A POLAROGRAPHIC STUDY.

THE ESTIMATION OF SODIUM AND POTASSIUM IN THE PRESENCE OF EACH OTHER.

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INTRODUCTION

In 1903, Kucera (1) modified Lippmann's method for measuring the surface tension of polarised mercury, by noting the weight of mercury dropping in a given time from a fine capillary tube. He suggested to J. Heyrovsky the study of the polarisation of dropping mercury. The latter's researches on electrolysis with the dropping mercury cathode and the significance of the current-voltage curves so obtained, led to the construction by Heyrovsky and Shikata of a device for the automatic increasing of the potential and registration of the curve. This was described in 1925 (2).

As will be described, certain analytical conclusions may be drawn from these curves, and the following advantages are claimed for this method of analysis (3):

(i) In many cases, simultaneous quantitative estimation of several constituents is possible.

(ii) Qualitative and quantitative Estimation may be performed simultaneously.

(iii) 0.1 ml. of a solution may be analysed.

(iv) Concentrations of 10^{-5} to 10^{-6} gram equivalents per litre may be estimated, and an accuracy of ± 2.5% is claimed for most cases.

(v) The method is rapid and convenient.

(vi) In addition, the method is economical in the use of chemicals.

The instrument has been employed in various industries for analytical purposes, in bio-chemistry for the examination of plant extracts, for the testing of reagents, etc.

Its use in the routine analysis of soil extracts has been suggested, and the present thesis is an investigation into one of the preliminary difficulties nl. the estimation of sodium and potassium in the presence of each other.

As this is the first thesis on the subject produced in South Africa, and as the best literature is not generally available, a fairly comprehensive treatment of the theoretical principles has been thought desirable.

I. POLAROGRAPHIC ANALYSIS

A. Its Electrochemical Principles

(a) Electrolysis.

The fundamental process in Polarography is that of Electrolysis. A potential difference applied to the electrodes of an empty electrolysis cell causes the latter to act as an electrical condenser. If an electrolyte is now introduced into the cell, electrostatic attraction causes ions to move towards the oppositely charged electrode, and unless the applied potential is sufficient to cause ionic oxidation or reduction, the accumulation of ions of one sign around the oppositely charged electrodes will set up a counter electromotive force. If, however, the potential is above a certain minimum value, known as the decomposition voltage, the stability of the ions will be overcome, and electronic transfers will occur at the electrodes, leading to the flow of an electric current.

The current we observe is additive, not in the sense that some is positive and some is negative, but in the sense that a part is due to the migration of anions and part to the migration of cations. As an illustration, let us consider a case where the cations move, say three times as fast as the anions. The positions at time zero, and after unit time may be represented diagrammatically by (a) and (b) respectively, in the following arrangement:

We have thus a polarisation phenomenon at each electrode, and because of the natural tendency to maintain electrical neutrality in the solution, four ions will be discharged at each electrode (for a uni-univalent electrolyte). The excess of four ions is due to the migration of three cations and one anion i.e. three-fourths of the current-producing electrode process is due to the migration of the cations, and the remaining one-fourth to that of the anions. That terminology which refers to the current as being carried partly by the anion and partly by the cation is liable to lead to confusion.

In the electrolysis, the cathode, by virtue of its function as an electron donor behaves as a reducing agent, the power of which depends on the applied potential. This variable reducing power was used in 1864 (4) for quantitative separation of metals, although no adequate explanation on these lines was available. If we have in solution a mixture of electrolytes containing different cations, and an increasing potential difference is applied across two inert electrodes dipping in the solution, then the most easily reducible cation will be the first to undergo reaction, with an accompanying increase in current. The other cations will enter into reaction as soon as the applied potential is sufficient to overcome the so-called "Reduction Potential", which is a measure of the tendency of the ion to remain in that particular valence state.

Now since the reaction

$$M^{n+} + nNe = M \quad \ldots(1)$$

where n = valency etc.

(n = valency
(N = avogadro's Number
(e = electronic charge.

is a definite chemical process, it must be accompanied by a no less definite Free Energy Decrease.

Further, since for an electrical process

$$-\Delta F = -E\,n\,F \,, \quad \ldots (2)$$

where
($-\Delta F$ = Free Energy Decrease
(F = Faraday
(E = the electromotive force

E must also be definite (5). This is not invalidated by the fact that certain ions have differing deposition potentials at electrodes of different material (the phenomenon of overvoltage, which has been defined by the relationship: Overvoltage = deposition potential - the reversible electrode potential (6)). In these cases, the reaction is accompanied by some other process, e.g. amalgam formation or solution, with its own characteristic Free Energy Decrease.

The determination of characteristic Potentials is the basic principle in the qualitative aspect of Polarographic Analysis.

(b) The Electrodes Employed.

