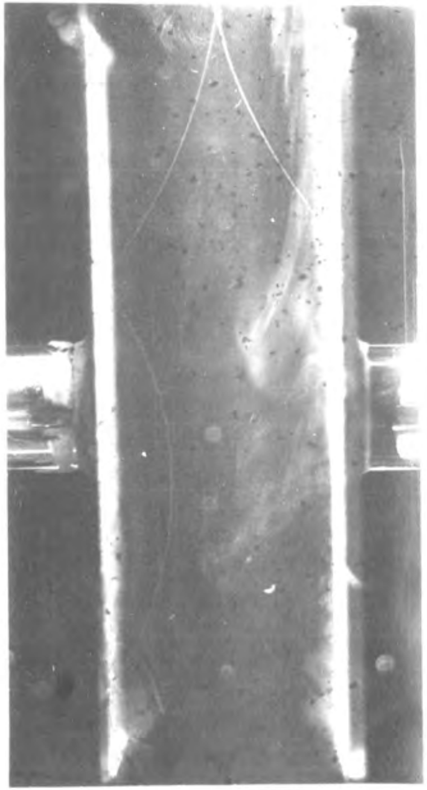
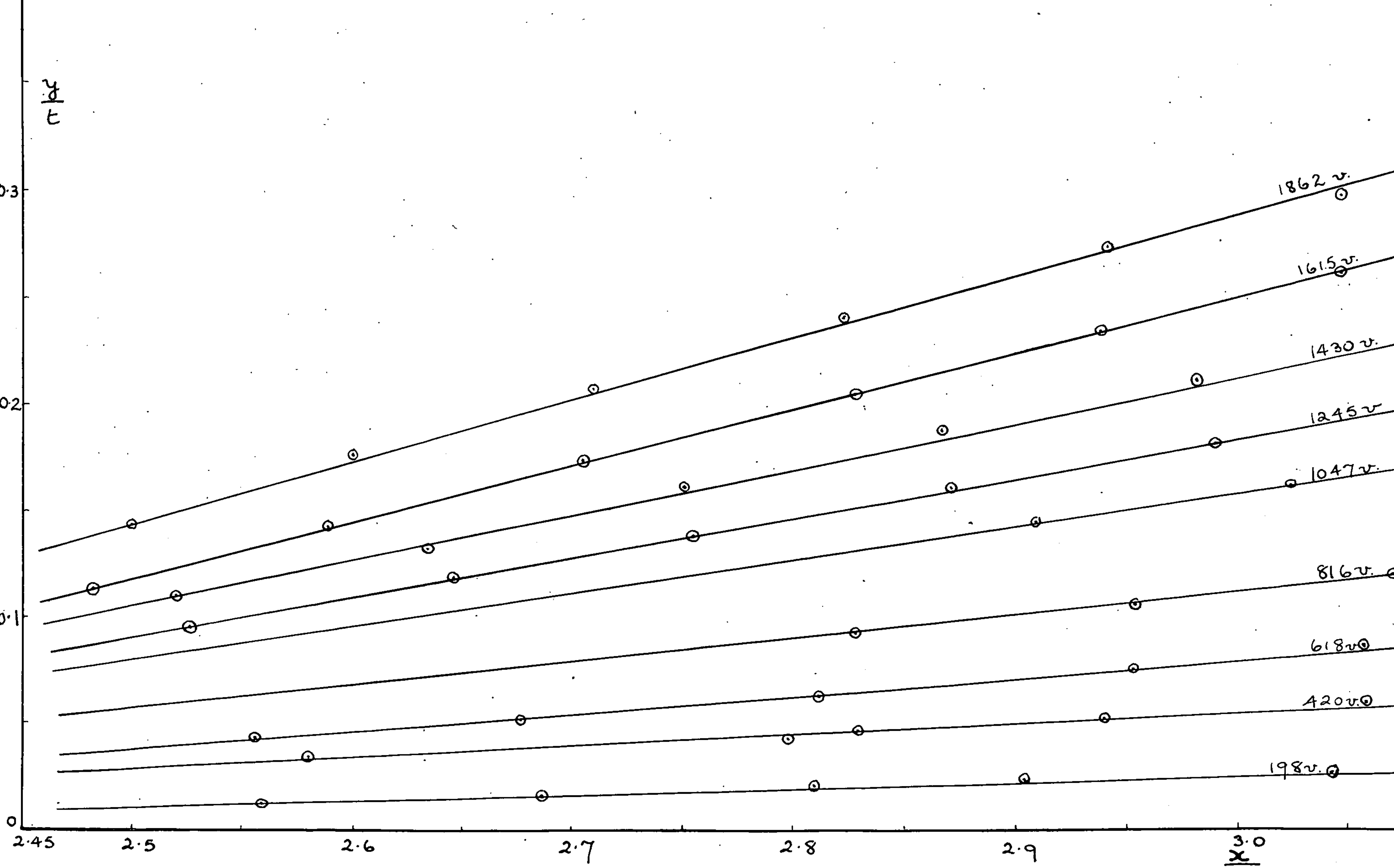
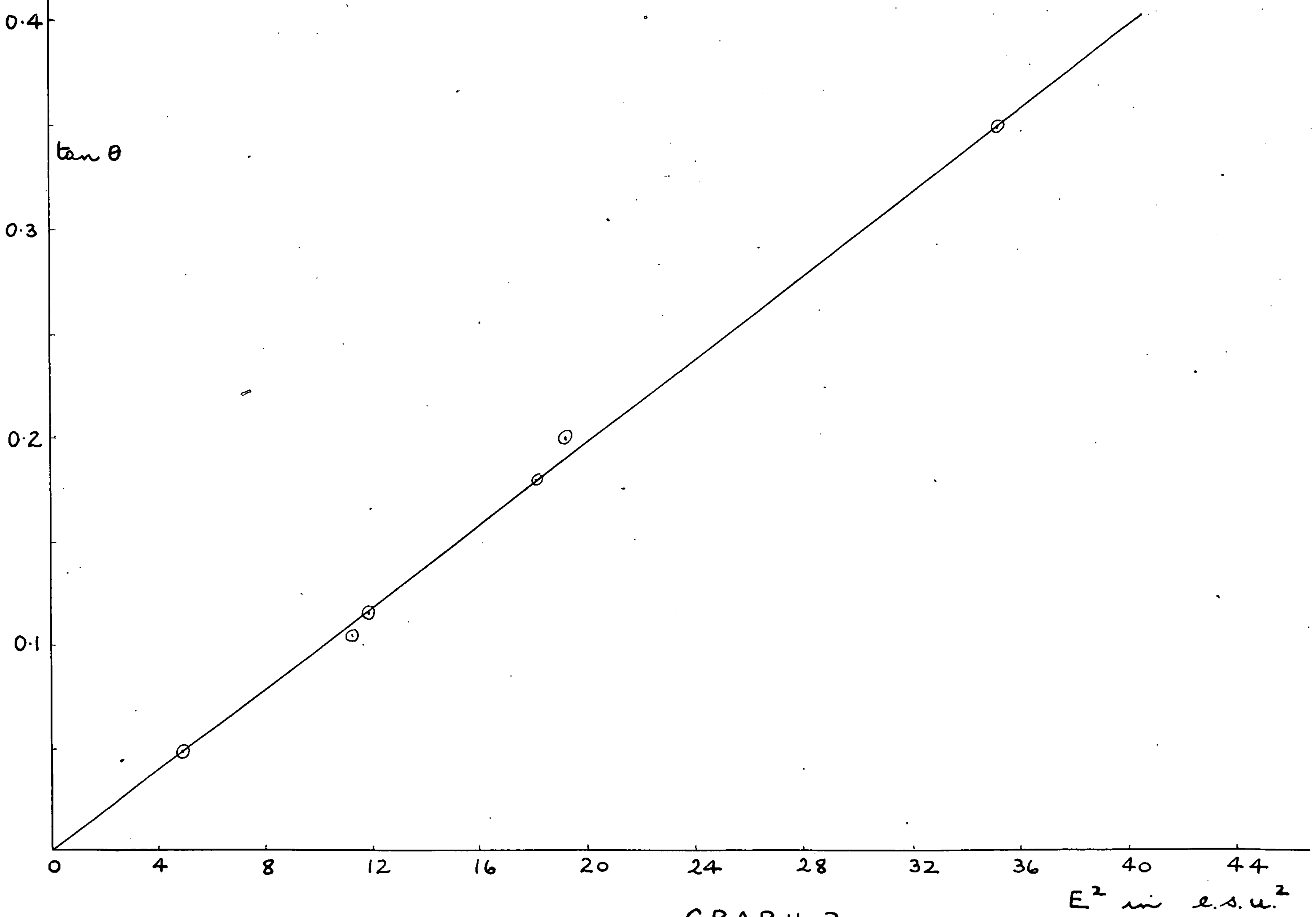


FIG. 45.

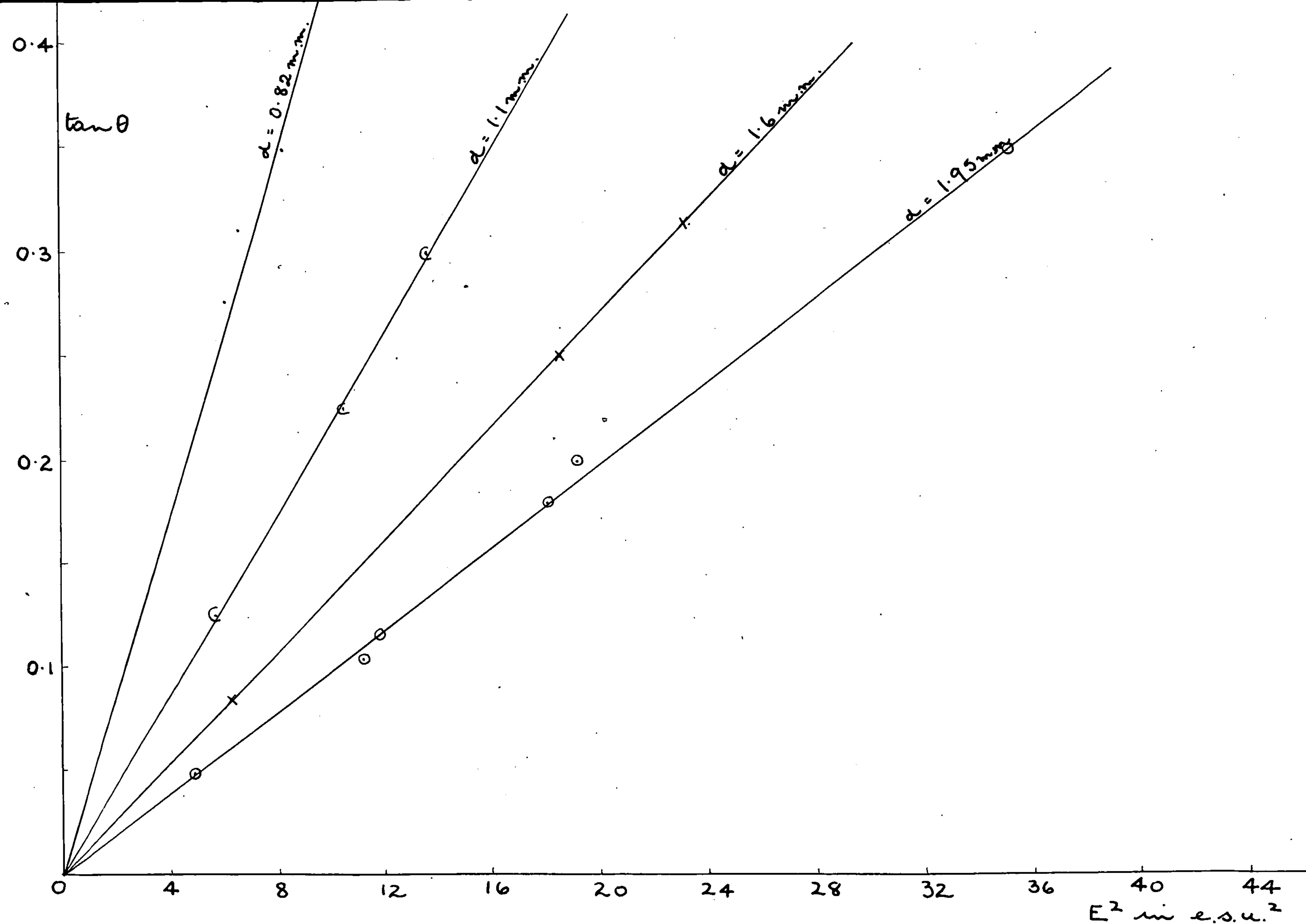


$\frac{y}{t}$
0·3
0·2
0·1
0
2·45
2·5
2·6
2·7
2·8
2·9
3·0
$\frac{x}{t}$
1862 v.
1615 v.
1430 v.
1245 v
1047 v.
816 v.
618 v
420 v.
198 v.

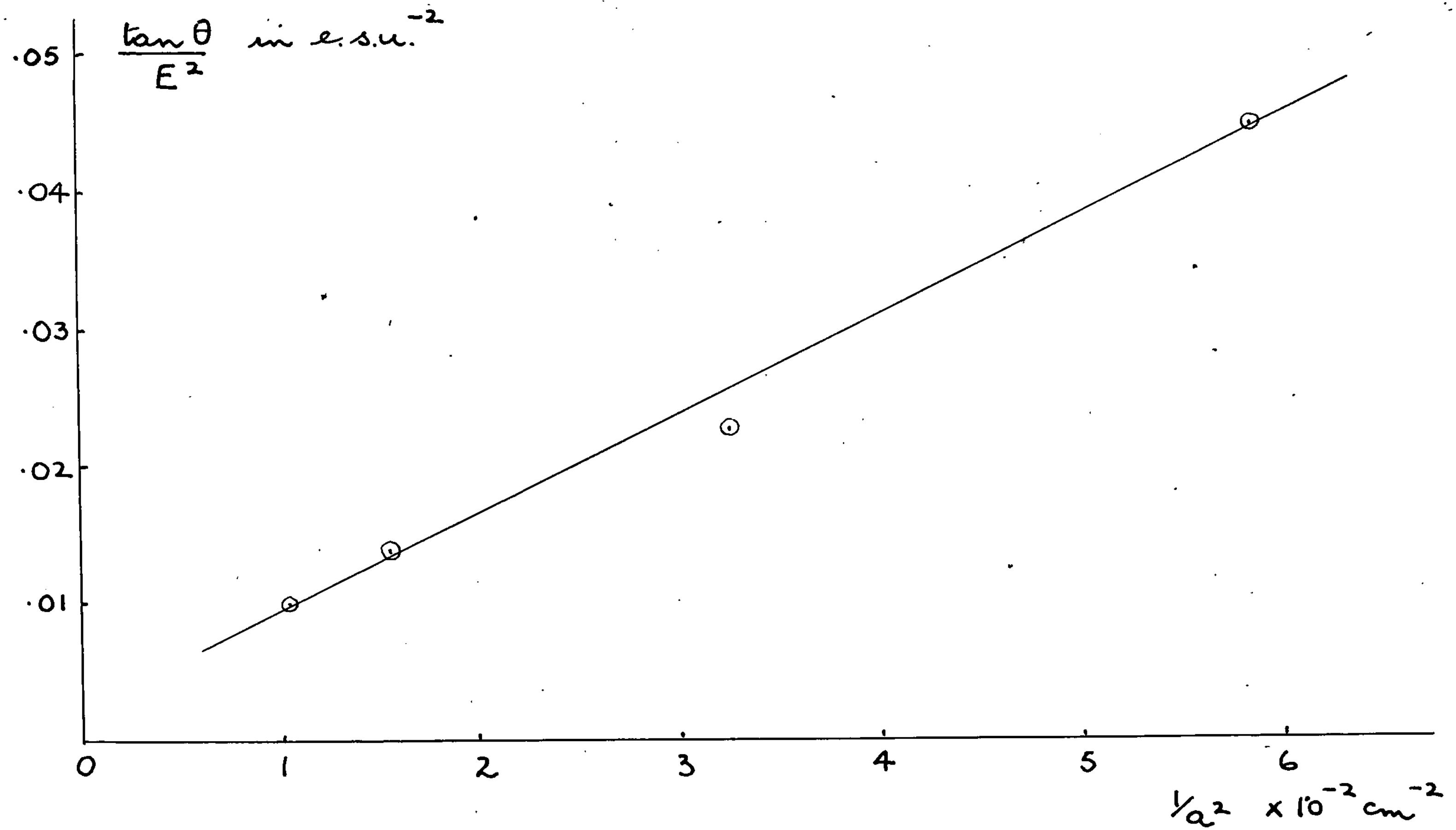
GRAPH I



GRAPH. 2.