The negative electrode is formed by the "dropping mercury cathode", introduced by Heyrovsky (7). Mercury is forced by hydrostatic pressure through a very finely drawn capillary tube dipping into the test solution, and as each drop breaks away from the end of the tube, a fresh cathode surface is exposed. A comparatively large surface of pure mercury serves as anode. A gradually increasing potential may be applied to the cathode. The advantages of this arrangement for the study of the electrolysis are as follows:

(1) The exclusion of Anodic Effects. The flow of a current through the solution soon depletes the layer in immediate contact with the small cathode surface, of the molecules or ions which are being reduced at the applied potential. The current intensity is thus limited entirely by the rate at which the reducible particles arrive at the cathode surface through the depleted volume. This movement may be due to thermal diffusion, either alone or in addition to electrostatic attraction. This limiting effect will be discussed in detail under the theoretical treatment. The much larger anode has in its immediate neighbourhood a much greater supply of ions than are needed for the supply of electrons to the electrode, and hence it remains unpolarised throughout the increase of potential. "In general, polarisation is any change produced at an electrode by electrolysis or by some other means which causes its potential to differ from its reversible or normal value." (8). Consequently the whole of the applied electromotive force affects only the cathode potential during the electrolysis (9).

(ii) Continual renewing of the cathode surface. This tends to reproducibility of results, as the cathode is restored to its initial condition, and traces of the reduction products are removed from the sphere where they might exert a catalytic influence. In addition, the very dilute amalgams formed provide the highest activity of the dissolved substance possible (10).

(iii) Overvoltage of hydrogen at a Mercury Cathode. If it were not for this, the high velocity of the H_3O^+ and its relatively easy reduction would make this ion play such an important part in the electrolysis of any acid solution that the effect of other ions would be lost. From a neutral or alkaline solution, even the alkali metals separate without evolution of hydrogen.

(iv) Stirring effect. The drops of mercury falling on the anode surface tend to stir the solution, thus preventing concentration polarisation.

B. THEORETICAL TREATMENT.

(a) The limiting current.

Let us consider the electrolysis in the polarographic cell of an aqueous solution of a uni - univalent strong electrolyte AB, which we may regard, from the point of view of modern theory, as being completely dissociated into ions, A' and $B^{\cdot}$. Commencing at zero, a gradually increasing potential is applied to the cathode. Below the deposition potential of $B^{\cdot}$, no appreciable current will be observed, but ions will be attracted towards the oppositely charged electrode until an electrostatic effect is set up in the cell sufficient to oppose the applied potential.

In practice, a very small current may be observed as in the case of $Na^{\cdot}$ and $K^{\cdot}$, which has been ascribed to a non-Faraday "condenser" current due to the charging of the molecular double layer at the surface of the dropping mercury cathode.(11).

As soon as the decomposition potential of the cation is reached, there will be a discharge of $B^{\cdot}$ at the cathode surface, yielding a current which will cause a deflection of a galvanometer in the circuit. This current will increase until the cations in contact with the electrode surface are discharged when the current will be limited by the number of cations which pass through the depleted volume to the cathode. See Fig. 1. In the case of positive ions, thermal diffusion and electrical migration both contribute to this effect, whereas with undissociated molecules or anions, diffusion alone will apply. This completely built-up current is termed the "limiting current" or "saturation current".

In the case of the electroreduction of neutral molecules, the rate of diffusion will be proportional to the number of molecules in the main body of the solution, and we should thus expect the limiting current formed by diffusion in this way to be proportional to the concentration of the electroreducible substance (assuming constant conditions of temperature, viscosity, dropping rate, etc.). Much practical evidence supports this conclusion (12). We are thus provided with a method available for quantitative analysis nl. the comparison of the height of the so-called "polarographic wave" in the test solution with that produced by a solution of known concentration.

Sand (13) has applied to the normal electrode process the equation evolved by Dieterici, stating that the number of molecular impacts against the surface was

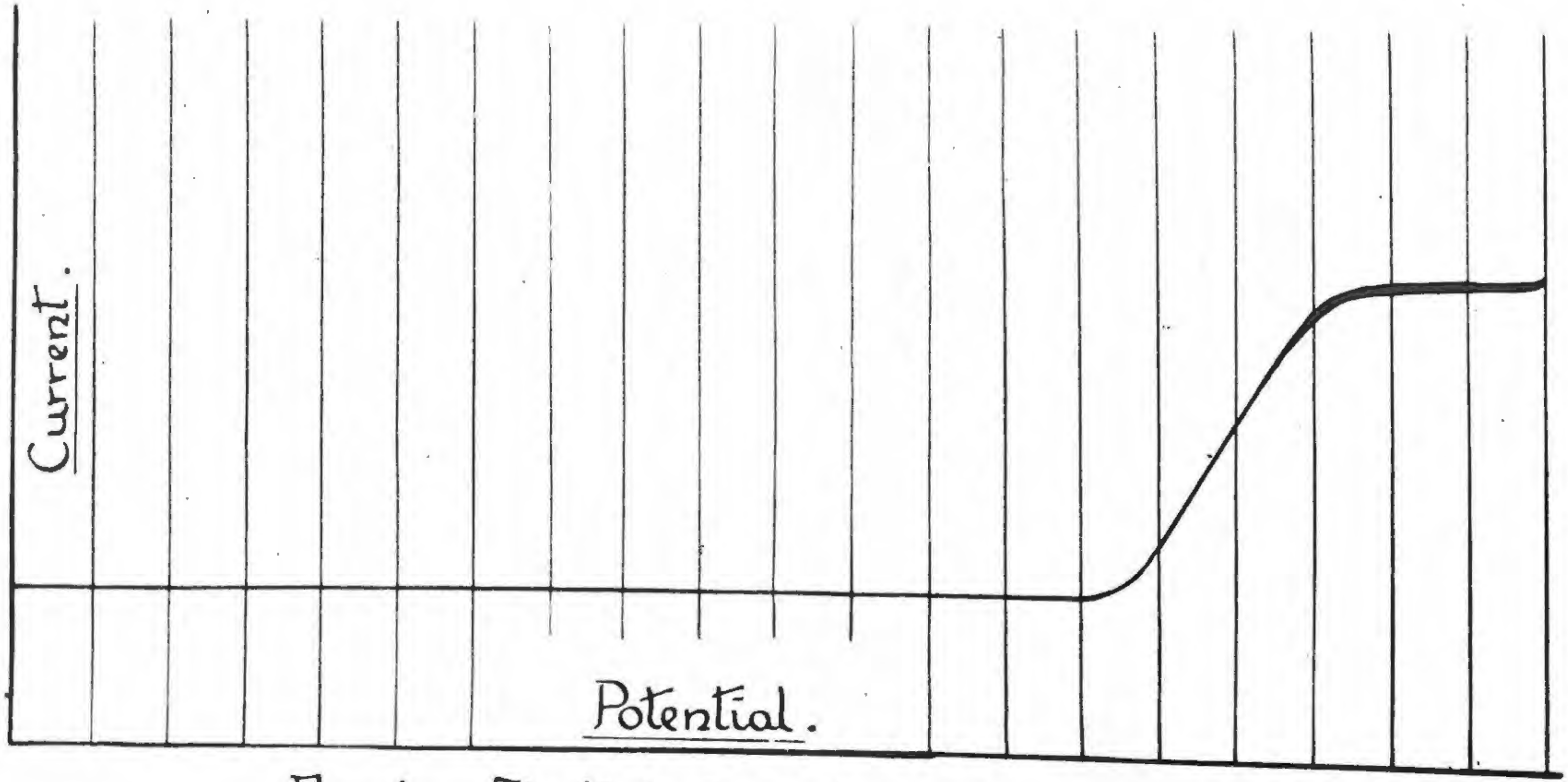


Fig. 1 Electrolysis of ·01 N NaCl solution.

proportional, not to c (the concentration in the main bulk of solution) but to $ce^{-\frac{A}{RT}}$, where A is the work done in transferring 1 mol. from the body of the solution to the surface.

In the case of cations, A = n x E x F, where E is the fall of potential, so that the rate of arrival at the electrode is proportional to $ce^{-\frac{nEF}{RT}}$ However, as explained in Section I. A. (c), E is, in effect, reduced to zero, so that the current is proportional to ce^{-0}, or to c. This aspect of the theory appears to have been overlooked, and although Hohn (14) refers to the exponential factor in passing, the significance of reducing E to zero was not mentioned.

(b) The effect of other electrolytes.

(1) In the case of undissociated molecules.

Limiting currents due to the reduction of non-electrolytes are not affected by the presence of those electrolytes whose cations are reduced at a more negative potential (12) (termed "indifferent" electrolytes). However, as Ilkovic states later in the paper, this is qualified by the assumption that the concentration of indifferent electrolyte is insufficient to cause any appreciable change in the viscosity of the solution, as in the latter case, diffusion rates are decreased.

Although the addition of electrolyte causes a drop of potential across the solution, this does not affect the movement of the neutral particles. Should the added electrolyte be reduced more easily than the undissociated molecules a current will flow before the decomposition potential of the latter is reached. At this point, a sudden increase of current intensity will occur, and the normal wave will be superimposed on the current already flowing. It should be noted that a high mobility cation should characterise an "indifferent electrolyte" (15).

(ii) <u>In the case of reduction of cations</u>.

The addition of indifferent electrolyte causes a depression of the limiting current due to the electro-reduction of cations, which current tends with increasing concentration of the added electrolyte, to a constant value, which is termed the "diffusion current". For further treatment see under Mathematical Analysis.

(iii) <u>In the case of reduction of anions</u>.

It may be mentioned here that a number of composite anions are reducible at the dropping mercury cathode e.g. NO_2^1, NO_3^1 (16), BrO_3^1 and IO_3^1(17). The anions tend to migrate away from the cathode, and are able to reach it only by diffusion. It is found that an excess of "indifferent electrolyte" causes an increase in the limiting current of the anionic reduction of about 50% (18).