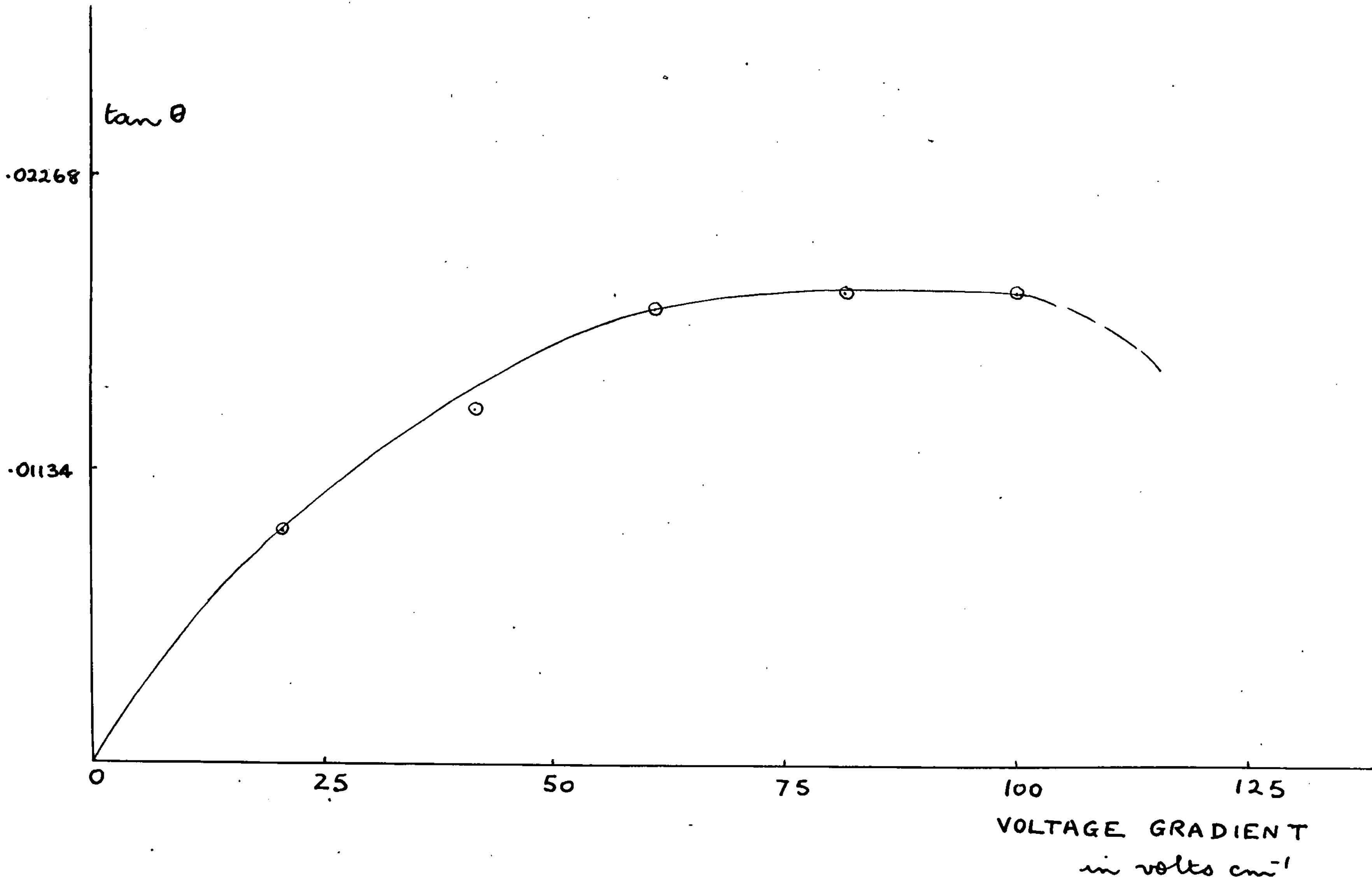

tan θ
0·4
0·3
0·2
0·1
0
4
8
12
16
20
24
28
32
36
40
44
E² in e.s.u.²
d = 0·82 m.m.
d = 1·1 m.m.
d = 1·6 m.m.
d = 1·95 m.m.

GRAPH 3



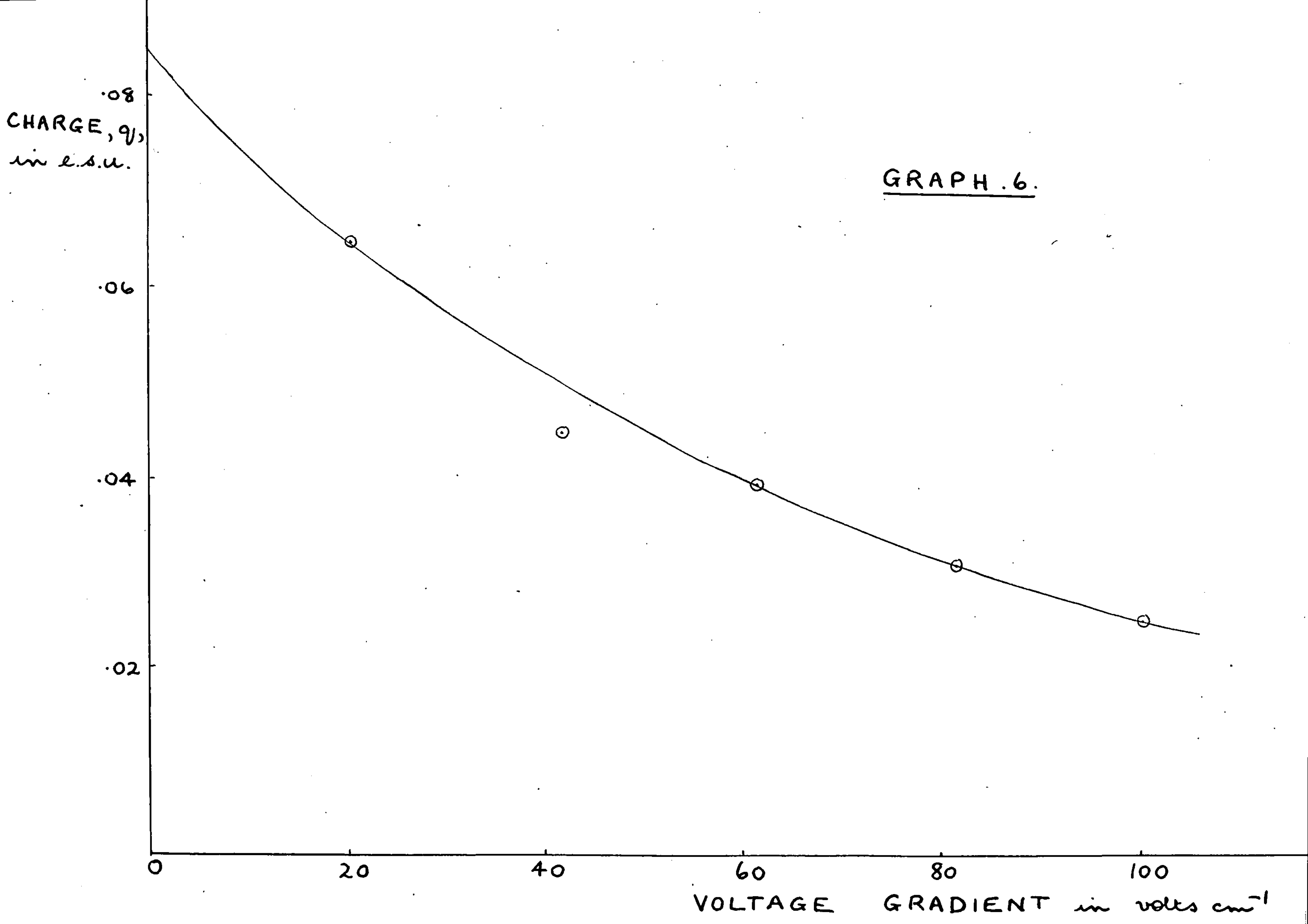
$\frac{\tan\theta}{E^2}$ in e.s.u.$^{-2}$
·05
·04
·03
·02
·01
0
1
2
3
4
5
6
$1/a^2 \times 10^{-2}$ cm^{-2}

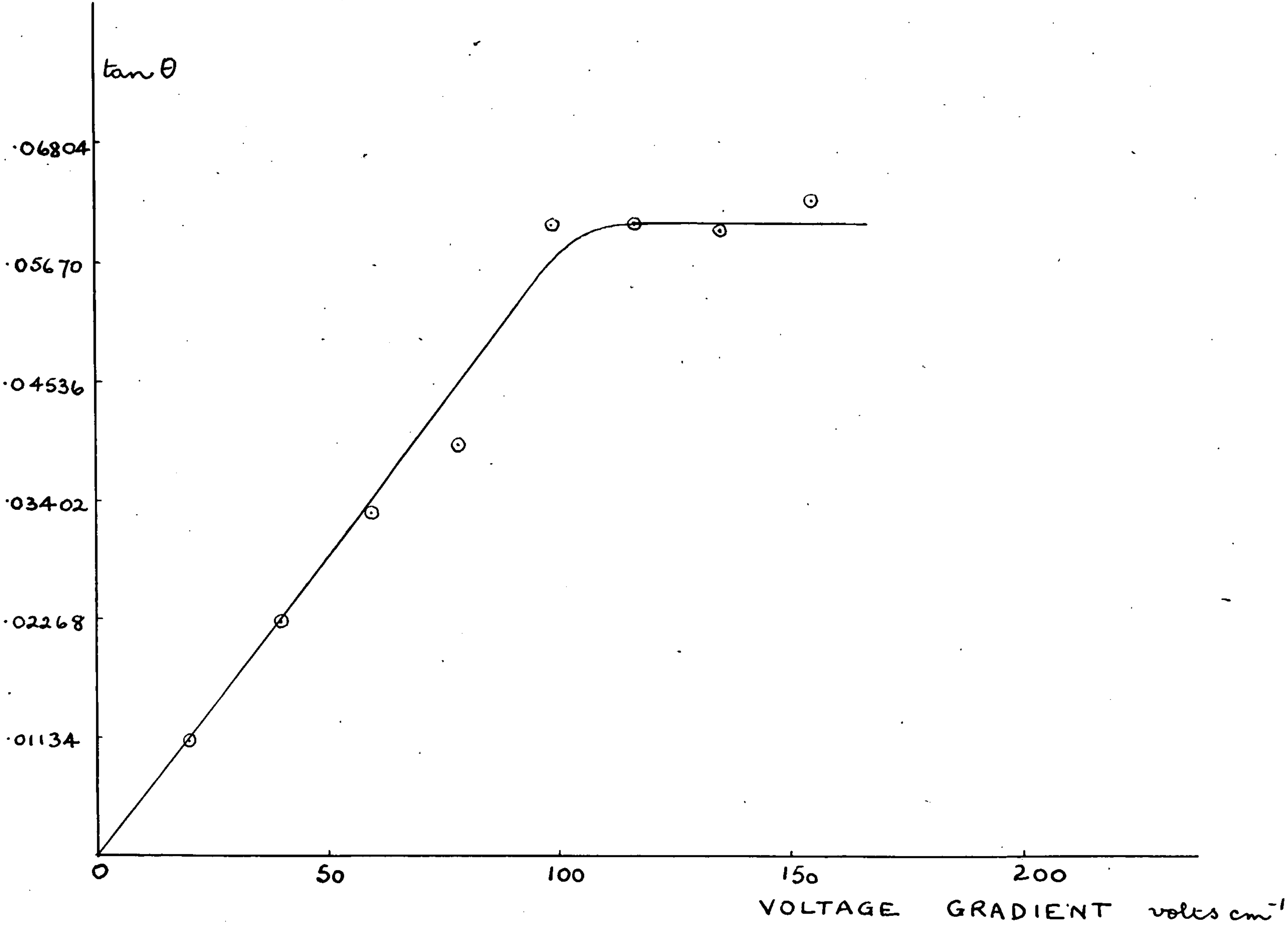
GRAPH 4


tan θ
·02268
·01134
0
25
50
75
100
125
VOLTAGE GRADIENT
in volts cm⁻¹

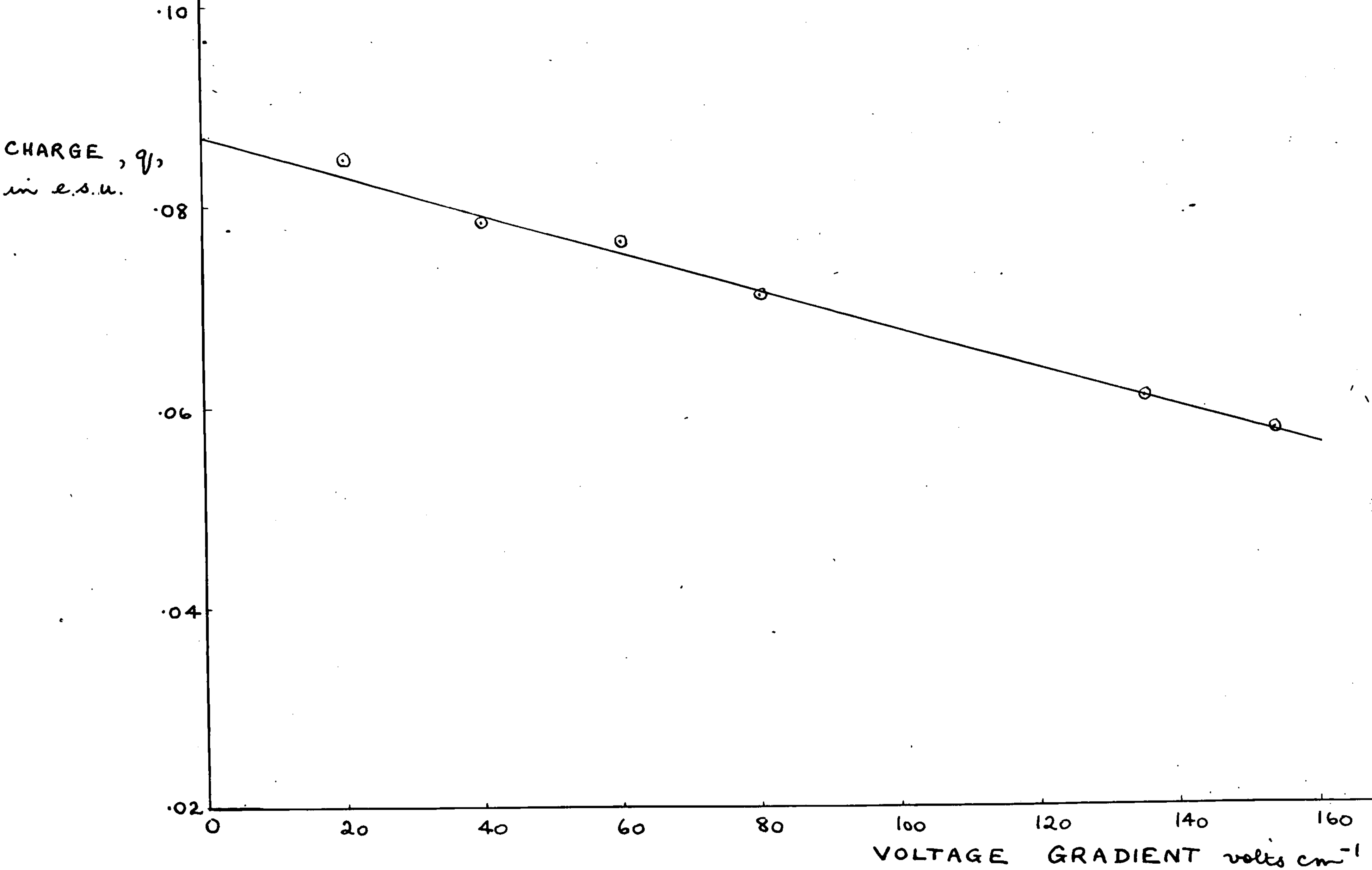
GRAPH. 5.

GRAPH .6.

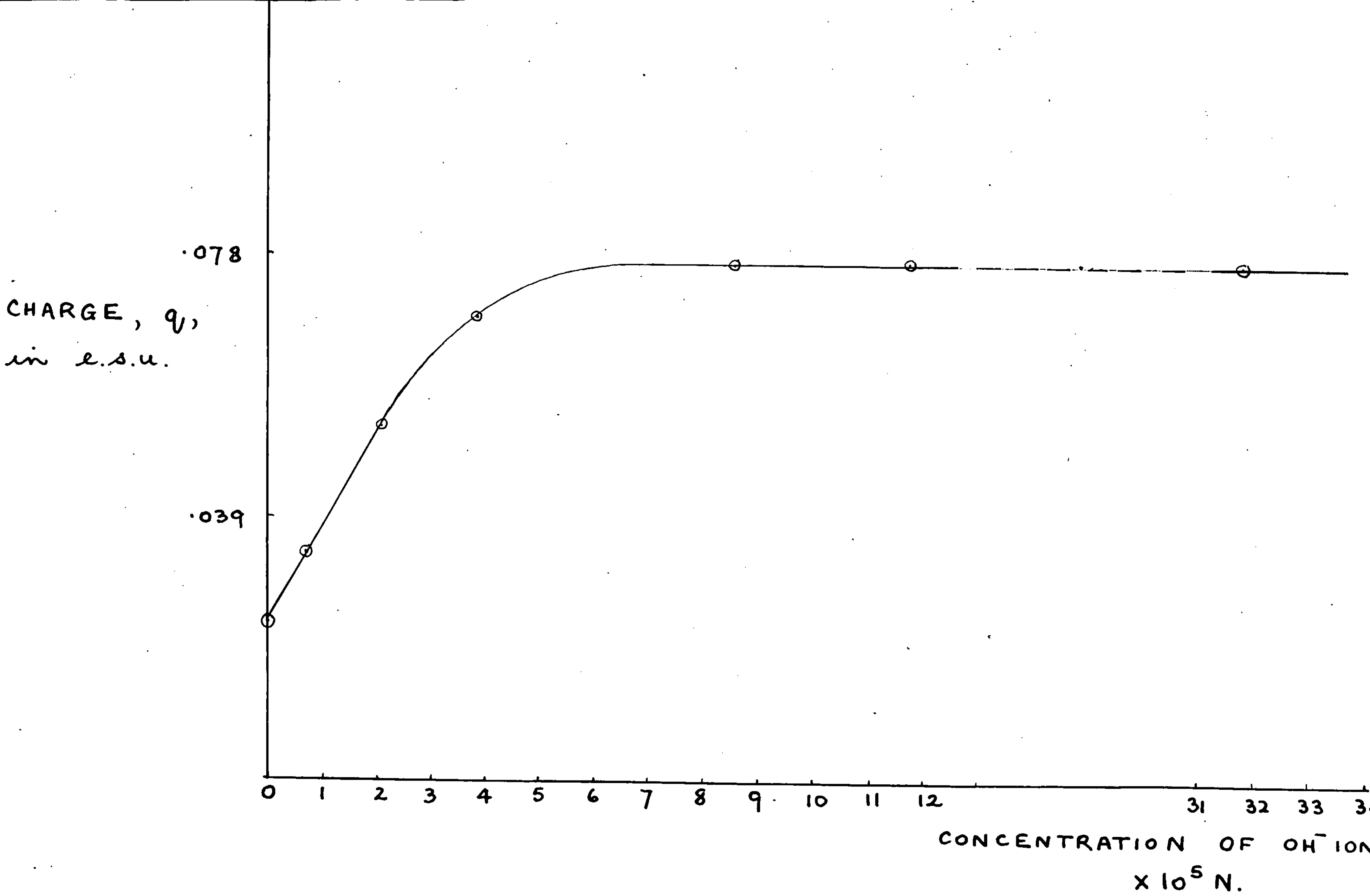

CHARGE, q, in e.s.u.
·08
·06
·04
·02
0
20
40
60
80
100
VOLTAGE GRADIENT in volts cm^{-1}


tan θ
·06804
·05670
·04536
·03402
·02268
·01134
0
50
100
150
200
VOLTAGE GRADIENT volts cm^{-1}