(c) Mathematical Analysis of the Limiting Current.

A. Eucken (19) has derived the following formula for the limiting current, due to the deposition of a metal from its pure salt solution based on Nernst's differential equations for the diffusion of electrolytes.

$$i = \frac{2\ c.\ U.R.T.F.q}{d.v.} \quad \ldots(3)$$

where c = concn.of pure salt from which the metal is being deposited.
U = mobility of the cation
R = Gas Constant.
T = Absolute Temp.
F = Faraday.
q = area of cathode.
d = thickness of the diffusion layer.
v = valency of the cation.

When another electrolyte with a higher decompostion potential is present e.g. KCl in deposition of

Cd from $CdCl_2$ the position is more complicated, and K^+ will accumulate at the cathode until the migration is balanced by diffusion into the area of weaker concentration. According to Eucken, the limiting current in this case will be given by

$$i_I = \frac{2\ c.U.R.T.F.q}{d.v.} \left\{ M - \sqrt{M(M-1} \right\} \quad - - - (4)$$

$$\text{where } M = \frac{\text{total concentration of anions.}}{\text{concentration of reducible cation.}}$$

As M increases, the expression $M - \sqrt{M(M)-1}$ tends to its limiting value of 0.5. Even when the indifferent electrolyte concentration is ten times that of the Cd^{++}, the limiting current falls to 0.51 of its original value in $CdCl_2$ solution alone.

In 1931 I. Slendyk (20) tested out the validity of Eucken's factor in equation 4 for the presence of indifferent electrolyte, using the dropping mercury cathode arrangement. For greater concentrations at least, he found satisfactory agreement with the theory in the relative values of the limiting current with and without added electrolyte. For the deposition of hydrogen ions, however, he observed, that the diffusion current in the presence of indifferent electrolyte was less than half of the expected value.

A simple analysis of the relationship between limiting and diffusion currents, made by Heyrovsky (21) and described by Ilkovic (22), is not only in better accord with experimental results, but explains the apparently anomalous behaviour of hydrogen ions referred to above. As the journals in which these papers appeared are not generally available, a summary of Ilkovic's report will be given.

(i) Limiting Currents in electroreduction of cations.

Consider the electrolysis of a solution containing one electrolyte only e.g. Thallous Chloride, the cation being deposited at the dropping mercury cathode. The current intensity is limited by the rate at which the cathode is supplied with cations, due to thermal diffusion, and migration due to the fall of potential. That is, the limiting current (i.l.) consists of two elements, a "diffusion" current (i.d.), and a "migration" current (i.m.).

i.e. $i_l = i_d + i_m$ ... (5)

Now by definition, that fraction of the total current which is due to the migration of the cations in a solution, is equal to the transport number of the cation.

i.e. $i_m = i_l \cdot \frac{u}{u+v}$ ... (6)

where u and v are the velocities of cation and anion respectively.

Hence the diffusion current,

$$i_d = i_l - i_m$$

$$= i_l \left(1 - \frac{u}{u+v}\right)$$

i.e. $i_d = i_l \cdot \frac{v}{u+v}$ ... (7)

That no accumulation of charge occurs at the cathode appears from the following considerations:

The diffusion current brings $\frac{il}{F} \cdot \frac{v}{u+v}$ equivalents of cations/second,

and $\frac{il}{F} \cdot \frac{v}{u+v}$ equivalents of anions/second.

The migration current brings $\frac{il}{F} \cdot \frac{u}{u+v}$ equivalents of cations/second

and removes $\frac{il}{F} \cdot \frac{v}{u+v}$ equivalents of anions/second

Thus the concentration of anions remains unchanged, and $\frac{i_1}{F} \cdot \frac{u}{u+v} + \frac{i_1}{F} \cdot \frac{v}{u+v}$ i.e. $\frac{i_1}{F}$ equivalents of cations are deposited per second.

The drop in potential driving the ions through the solution is equal to $i_1 \times r$ (where r is the resistance of the solution between the electrodes). Suppose we add an excess of indifferent electrolyte: Although its cations will not be reduced at the potential which we are considering at the moment, they will, by their migration, build up an excess of charge around the cathode, which will oppose the applied potential. It is customary to explain the effect by stating that the indifferent electrolyte provides an "excess of current carriers". (although the cations are not reduced), hence there is a lowering of the resistance and a consequent fall of potential driving the ions through the solution. This argument appears somewhat forced, and it would seem much more reasonable to regard the accumulation of undischargeable cations to nullify the effect of the applied e.m.f. on cations in the solution, and thus cause a falling off in the current.

In this paper under discussion, Ilkovic states that an excess of indifferent electrolyte "practically eliminates" the migration current, due to the reduction of the force driving the ions through the solution.