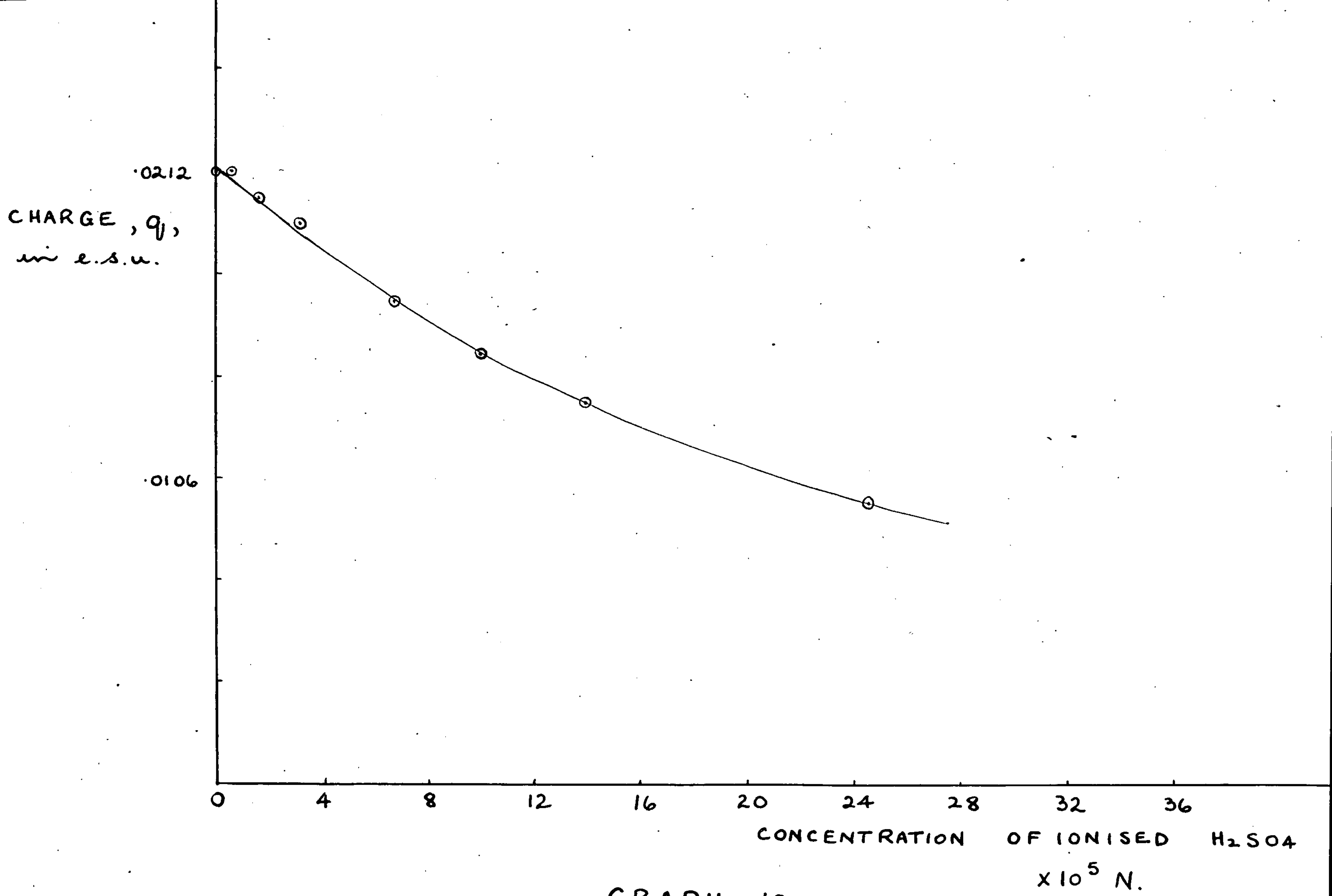
GRAPH. 7.


CHARGE, q, in e.s.u.
·10
·08
·06
·04
·02
0
20
40
60
80
100
120
140
160
VOLTAGE GRADIENT volts cm^{-1}

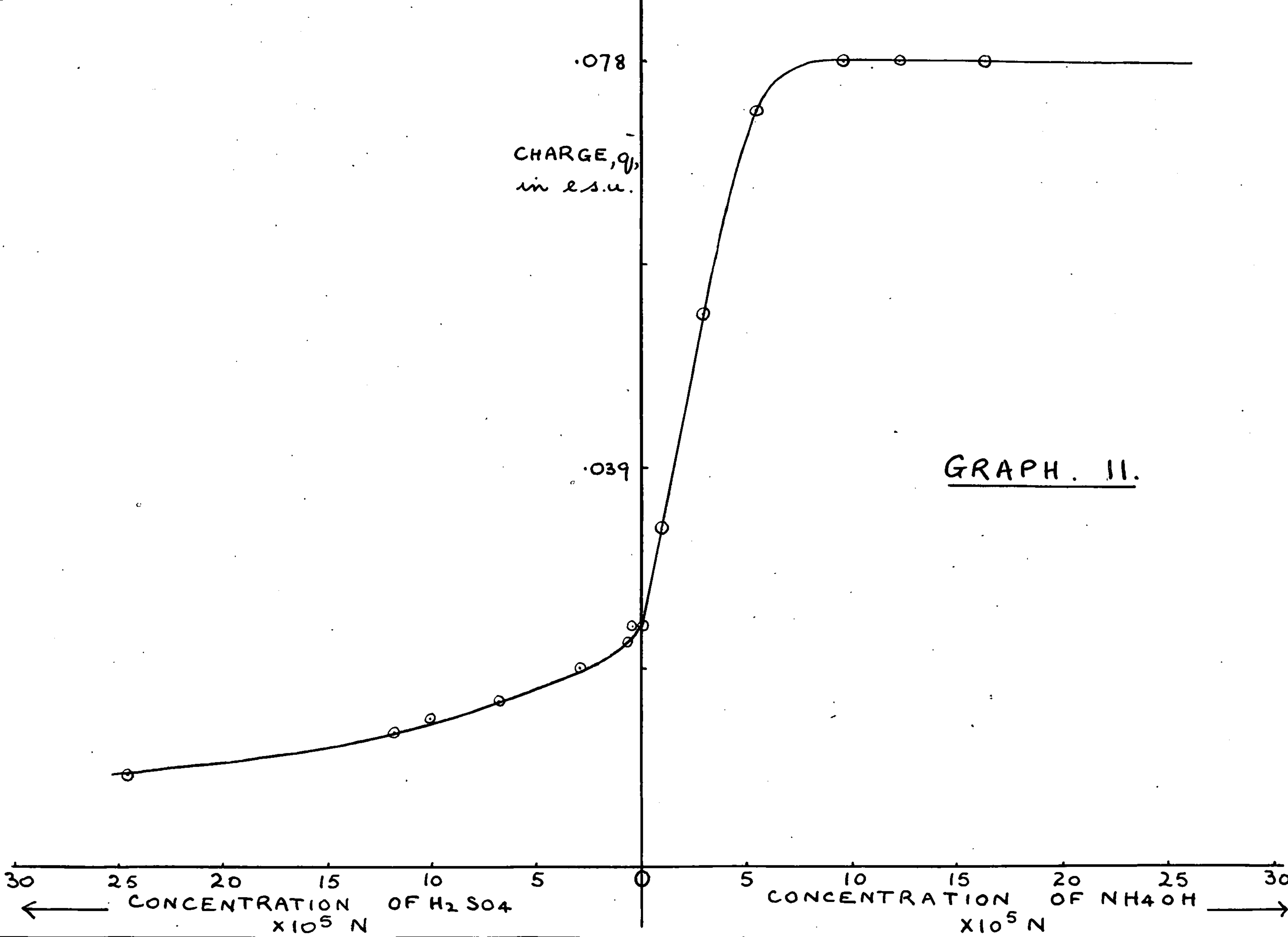
GRAPH. 8.

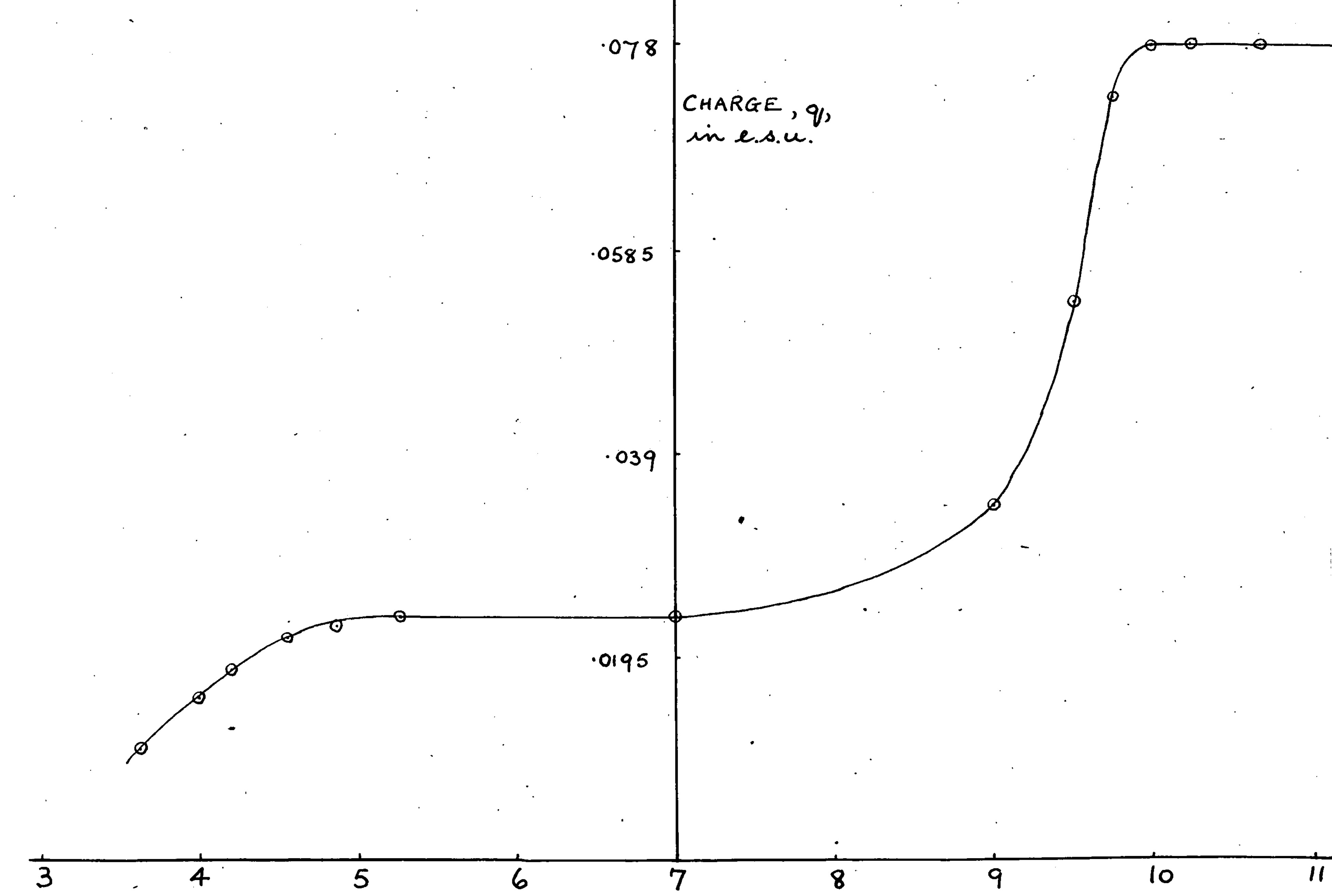

·078
·039
CHARGE, q,
in e.s.u.
0
1
2
3
4
5
6
7
8
9
10
11
12
31
32
33
CONCENTRATION OF OH^- ION
$\times 10^5$ N.

GRAPH . 9.

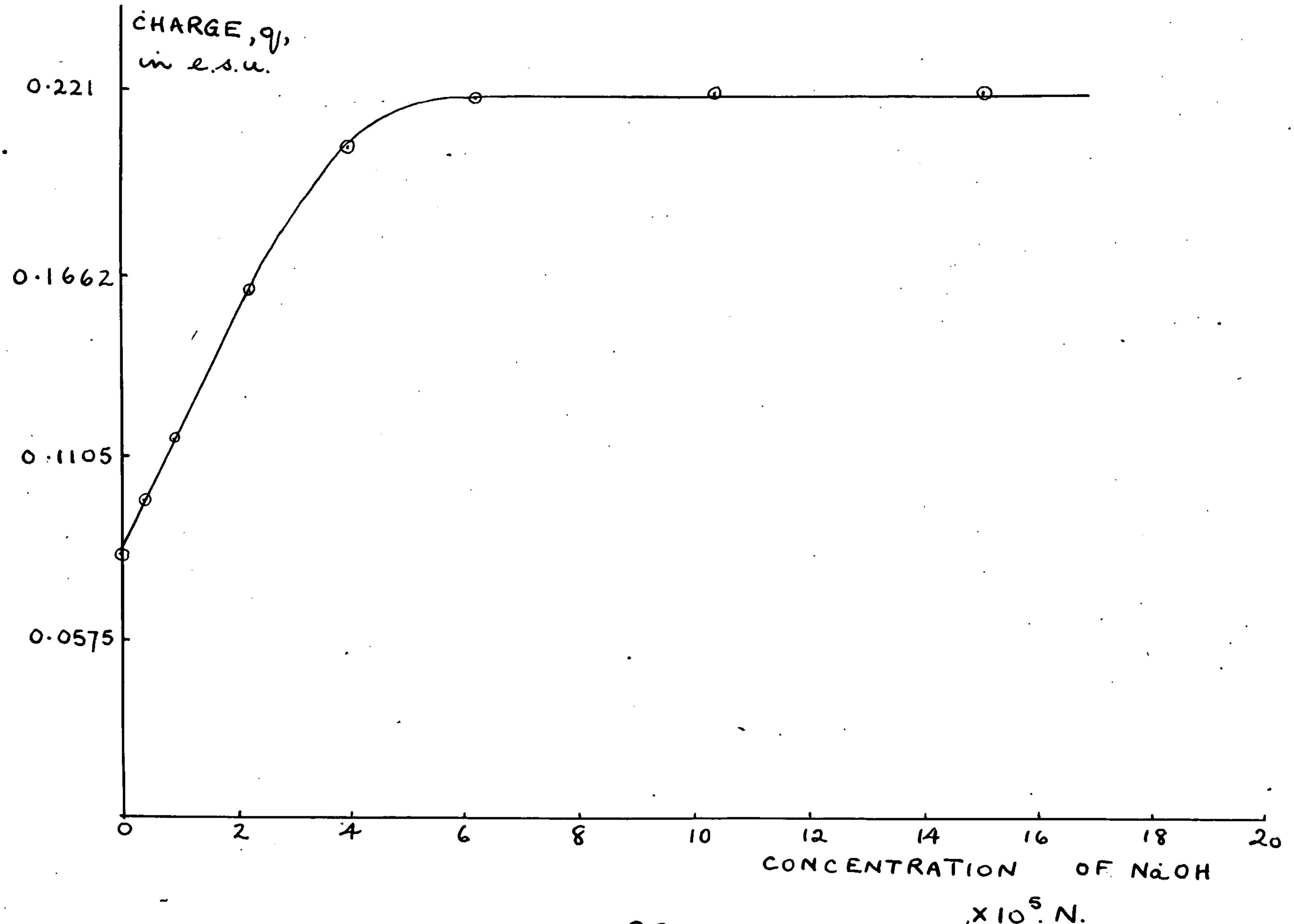

·0212
CHARGE, q, in e.s.u.
·0106
0
4
8
12
16
20
24
28
32
36
CONCENTRATION OF IONISED H_2SO_4 $\times 10^5$ N.

GRAPH . 10.

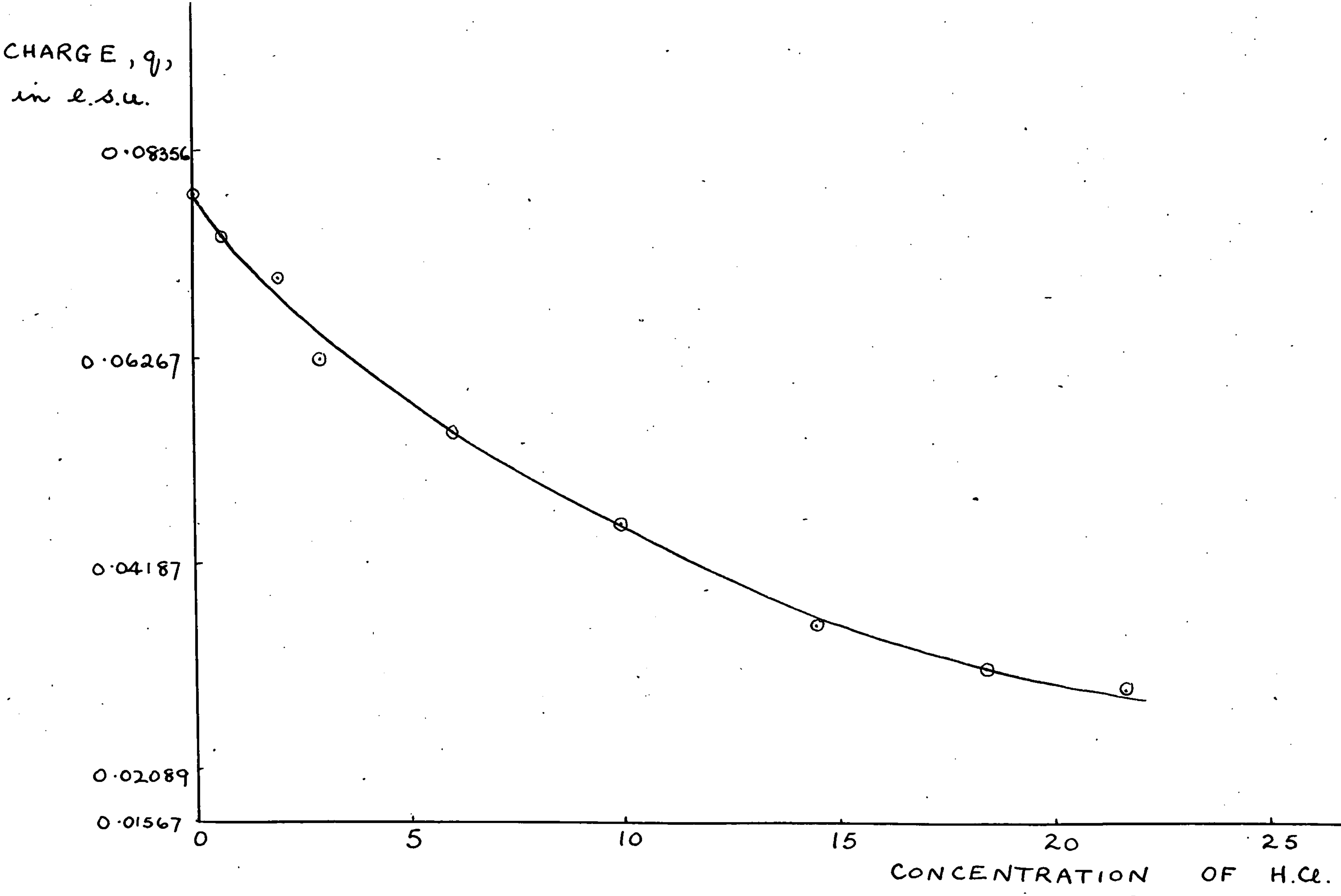

GRAPH. II.
.078
CHARGE, q, in e.s.u.
.039
30
25
20
15
10
5
0
5
10
15
20
25
30
CONCENTRATION OF H_2SO_4 ×10^5 N
CONCENTRATION OF NH4OH ×10^5 N



GRAPH. 12.

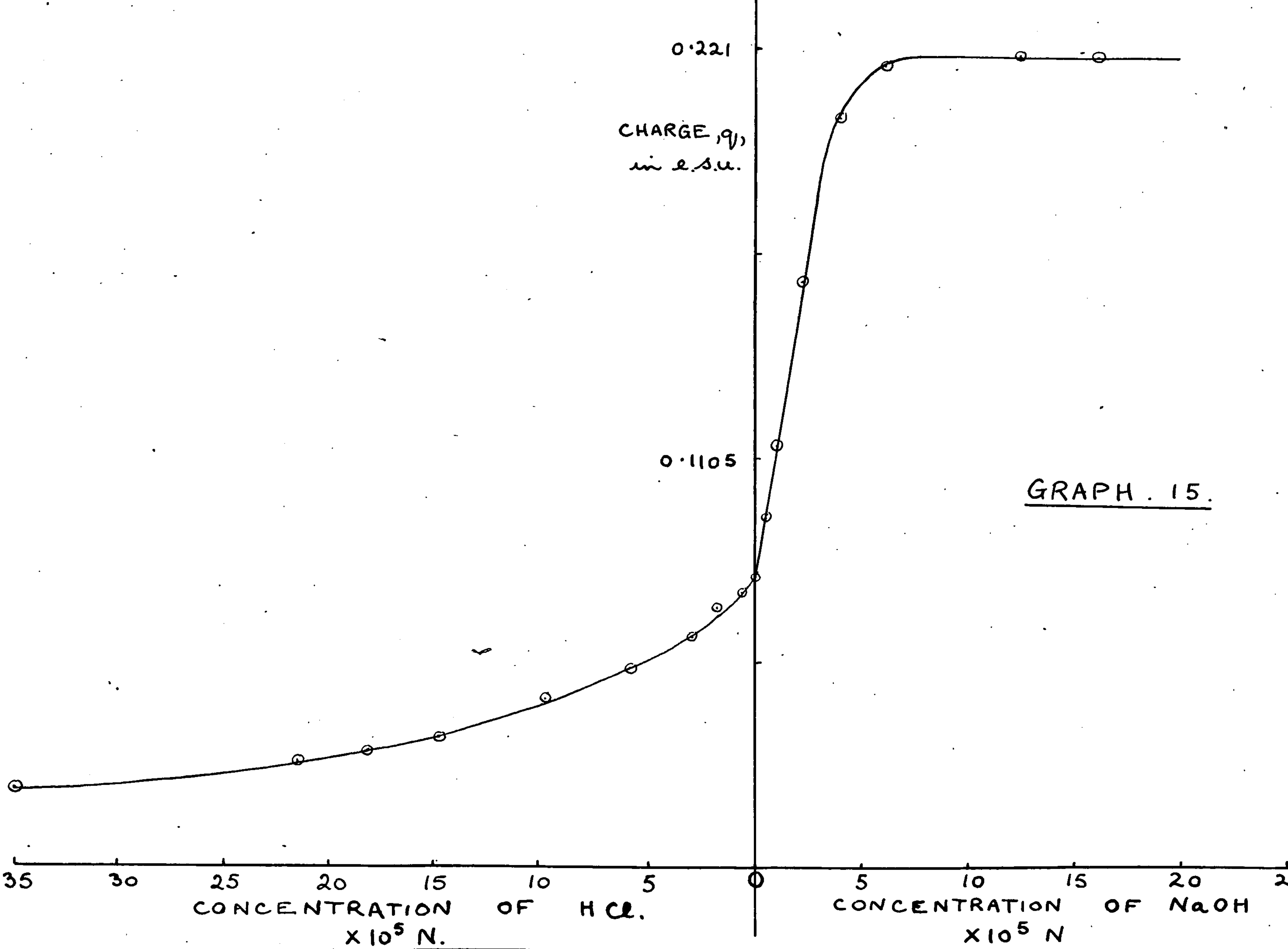

CHARGE, q, in e.s.u.
0·221
0·1662
0·1105
0·0575
0
2
4
6
8
10
12
14
16
18
20
CONCENTRATION OF NaOH ×10⁵ N.

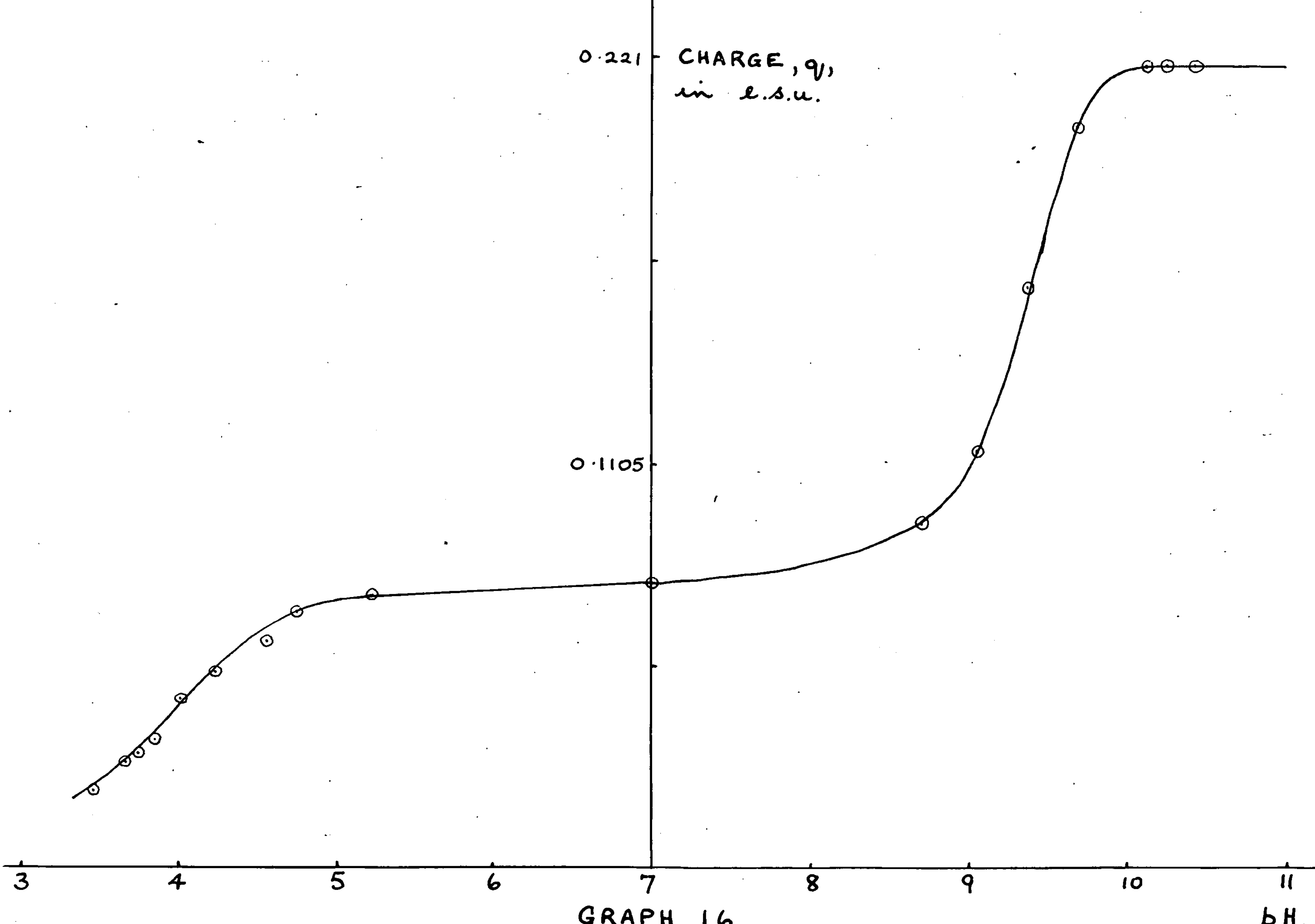
GRAPH. 13.


CHARGE, q,
in e.s.u.
0·08356
0·06267
0·04187
0·02089
0·01567
0
5
10
15
20
25
CONCENTRATION OF H.Cl.
X10^5 N.

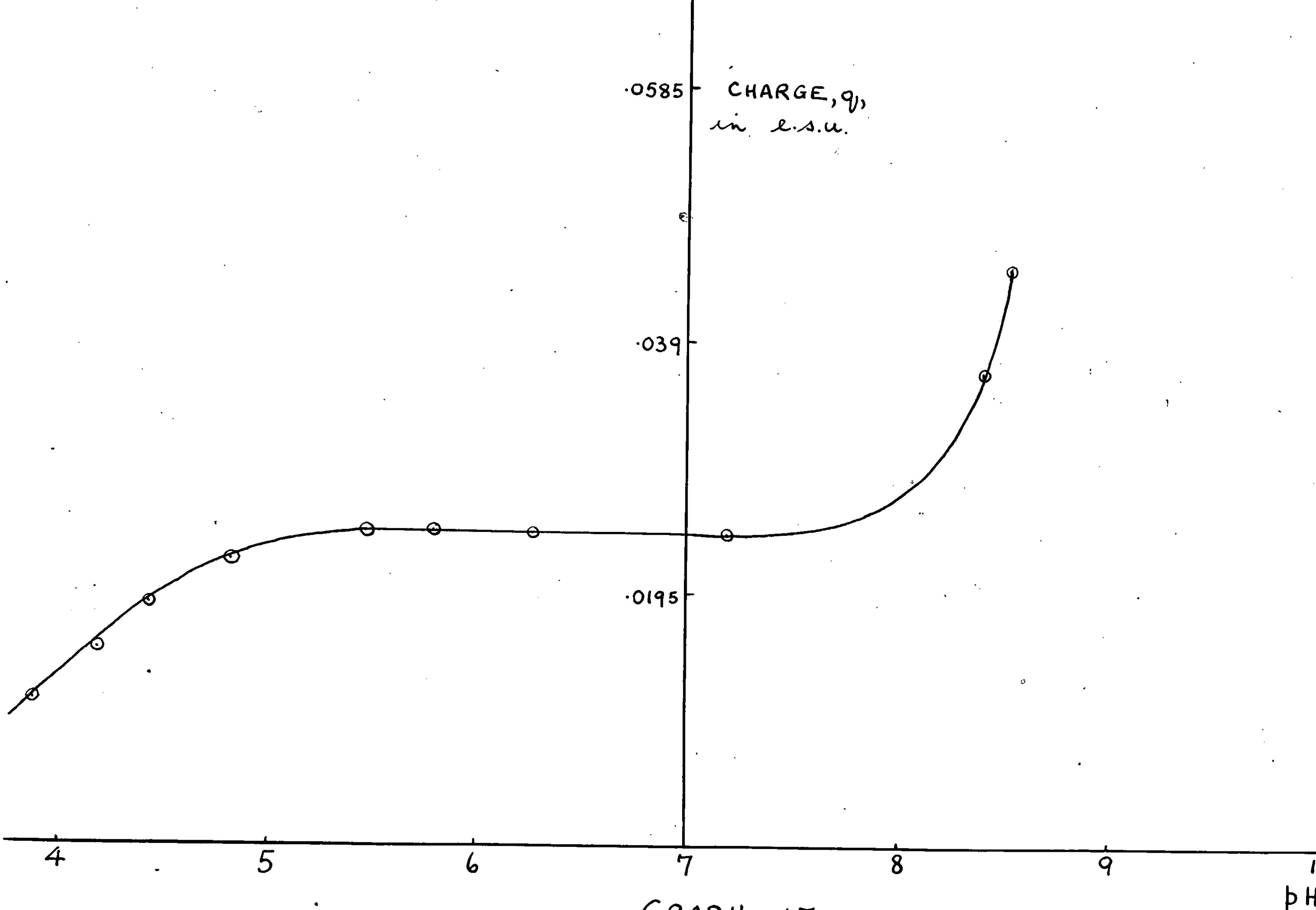
GRAPH 14

GRAPH. 15.

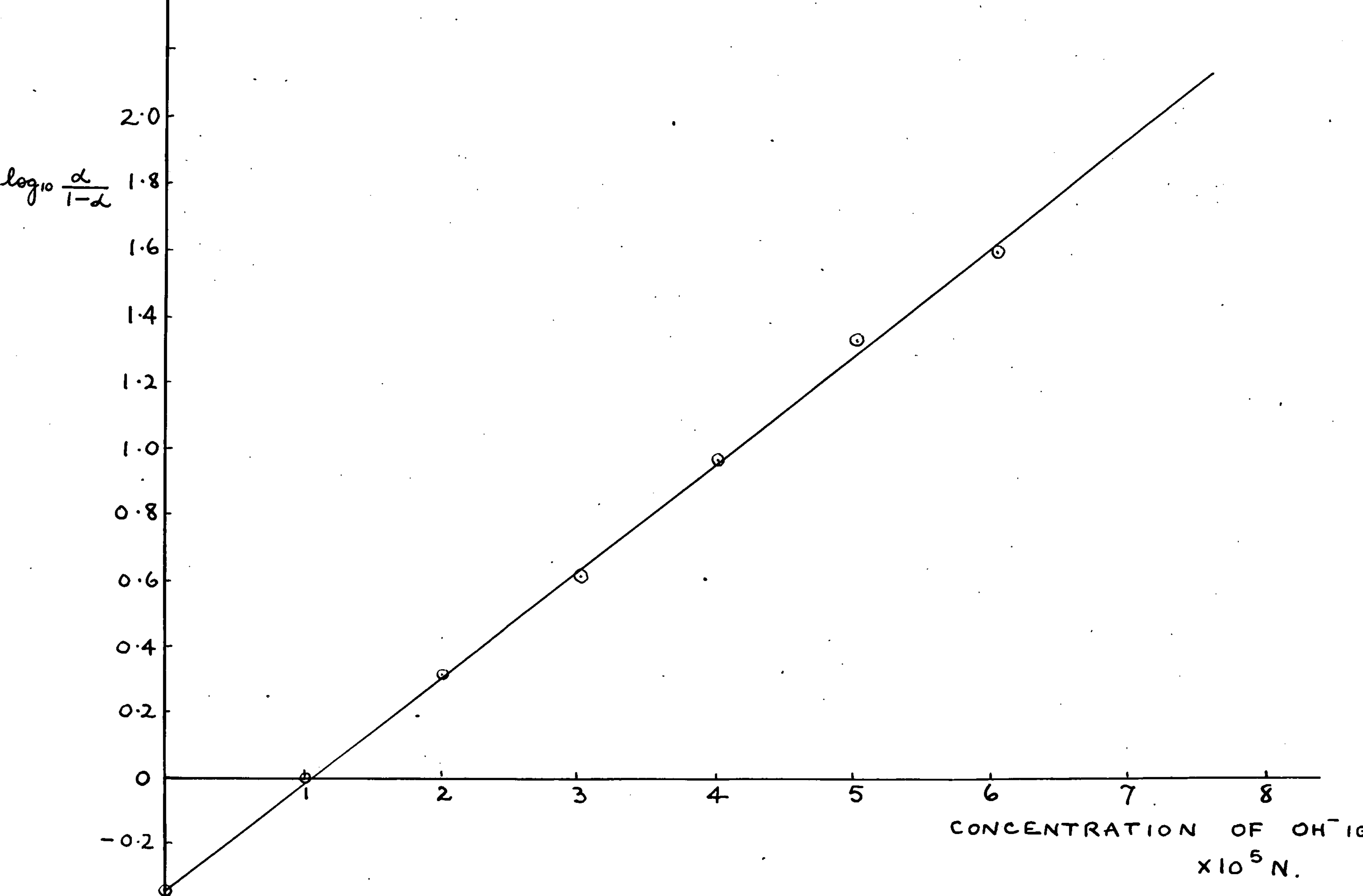

0·221
CHARGE, q, in e.s.u.
0·1105
35
30
25
20
15
10
5
0
5
10
15
20
CONCENTRATION OF HCl. ×10⁵ N.
CONCENTRATION OF NaOH ×10⁵ N