Now, according to equation (7)

$$\frac{i_d}{i_l} = \frac{v}{u + v}$$

By the above theory, the maximally reduced current becomes equal to the diffusion current (since the migration factor is removed). This explains the partial experimental confirmation of Eucken's equation found by Slendyk, as for the majority of salts u approximately equals v, and hence $\frac{v}{u+v}$ is of the order 0.5

The behaviour of the hydrogen ion ceases to be anomalous on account of the high velocity of this ion. For HCl, v = approx. $\frac{1}{5}$ u, and the ratio falls to about 1/6. . This is in good agreement with Slendyk's ratio of $\frac{10}{58}$, for the suppression of the current in 10^{-3}N HCl by 10^{-1}N $BaCl_2$.

Ilkovic (loc. cit.) states that "the limiting current due to the deposition of hydrions, however, in the presence of electrolytes falls to about 1/5, as for the HCl v = 1/5 u. It would appear that either the first 1/5 is a misprint for 1/6 (the latter being correct according to equation (7), or Ilkovic has used some of Slendyk's results in which the current was not maximally reduced.

The converse effect of increasing the migration current may be obtained by raising the drop of potential across the solution. This may be done (a) by adding a more easily reducible non-electrolyte which will increase i_1, but not affect r. Note that not only is the total limiting current increased by this procedure, but also that part of the current due to the reduction of the cations being examined owing to the increase in potential gradient.

A proposed application of method (a) to polagraphic analysis has been described under Experimental Section.

(b) The addition of an easily reducible electrolyte will also increase the current, but since the final current increases inversely to r, the drop of potential ir remains practically constant. However, if excess indifferent electrolyte is present, r is not affected, so that ir is increased, and the migration of the original cation is hastened. This phenomenon has been described by Kemula as "exaltation".

(ii) Limiting currents in electro-reduction of anions.

In this case, any tendency of anions to diffuse to the cathode is diminished by migration,

i.e. $i_l = i_d^{'} - i_m^{'}$. (8)

Hence the effect of indifferent electrolyte of decreasing the potential gradient will result in an increased limiting current.

(iii) Limiting currents due to electro-reduction of undissociated molecules.

It is found experimentally that the limiting current in this case is unaffected by the presence of indifferent electrolytes, except at very great concentrations of the latter, when viscosity effects reduce the rate of diffusion. This is in complete accord with the above theory, as the fall of potential should not affect the diffusion of the neutral molecules e.g. oxygen or nitrobenzene.

The effect of electrolyte addition thus enables us to determine whether a wave on the current-voltage curve is due to the electro-reduction of cations, anions or undissociated molecules.

(d) The Exponential form of the Limiting Current.

A potential E applied to the cathode will be opposed by a counter electromotive force from within the cell, equal to $P_a - P_c$,

where P_a = the potential of the anode with respect to the solution

and P_c = " cathode " " " " "

If i is the current produced, and r is the electrolytic resistance of the cell, then

$$i. r = E - (P_a - P_c)$$

$$\text{i.e. } P_c = -E + P_a + i.r. \quad \ldots (9)$$

Owing to the relatively large size of the anode compared with that of the cathode, P_a remains constant during the electrolysis. Heyrovsky proceeds by stating that for simplicity, the potential of the unpolarisable anode may be put equal to zero. This seems, however, an unnecessary step, and rather illogical, as P_a has in fact to be determined experimentally in order to find P_c.

When the maximum sensitivity of the galvanometer is used, the current may not exceed $100 \times 3 \times 10^{-9}$ amps. i.e. 3×10^{-7} amps, being limited by the dimensions of the recording apparatus (100 mm. is the maximum possible deflection for record). Even at a sensitivity of 1/30, the maximum permissible current is less than 10^{-5} amps. The resistance of the cell is kept below 1000 ohms by the presence of indifferent electrolyte, and hence the effect on P_c of i.r. is under 10 millivolts, corresponding to less than 1 m.m. on the polarogram. In the determination of the potential for qualitative analysis, the practical value of this factor may, in general, be neglected.

Consequently, for electrolysis in the presence of excess indifferent electrolyte equation (9) reduces to

$$P_c = -E + P_a \qquad \ldots \qquad (10)$$

It is generally assumed that when a metal is deposited, an amalgam of concentration c is formed (23) (10). The relationship between P_c and the concentration c is given by Nernst's formula

$$P_c = -\frac{RT}{nF} \cdot \ln \frac{c.k.}{\{Me^{n+}\}} \qquad \ldots \qquad (11)$$

where R.T.F. have the usual thermodynamic significance.

$\{Me^{n+}\}$ is concentration in solution of the reducible ion,

n the valency of the above ion

k is a constant characteristic of the metal, depending on the solution-tension of the amalgam.

By Faraday's Law, $c = k^1 i$

By re-writing equation (11) as an exponential function, and substituting for c, we have

$$i = \frac{\left\{ Me^{n+} \right\}}{k.k^1} \cdot e^{-\frac{nF.Po}{RT}} \qquad \ldots \qquad (12)$$

(12) reveals not only the exponential form of the current, but also the linear relationship between i and the concentration of reducible ions, at the same values of Po (i.e. in the presence of excess indifferent electrolyte).

Heyrovsky (24) discusses the deposition of Arsenic at the dropping mercury cathode, a case in which no amalgam can be formed. The sudden increase in current should therefore occur when a layer of arsenic begins to be deposited. The deposition potential does not appear to be reproducible. Semerano (25) shows a curve for the reduction of As_2O_3 in H_2SO_4, and the two waves (probably due to the reductions $As_2O_3 \rightarrow As \rightarrow AsH_3$) are neither exponential in appearance nor easy of measurement.

(e) A Quantitative Demonstration of the Cathode Process.

Consider the electrolysis of a solution .0005N with respect to KCl.

i.e. Solution contains $\frac{6.06 \times 10^{23}}{2 \times 10^{3}}$ ions/litre

$=$ approx. 3×10^{20} ions/litre

Now 81 drops of mercury from the dropping cathode (in distilled water, at a drop rate of 4 seconds/drop), weighed 0.3033 gm.

$$\therefore \quad \frac{4 \times 3.142 \times r^3 \times 13.6}{3} = \frac{0.3033}{81}$$

whence r = .0403 cm = approx. 0.4 m.m.

Now the diameter of K' in aqueous soln. is of the order of 3 Å (26),

Volume around the sphere to the diameter of K' will be

$$4 \times 3.142 \times .4 \times .4 \times 3 \times 10^{-7} \text{ cu. mm.}$$

and
No. of K' in this volume is

$$\frac{3 \times 10^{20} \times 4 \times 3.142 \times .4 \times .4 \times 3 \times 10^{-7}}{10^6}$$

= (approx.) 1.8×10^8 K' in contact with the cathode before electrolysis.

A current of 1 amp. flowing for 1 sec. will deposit

$$\frac{6 \times 10^{23}}{96500} \text{ ions = approx. } 6.2 \times 10^{18} \text{ K'}$$

The sensitivity of the galvanometer used in experiment is 2.7×10^{-9} amps for 1 mm. deflection at a distance of 1 metre.

Electrolysis of this solution (excess indifferent electrolyte being present) yielded a curve showing a galvanometer deflection of 50 mm., 75 seconds after the commencement of deposition. As the galvanometer was shunted to 1/10 of its sensitivity the average flow of coulombs current per second was

$$\frac{2.7 \times 10^{-9} \times 30 \times 10}{75} = \text{(approx) } 1.1 \times 10^{-8}$$

$\therefore$ at this rate, approximately

$$6.2 \times 10^{18} \times 1.1 \times 10^{-8} \text{ potassium ions}$$

will be deposited in one second.

i.e. approx. 6.8×10^{10} ions, a quantity far in excess of the number of potassium ions originally in contact with the cathode surface. As the current rises exponentially, the initial current intensity will be less than this, but some idea is given of the short time necessary for establishing diffusion conditions through the depleted volume. As such a minute fraction of the concentration is used up during electrolysis, the same solution may be analysed thus repeatedly.

(f) Further types of Polarographic Analysis.

For the sake of completeness, three other types of polarographic analysis will be mentioned. For a detailed study, the literature should be consulted e.g.(27)

(i) Adsorption Analysis.

In cases where the substance in solution is simultaneously reducible and adsorbable, the current will rise above its expected value due to the second effect. According to Hohn (28), Heyrovsky states that the adsorbing power gradually decreases with increasing potential, and consequently as the potential passes the decomposition value, the current rises to a maximum, and then falls to the normal diffusion value. If a more easily adsorbable and non-reducible substance e.g. a dye or colloid, preferential adsorption will cause a depression of this maximum, and at sufficient concentrations will cause its eliminations. From the depression we can find the concentration or the adsorbing power of the more easily adsorbed substance.

(ii) Catalytic Analysis.

Some substances in solution appear to have a catalytic effect on the deposition of other substances e.g. Pt in the reduction of H^+. It is noted that the wave height is proportional to the concentration of both reducible substance and catalyst, and consequently may be used for the estimation of traces of the latter.

(iii) Estimation at the Dropping Mercury Anode.

Provided that the anions form insoluble or complex salts with mercury, they will provide current waves which may be used for estimation in a way corresponding to the reduction of cations at the dropping mercury cathode.

(g) Limits of application.

Only cathodically reducible susbtances can in general be determined, and these must be made up in a solution which conducts electricity.

The concentration of the substance to be examined should lie between 10^{-2} and 10^{-7} moles/litre, The optimum concentration according to the handbook, being 10^{-3} .