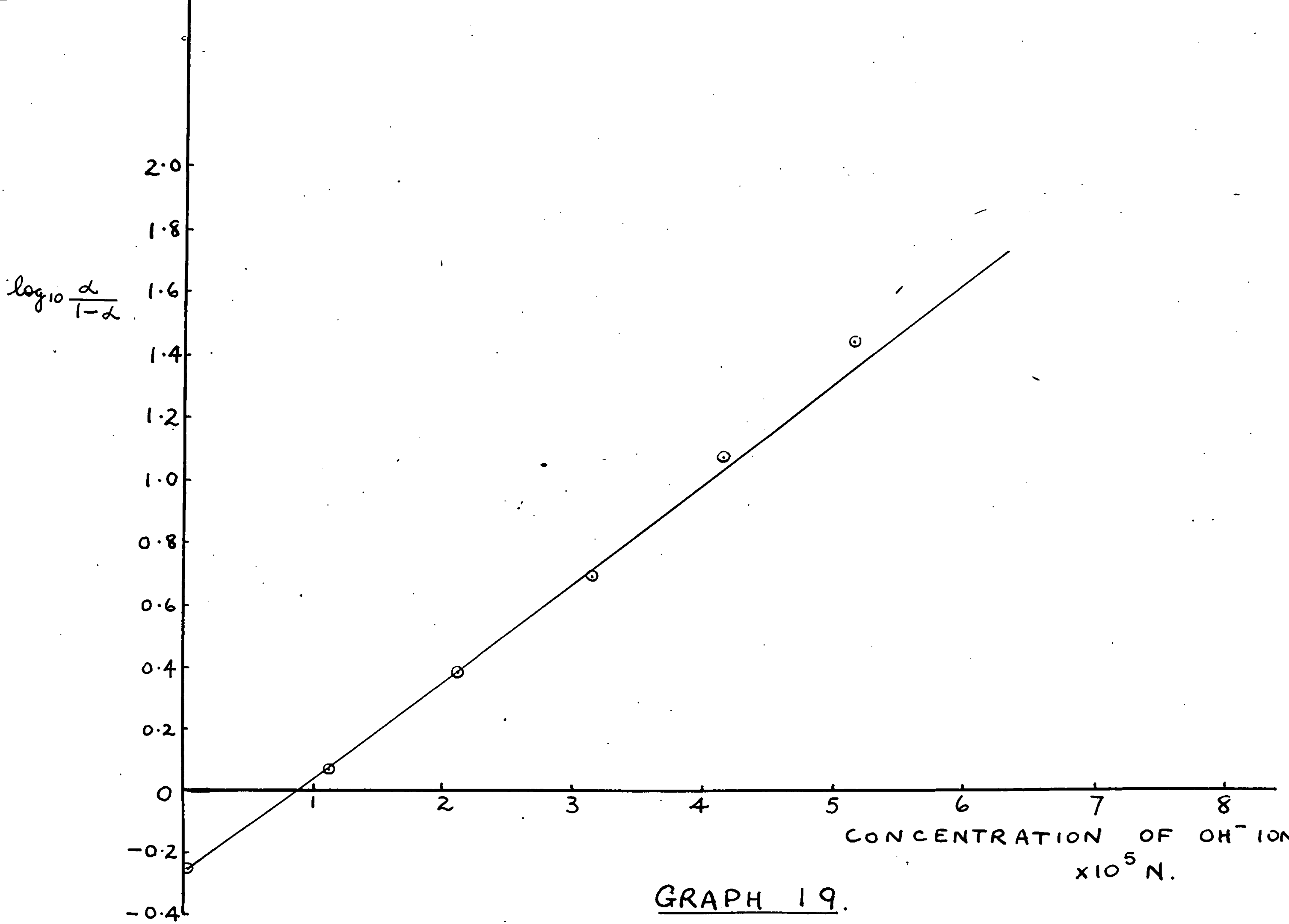
GRAPH 16.



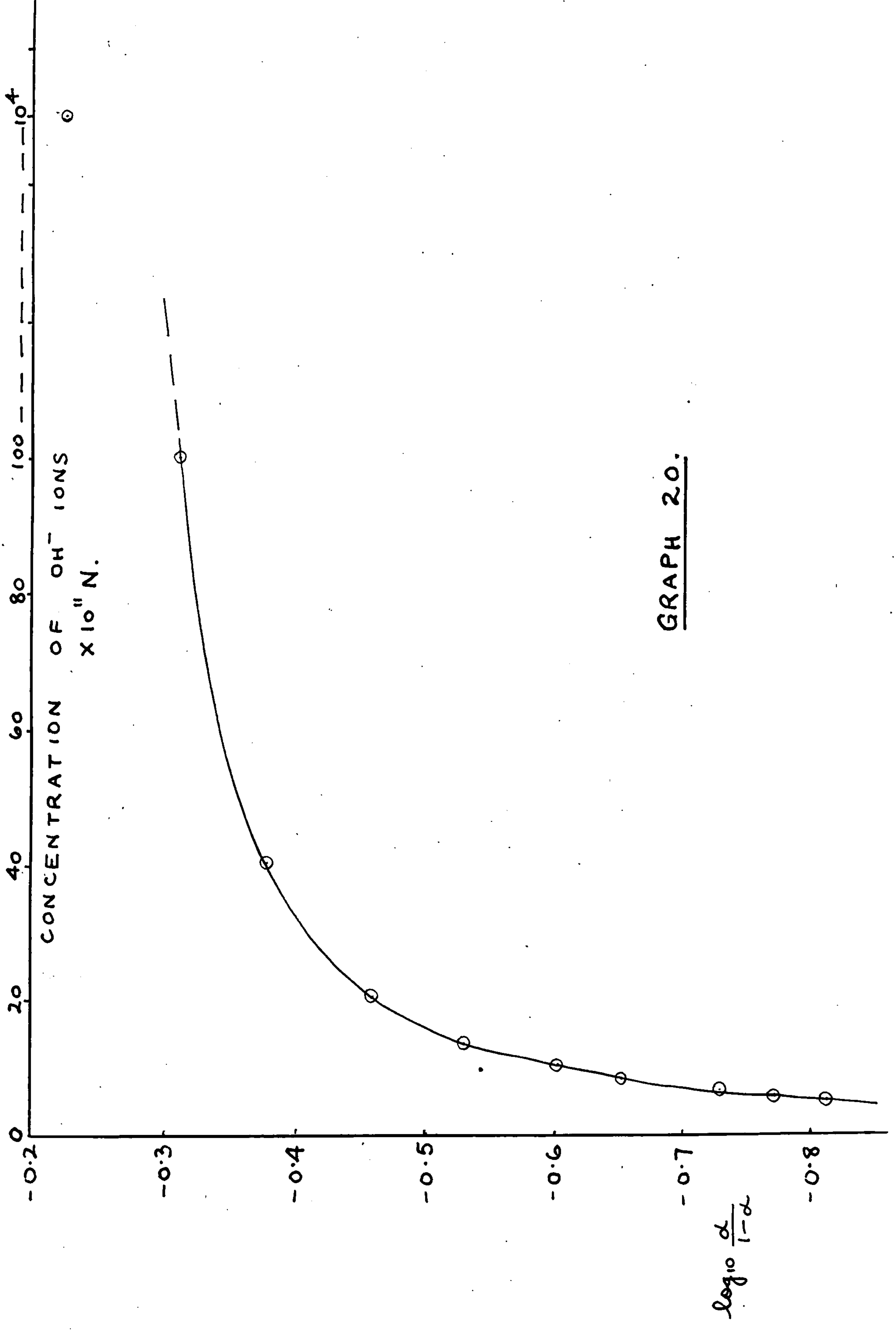
GRAPH 17.


$\log_{10} \frac{\alpha}{1-\alpha}$
2·0
1·8
1·6
1·4
1·2
1·0
0·8
0·6
0·4
0·2
0
−0·2
−0·4
1
2
3
4
5
6
7
8
CONCENTRATION OF OH^- IO
$\times 10^5$ N.

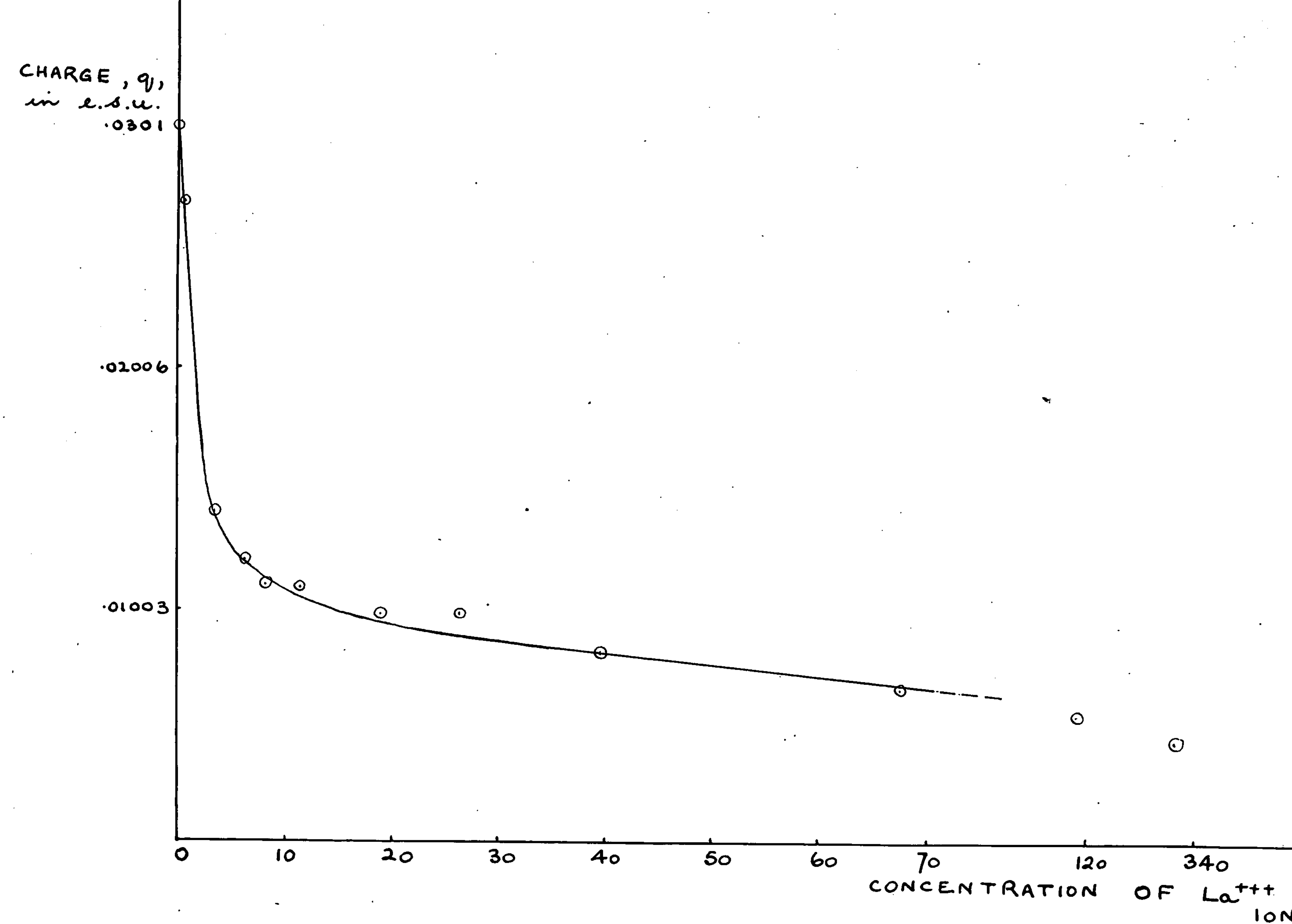
GRAPH 18


$\log_{10}\frac{\alpha}{1-\alpha}$
2·0
1·8
1·6
1·4
1·2
1·0
0·8
0·6
0·4
0·2
0
−0·2
−0·4
1
2
3
4
5
6
7
8
CONCENTRATION OF OH^- ION
$\times 10^5$ N.

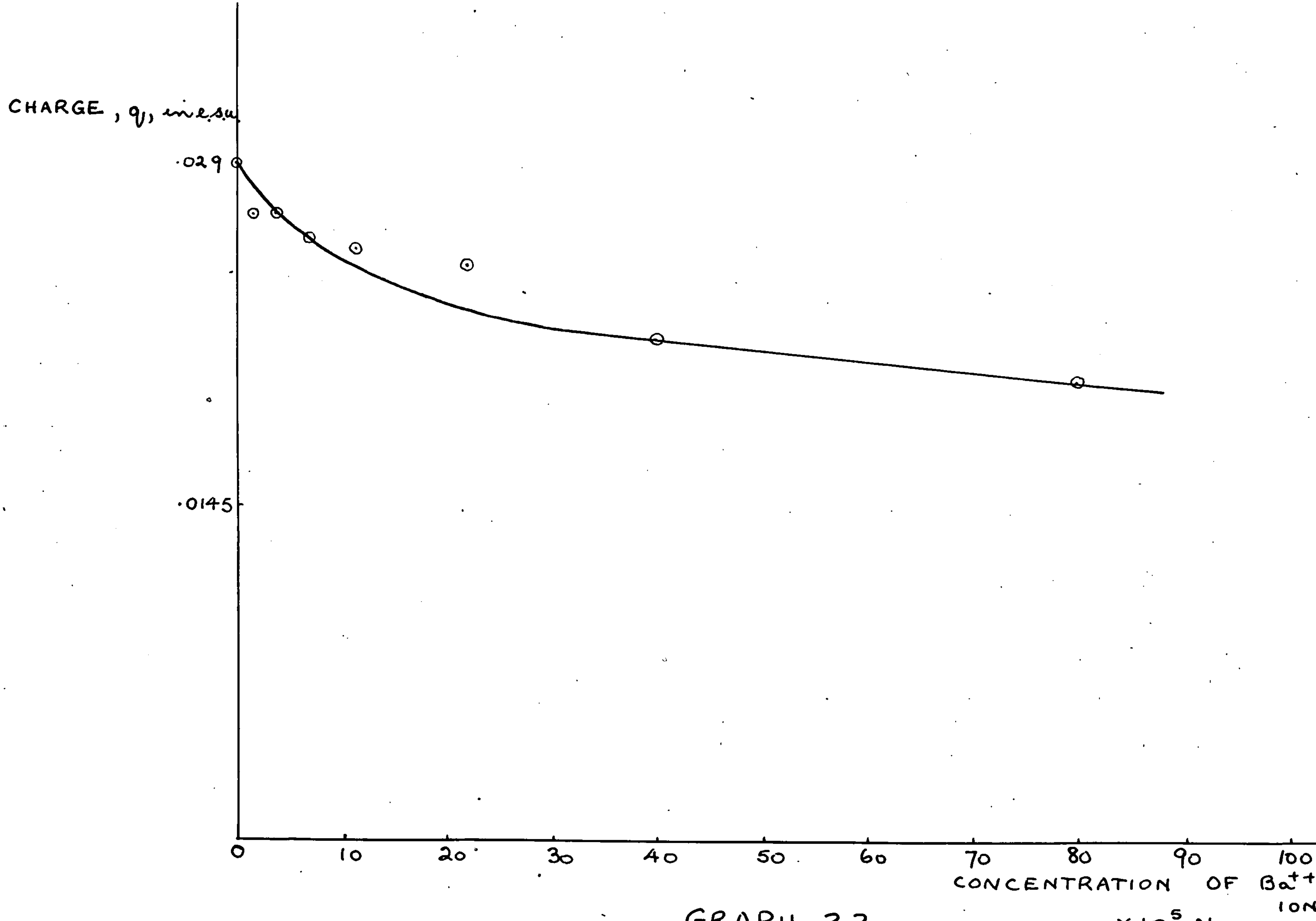
GRAPH 19.


CONCENTRATION OF OH⁻ IONS
× 10¹¹ N.
0
20
40
60
80
100
10⁴
-0·2
-0·3
-0·4
-0·5
-0·6
-0·7
-0·8
log₁₀ α/(1-α)

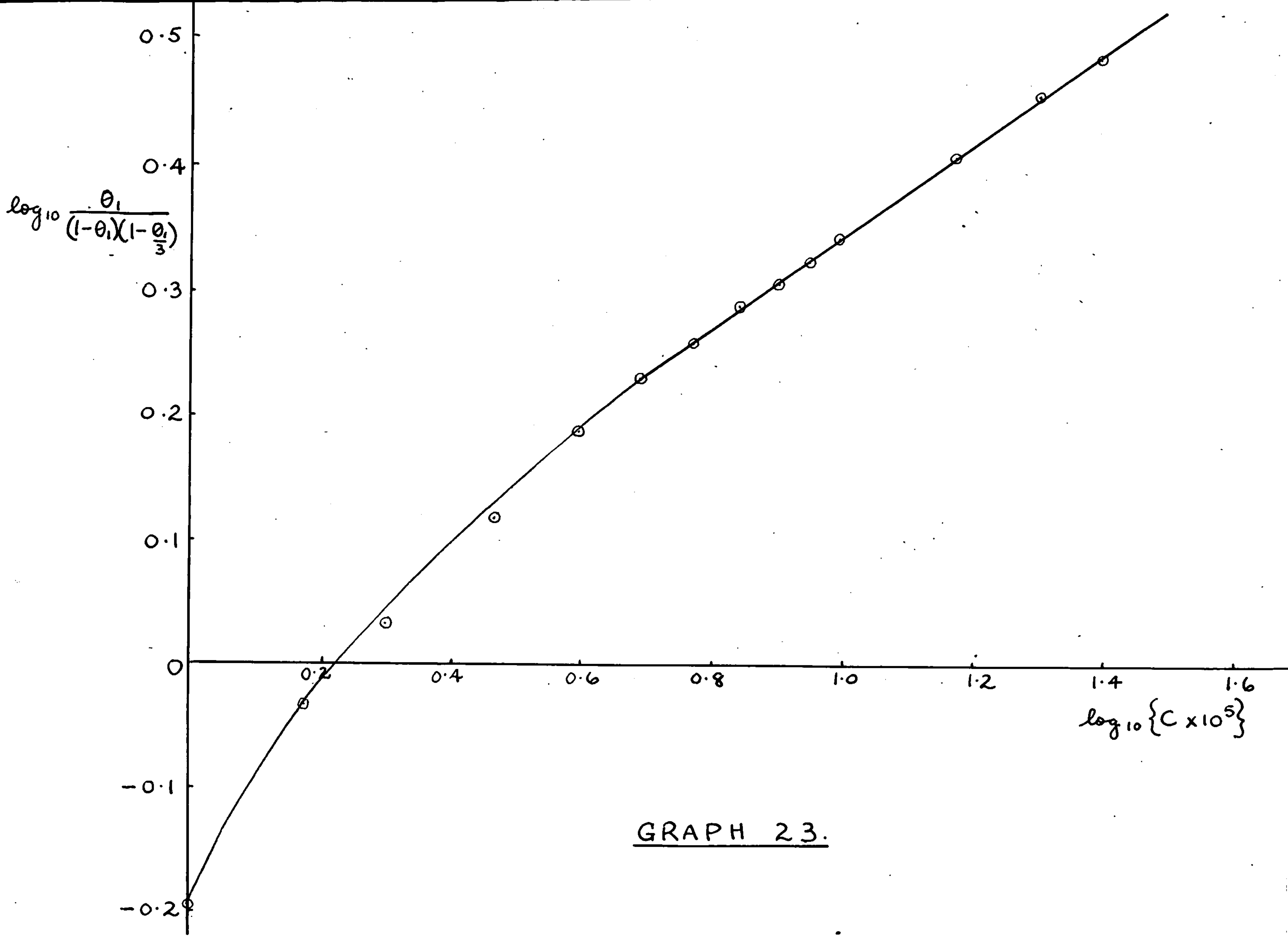
GRAPH 20.


CHARGE, q, in e.s.u.
·0301
·02006
·01003
0
10
20
30
40
50
60
70
120
340
CONCENTRATION OF La^{+++} ION
$\times 10^5$ N.

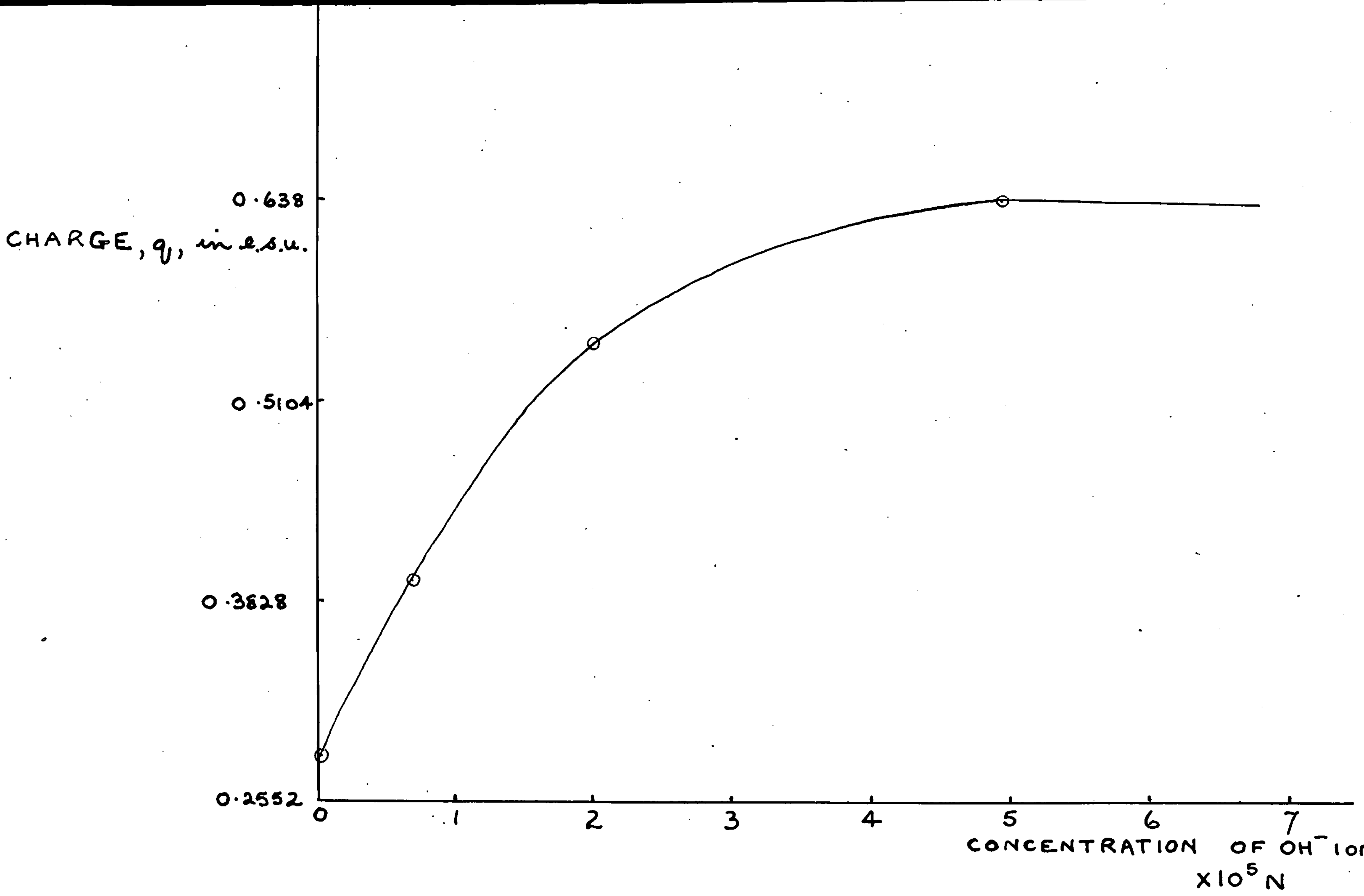
GRAPH 21


CHARGE, q, in e.s.u.
·029
·0145
0
10
20
30
40
50
60
70
80
90
100
CONCENTRATION OF Ba++ ION
×10⁵ N.

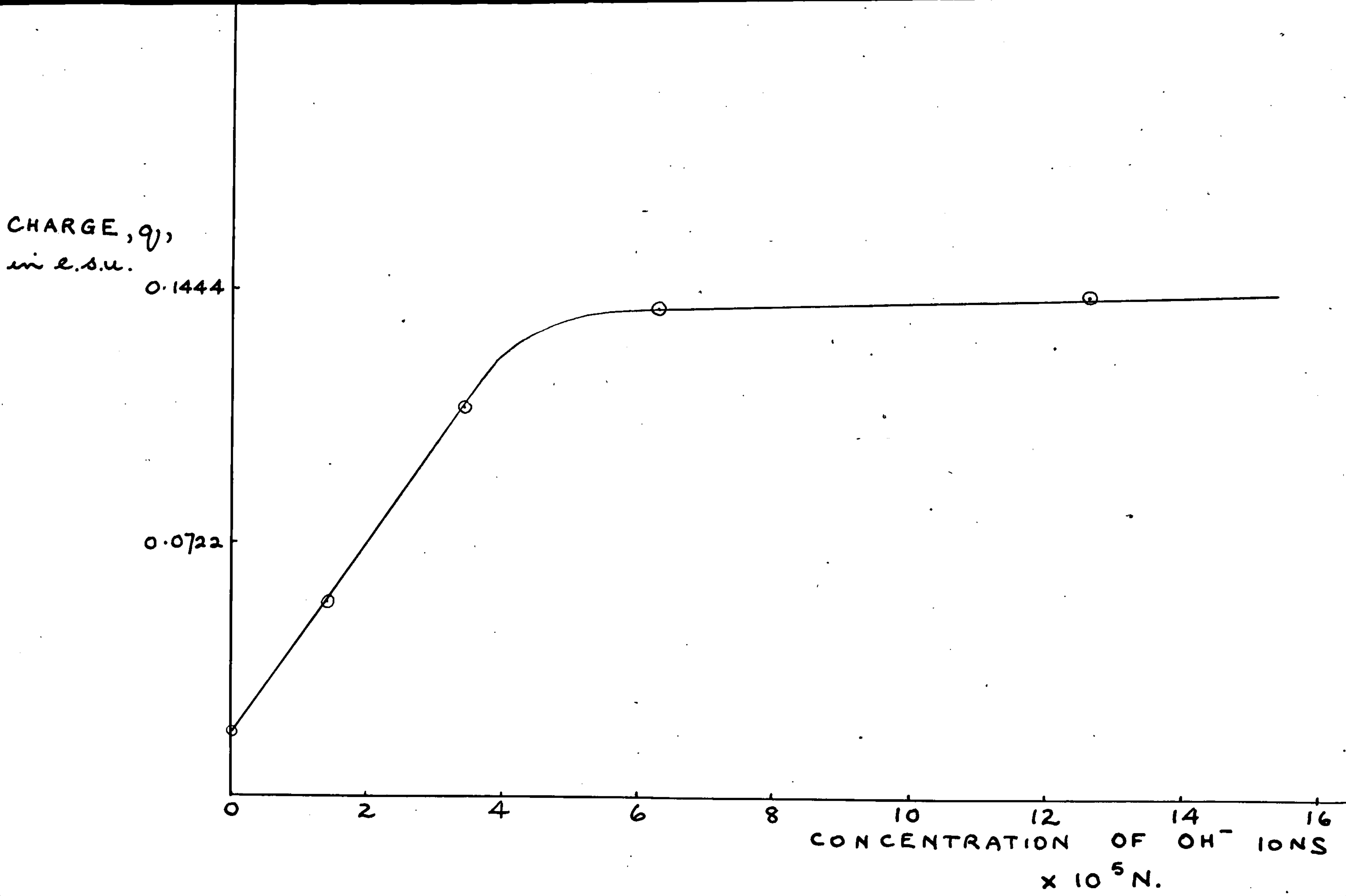
GRAPH. 22.


0·5
0·4
0·3
0·2
0·1
0
-0·1
-0·2
$\log_{10} \frac{\theta_1}{(1-\theta_1)(1-\frac{\theta_1}{3})}$
0·2
0·4
0·6
0·8
1·0
1·2
1·4
1·6
$\log_{10}\{C \times 10^5\}$

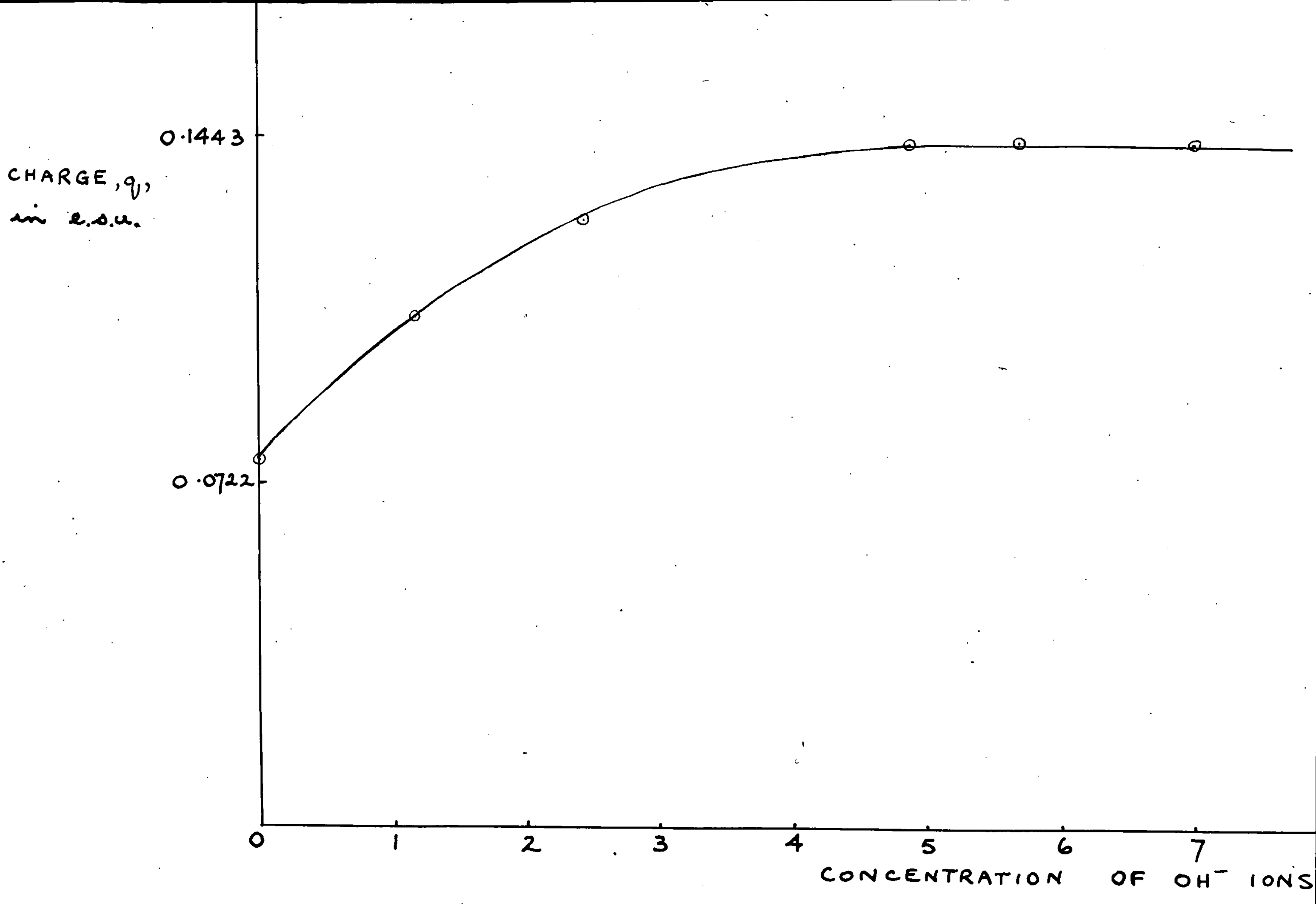
GRAPH 23.


CHARGE, q, in e.s.u.
0·638
0·5104
0·3828
0·2552
0
1
2
3
4
5
6
7
CONCENTRATION OF OH^- IO
$\times 10^5$ N

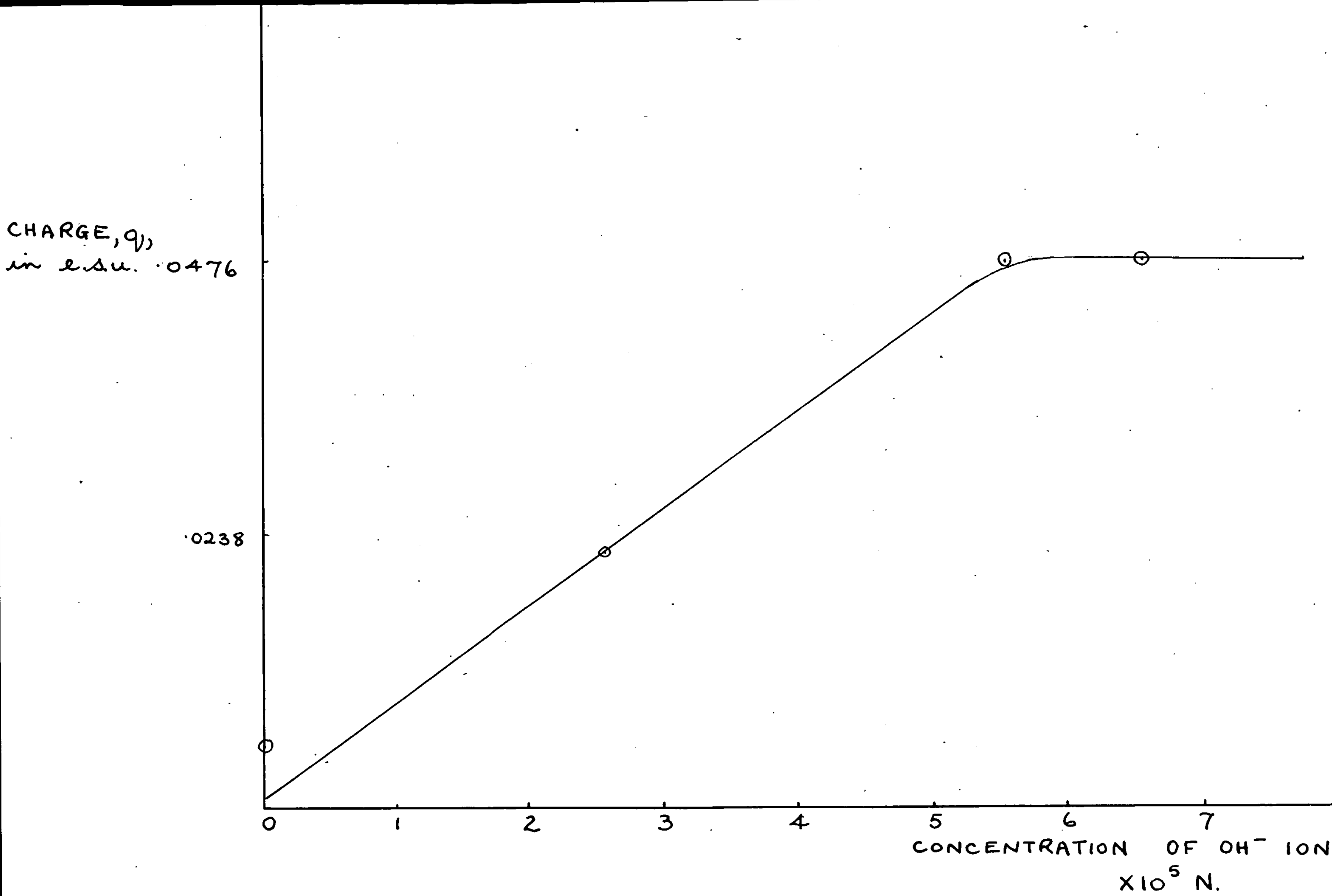
GRAPH 24.