From a study of the theory, one might be led to suppose that any solution is electrolysed, and the resulting polarogram simply evaluated, but in practice it is found that unless the reduction potentials of two ions differ by more than 0.2 volts, the current increases due to their deposition merge, and one wave results instead of two. In this case, resource must be had to some means of

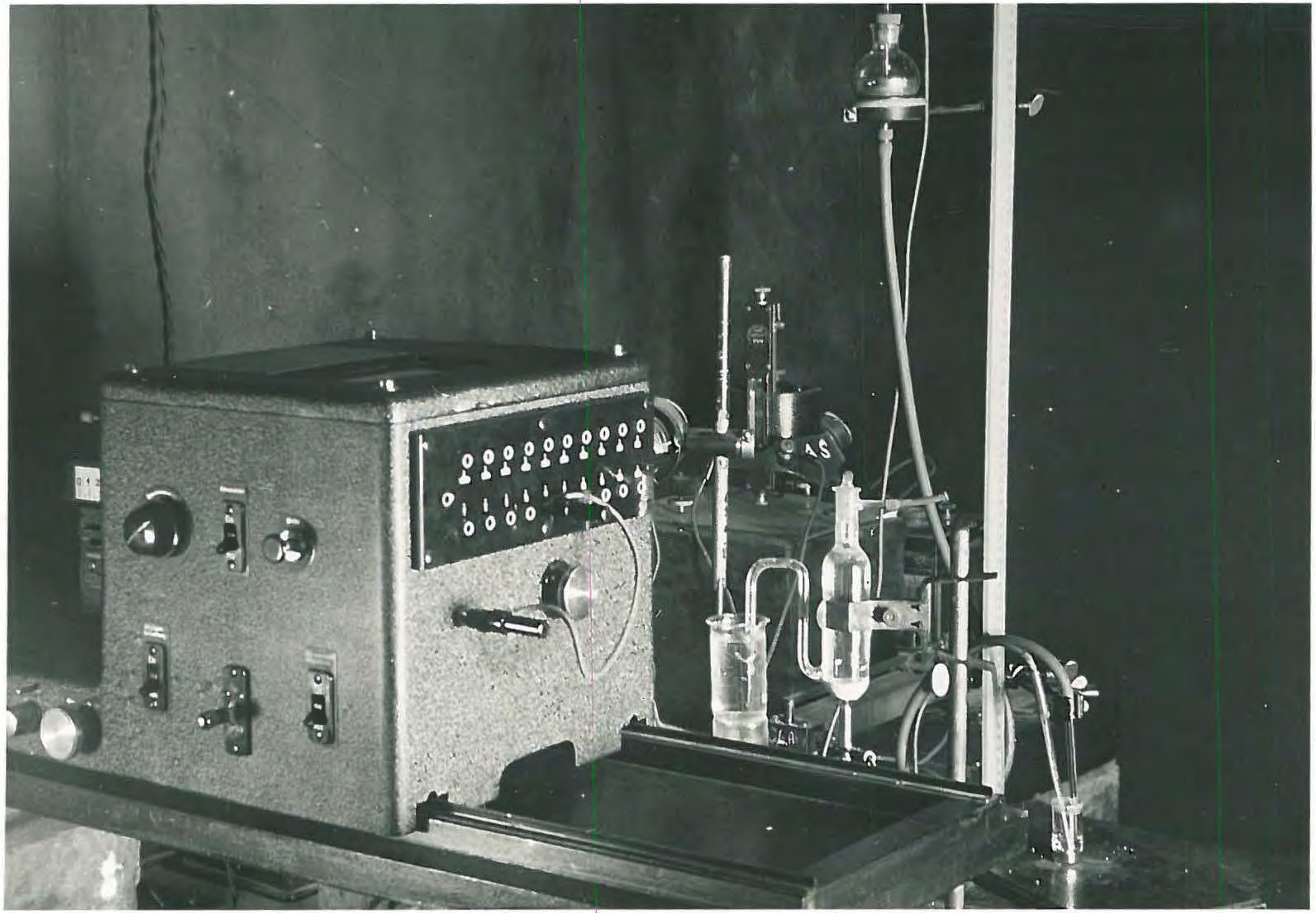


Fig. 2.

separating the substances or their potentials.

C. A Description of the Apparatus.

The machine was supplied by E. Leybold's Nachfolger A. G. and is illustrated, with its accessories in Fig. 2. The apparatus is mounted in a dark-room on a cement slab 37" x 33", supported by a brick structure. The galvanometer and accumulators rest on an adjoining brick pillar 16" x 16". The floor is of concrete. It is recommended that the apparatus be installed so as to be unaffected by vibrations, but in the local situation no trouble of this kind was experienced. Fig. 3 shows the apparatus from another angle, and in the left background may be seen the galvanometer mounted on a glass sheet at such a height that its mirror and the slit at the back of the drum casing are in the same horizontol plane.