CHARGE, q, in e.s.u.
0·1444
0·0722
0
2
4
6
8
10
12
14
16
CONCENTRATION OF OH⁻ IONS × 10⁵ N.

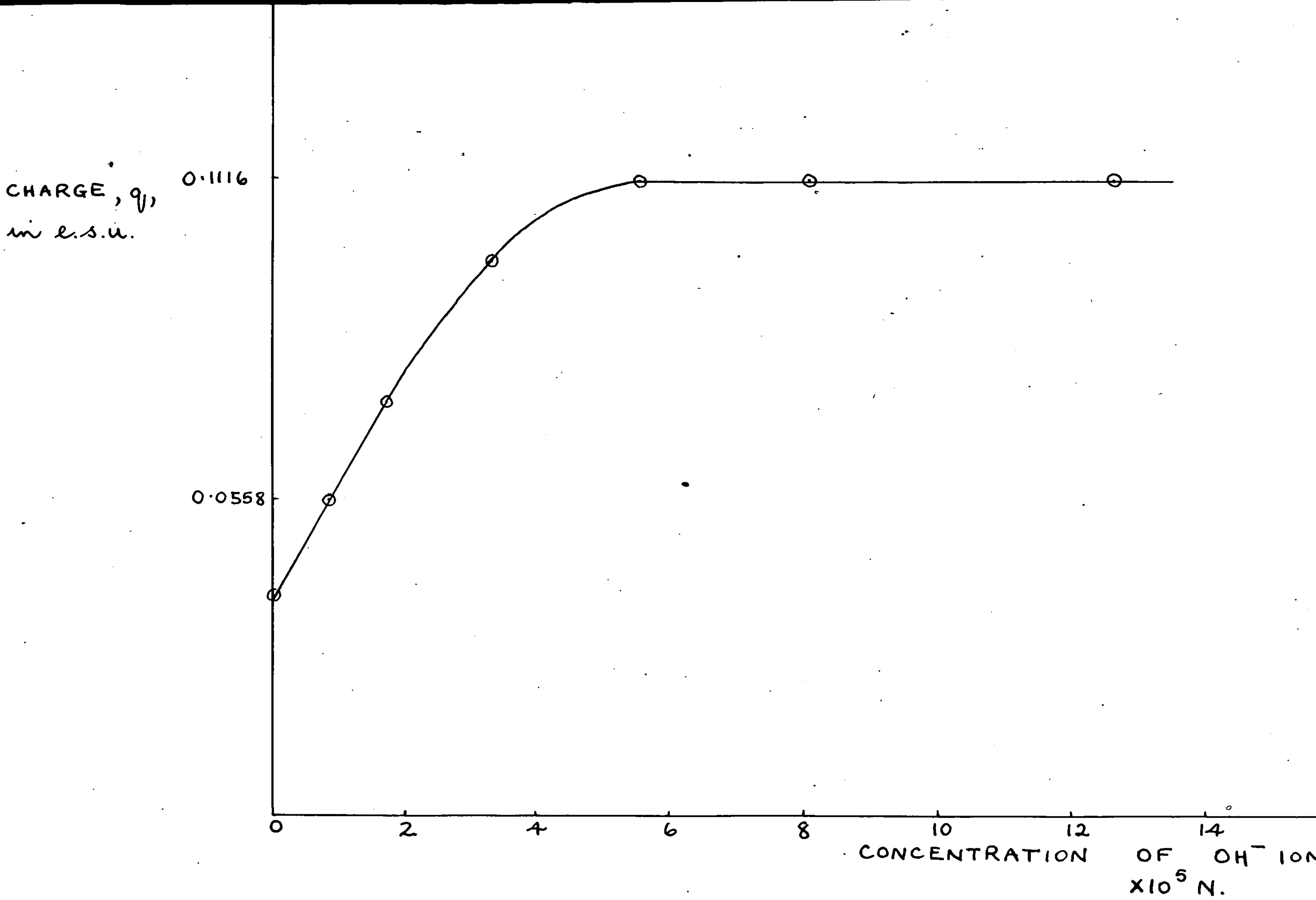
GRAPH 25.

0·1443
0·0722
CHARGE, q, in e.s.u.
0
1
2
3
4
5
6
7
CONCENTRATION OF OH⁻ IONS ×10⁵ N

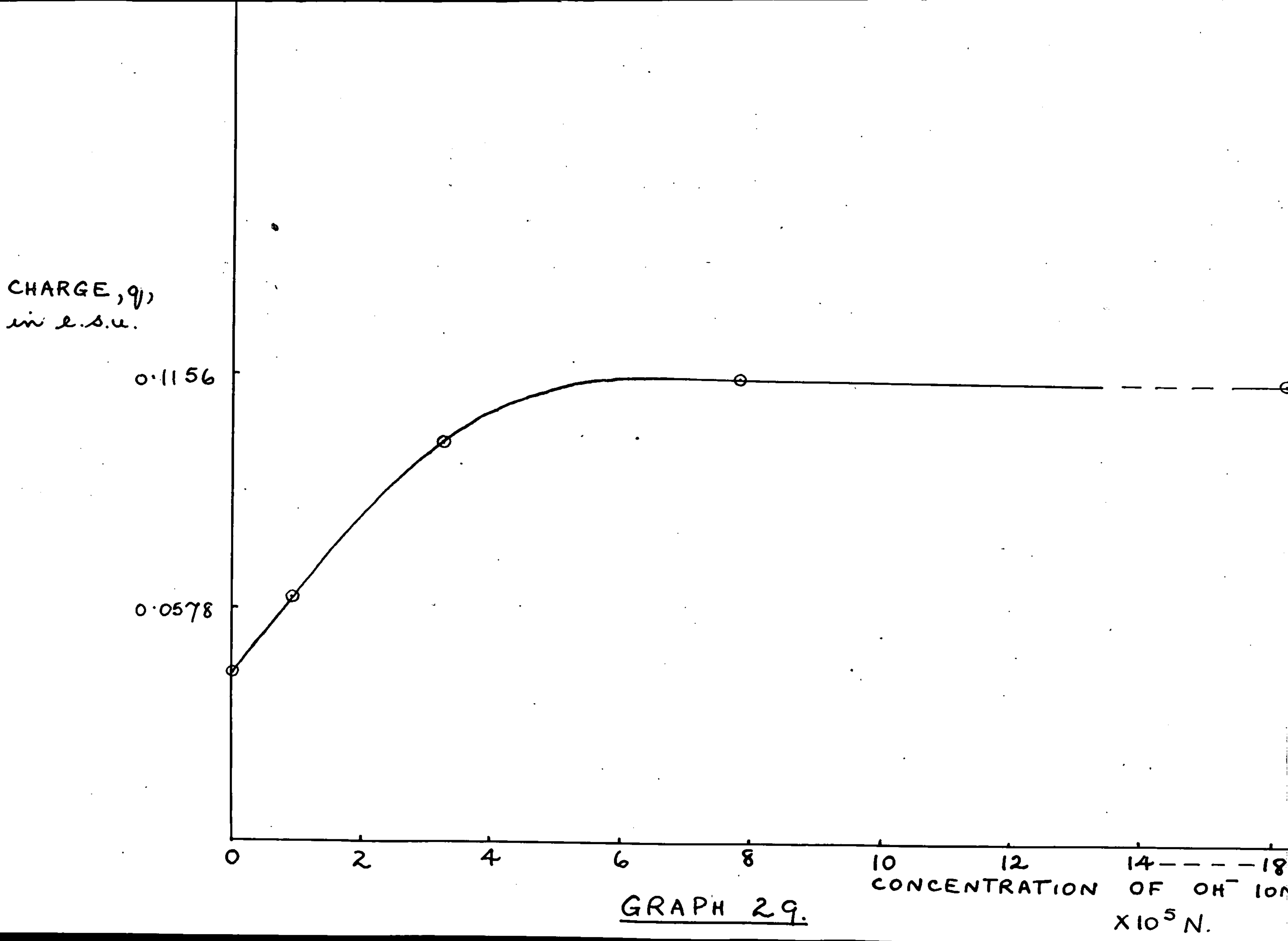
GRAPH 26.


CHARGE, q, in e.s.u.
·0476
·0238
0
1
2
3
4
5
6
7
CONCENTRATION OF OH⁻ ION ×10⁵ N.

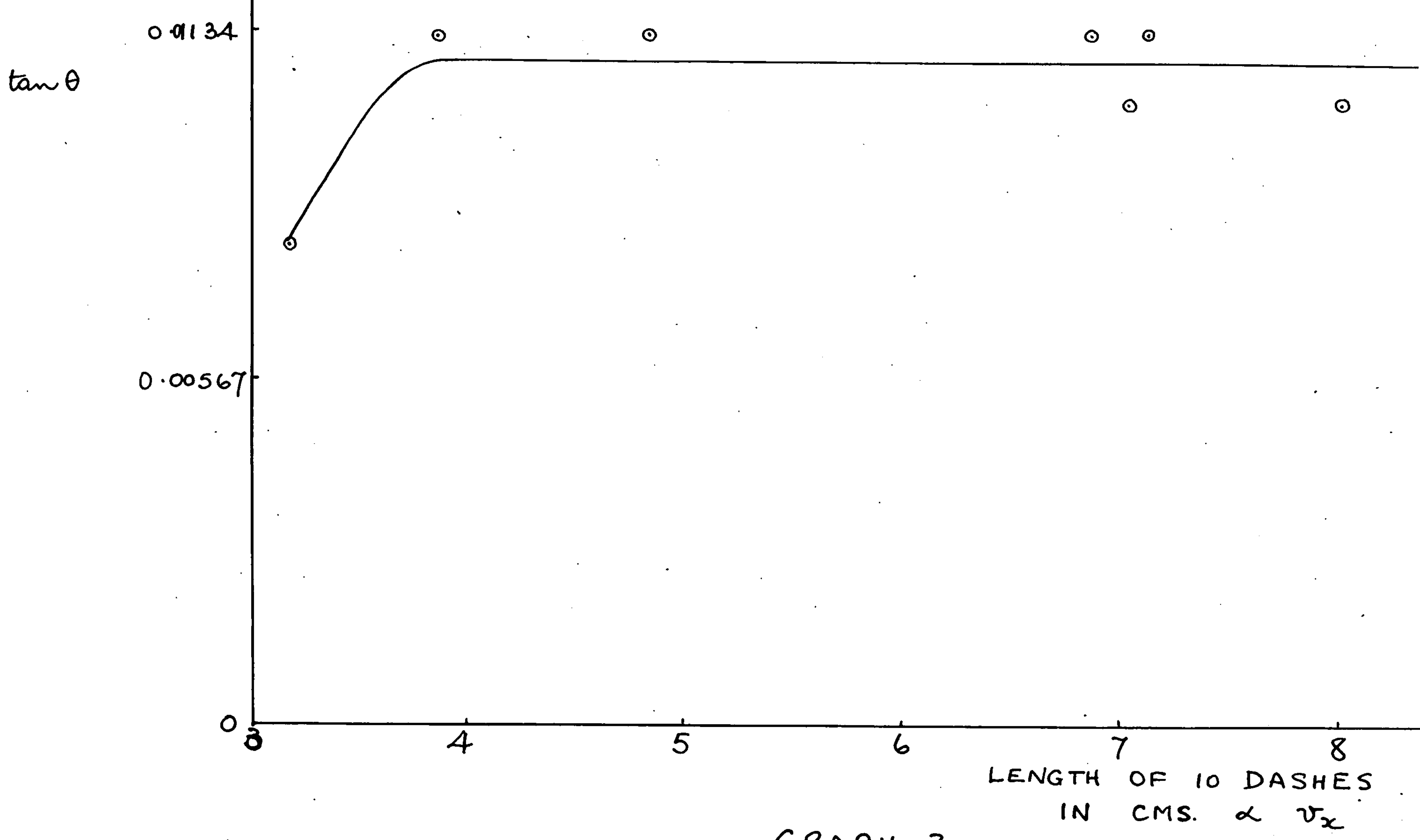
GRAPH 27.


CHARGE, q, in e.s.u.
0·1116
0·0558
0
2
4
6
8
10
12
14
CONCENTRATION OF OH^- IO
$\times 10^5$ N.

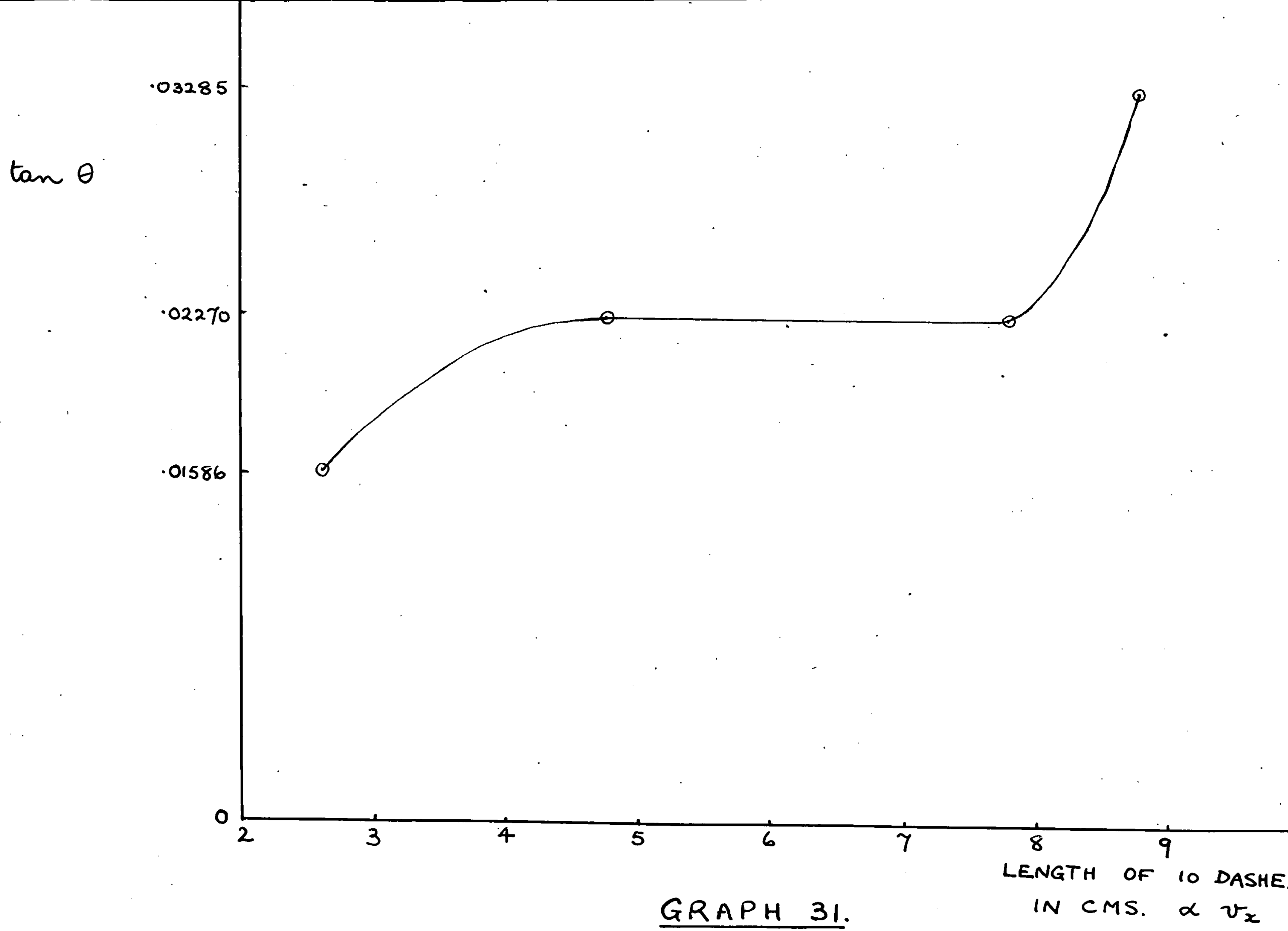
GRAPH 28.


CHARGE, q, in e.s.u.
0·1156
0·0578
0
2
4
6
8
10
12
14 - - - - 18
CONCENTRATION OF OH^- ION
$\times 10^5$ N.

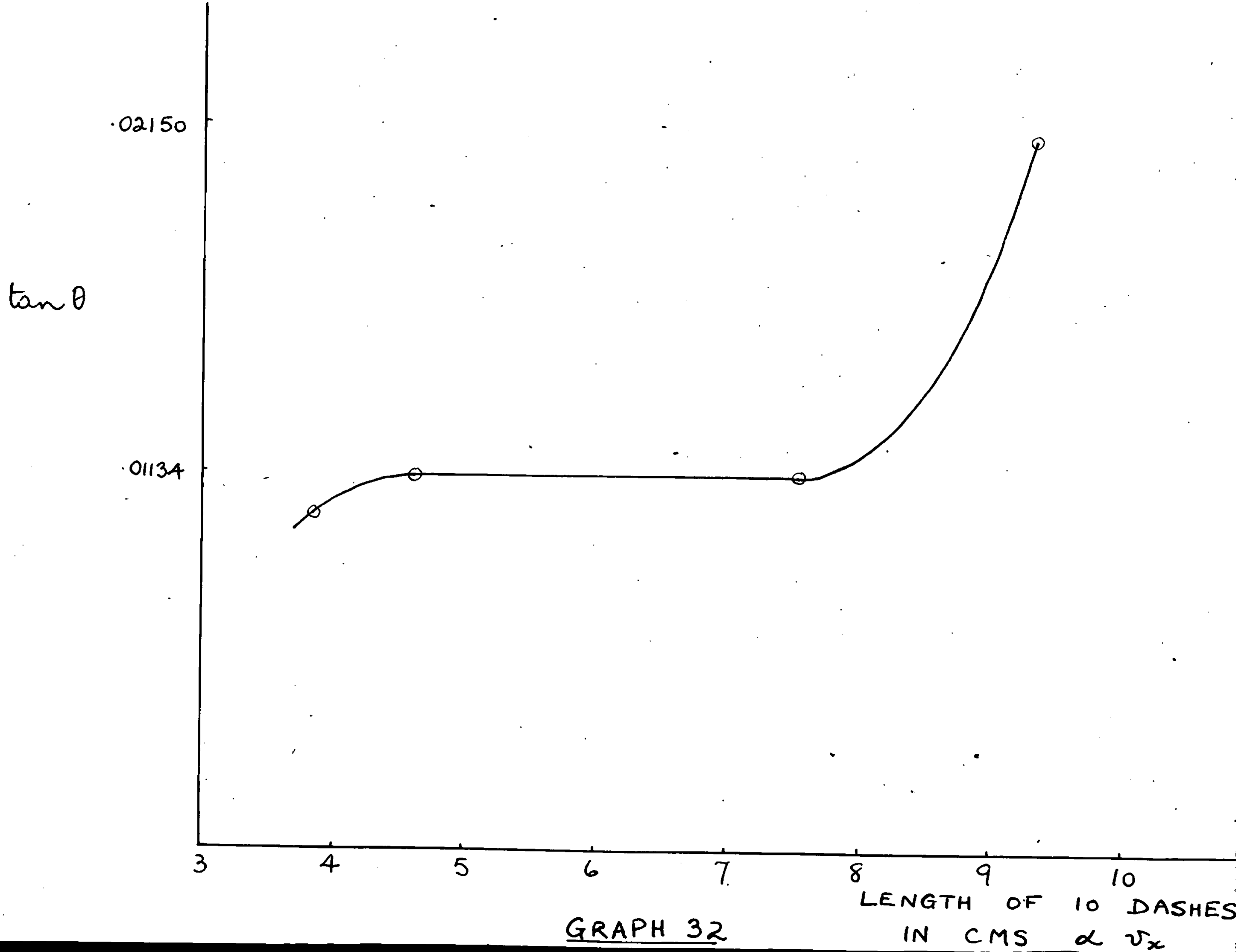
GRAPH 29.



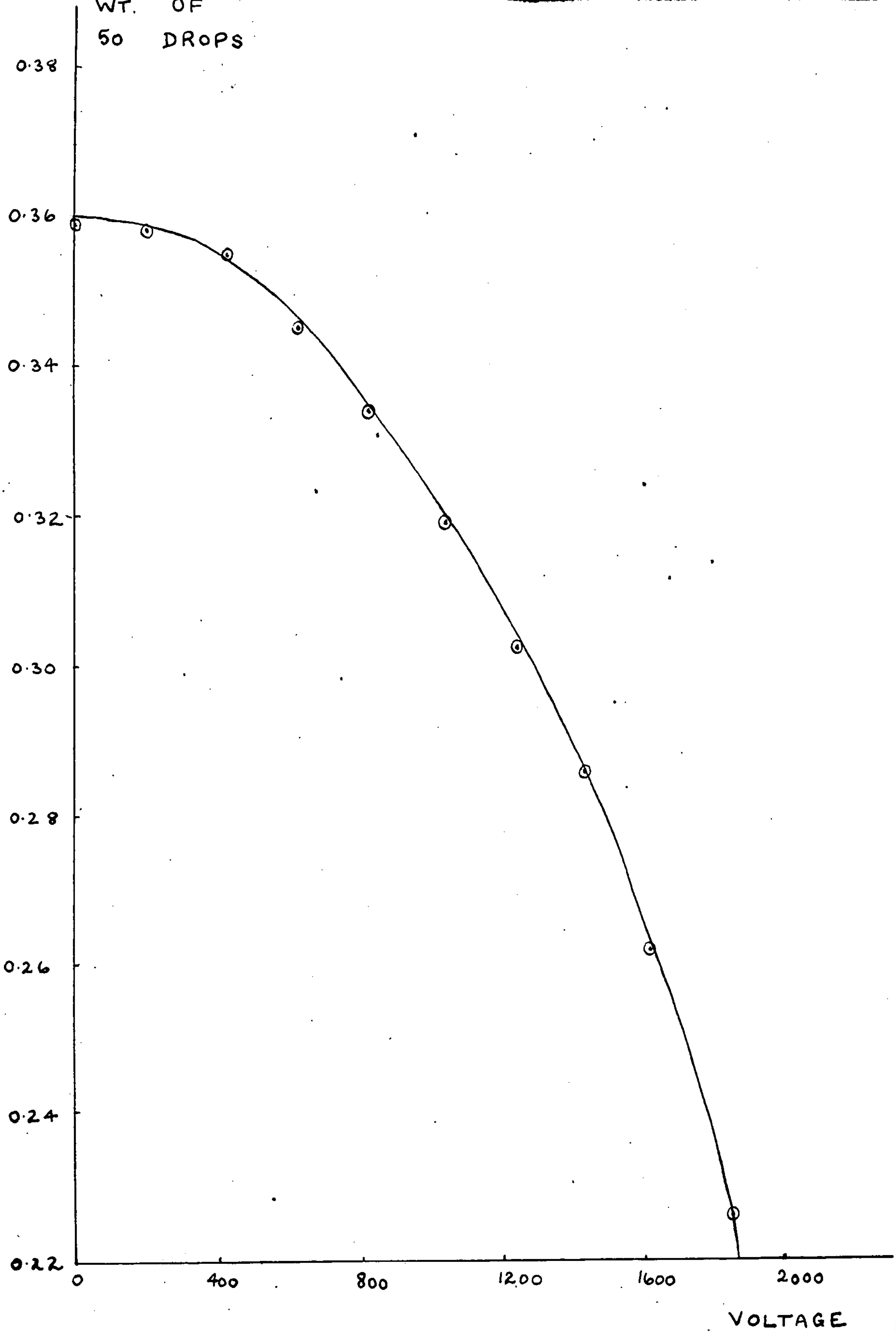
GRAPH 30.


tan θ
·03285
·02270
·01586
0
2
3
4
5
6
7
8
9
LENGTH OF 10 DASHE
IN CMS. ∝ v_x

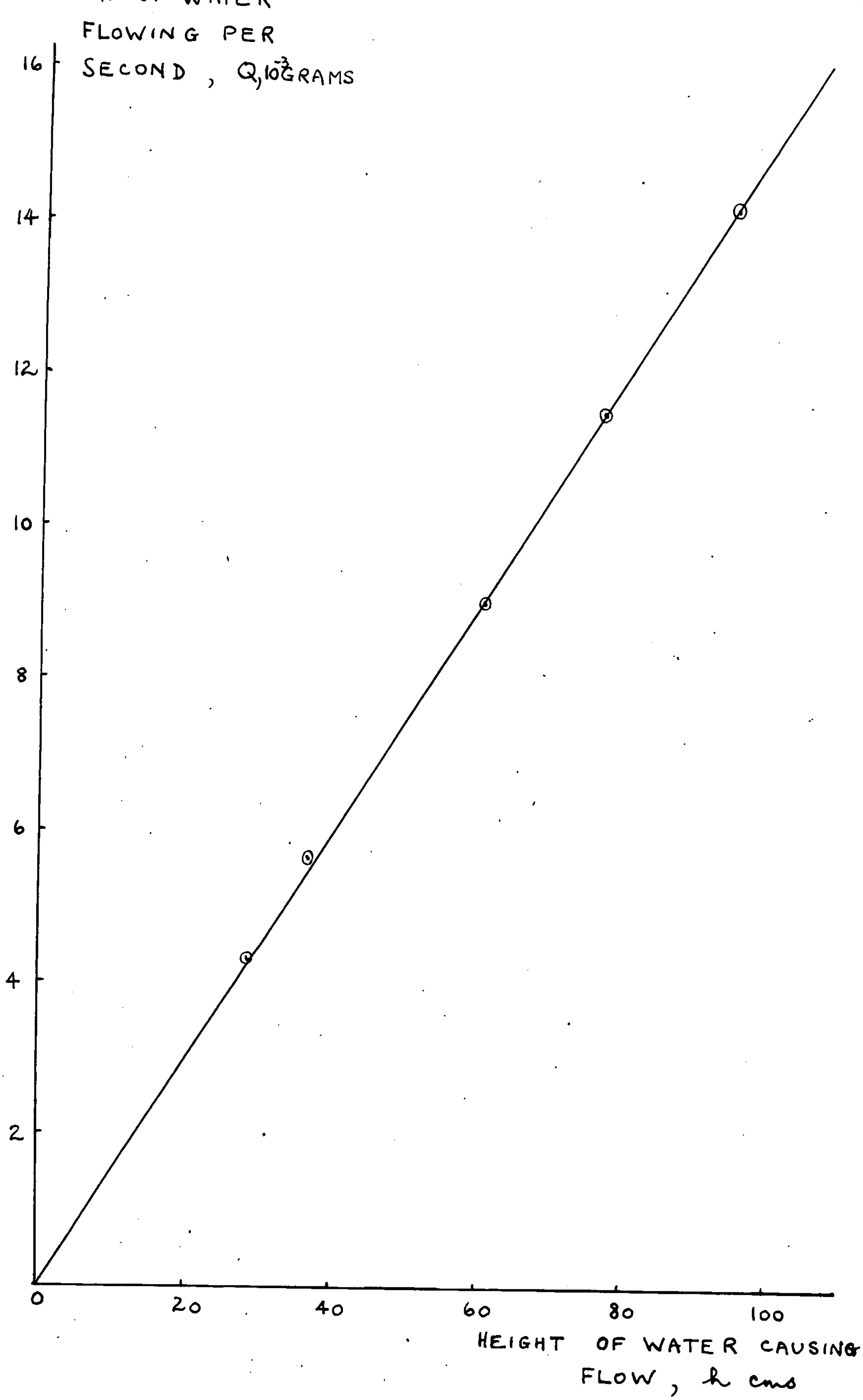
GRAPH 31.


tan θ
·02150
·01134
3
4
5
6
7
8
9
10
LENGTH OF 10 DASHES
IN CMS $\propto v_x$

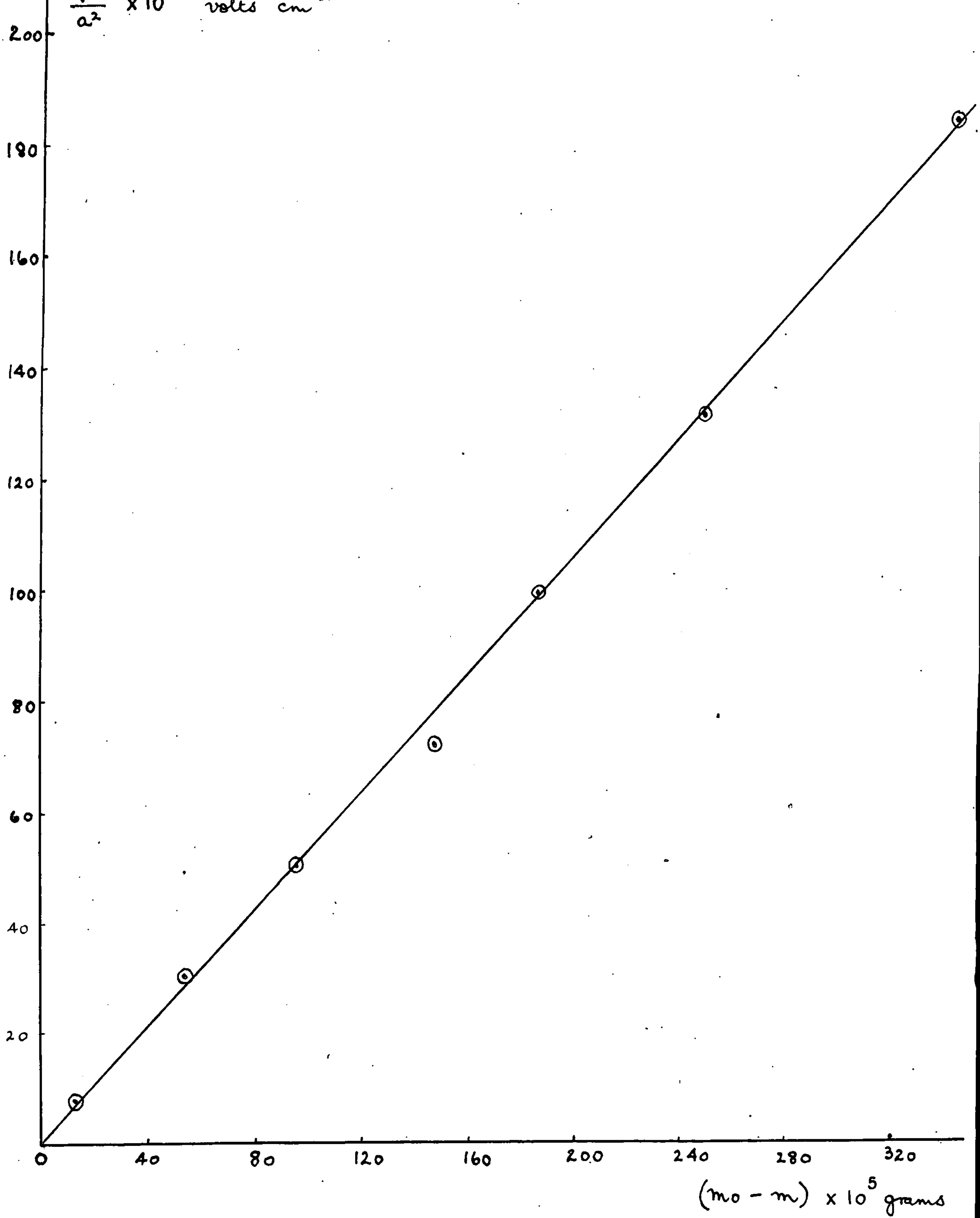
GRAPH 32


WT. OF
50 DROPS
0·38
0·36
0·34
0·32
0·30
0·28
0·26
0·24
0·22
0
400
800
1200
1600
2000
VOLTAGE

GRAPH 33

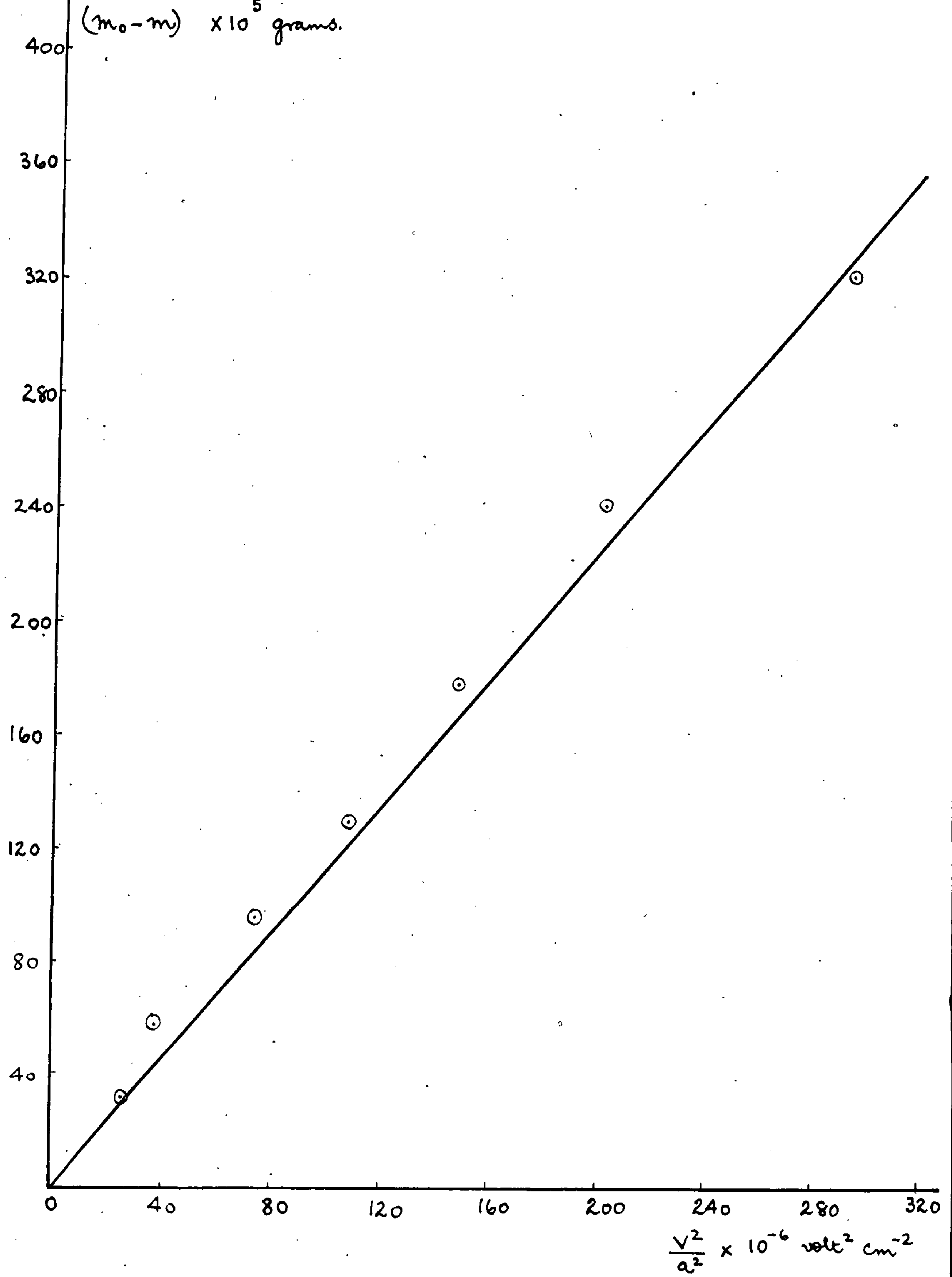

FLOWING PER
SECOND, Q, 10^{-3} GRAMS
16
14
12
10
8
6
4
2
0
20
40
60
80
100
HEIGHT OF WATER CAUSING
FLOW, h cms

GRAPH 34



$\frac{\ }{a^2}$ x 10 volts cm
200
180
160
140
120
100
80
60
40
20
0
40
80
120
160
200
240
280
320
$(m_0 - m) \times 10^5$ grams

GRAPH 35


$(m_0 - m) \times 10^5$ grams.
400
360
320
280
240
200
160
120
80
40
0
40
80
120
160
200
240
280
320
$\frac{V^2}{a^2} \times 10^{-6}$ volt^2 cm^{-2}

GRAPH 36