A simplified diagram of the polarograph and its main circuit appears in Fig. 4. One or more accumulators A, act as a source of potential which is applied to the ends of twenty windings of resistance wire on the drum D, which is rotated by an electric motor whose speed is controlled by

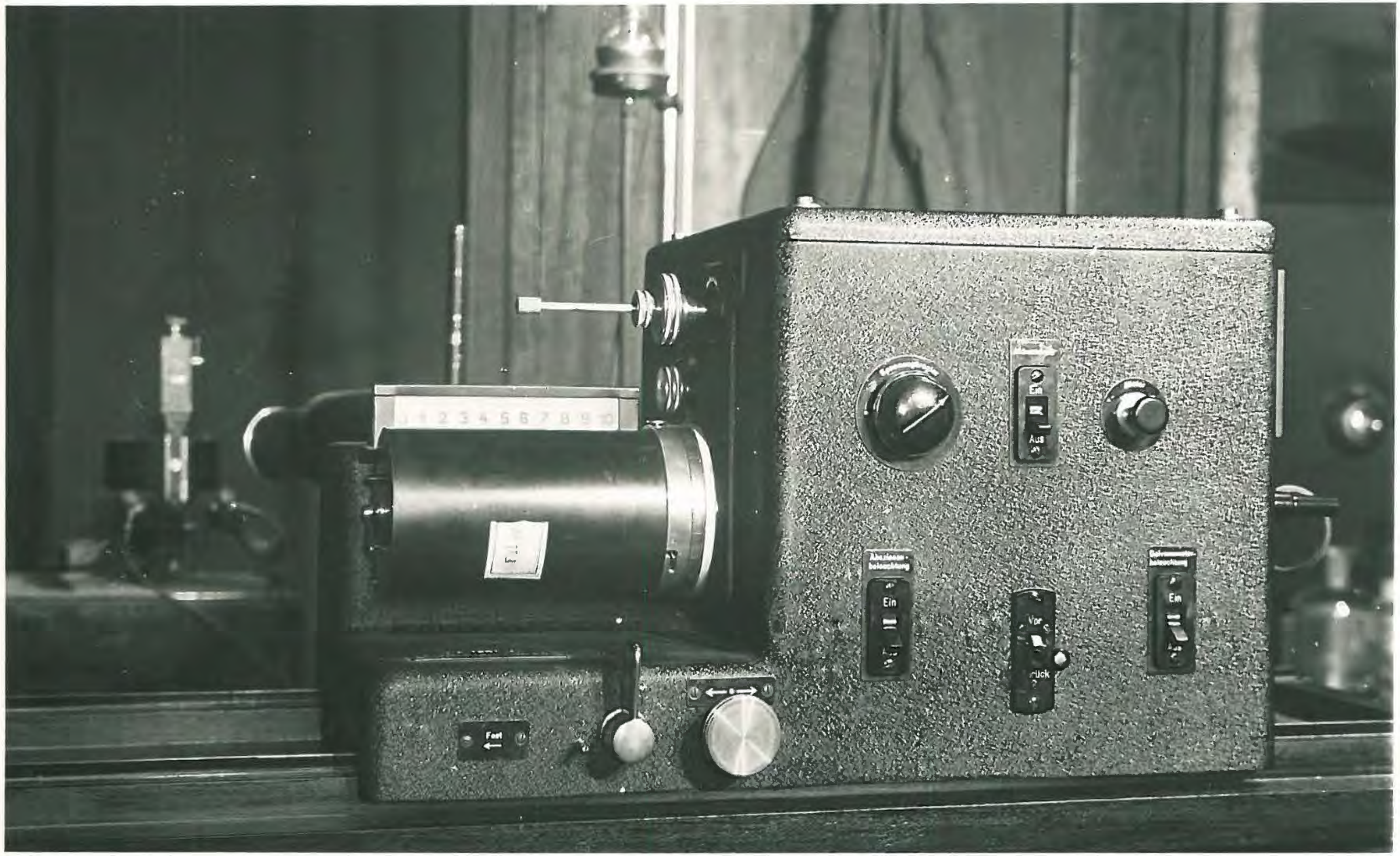


Fig. 3.

a governor. A voltmeter V is connected across the drum, and a resistance B is supplied for accurate setting of the potential at the desired value. Actually B consists of a rheostat in the external circuit, and a fine adjustment built into the machine.

A travelling contact wheel taps off from the drum a continuously increasing or decreasing potential, according to the direction of motion. A condenser C is fitted between the positive end of the drum windings and the contact wheel to smooth out current oscillations caused either by impurities settling momentarily on the drum windings, or by the cathode processes. The potential is finally applied to the electrodes in the electrolysis vessel E.

By means of a plug and a series of sockets various fractions of the current may be passed through the galvanometer circuit. The galvanometer light source is the lamp L , which is provided with a casing, and a slit and lens system which makes it possible to produce a sharp vertical line of light. The lamp, to which 6 volts and 4.35 amps. are applied, may be accurately centred by means of screws. The pencil of light falls on a ground glass

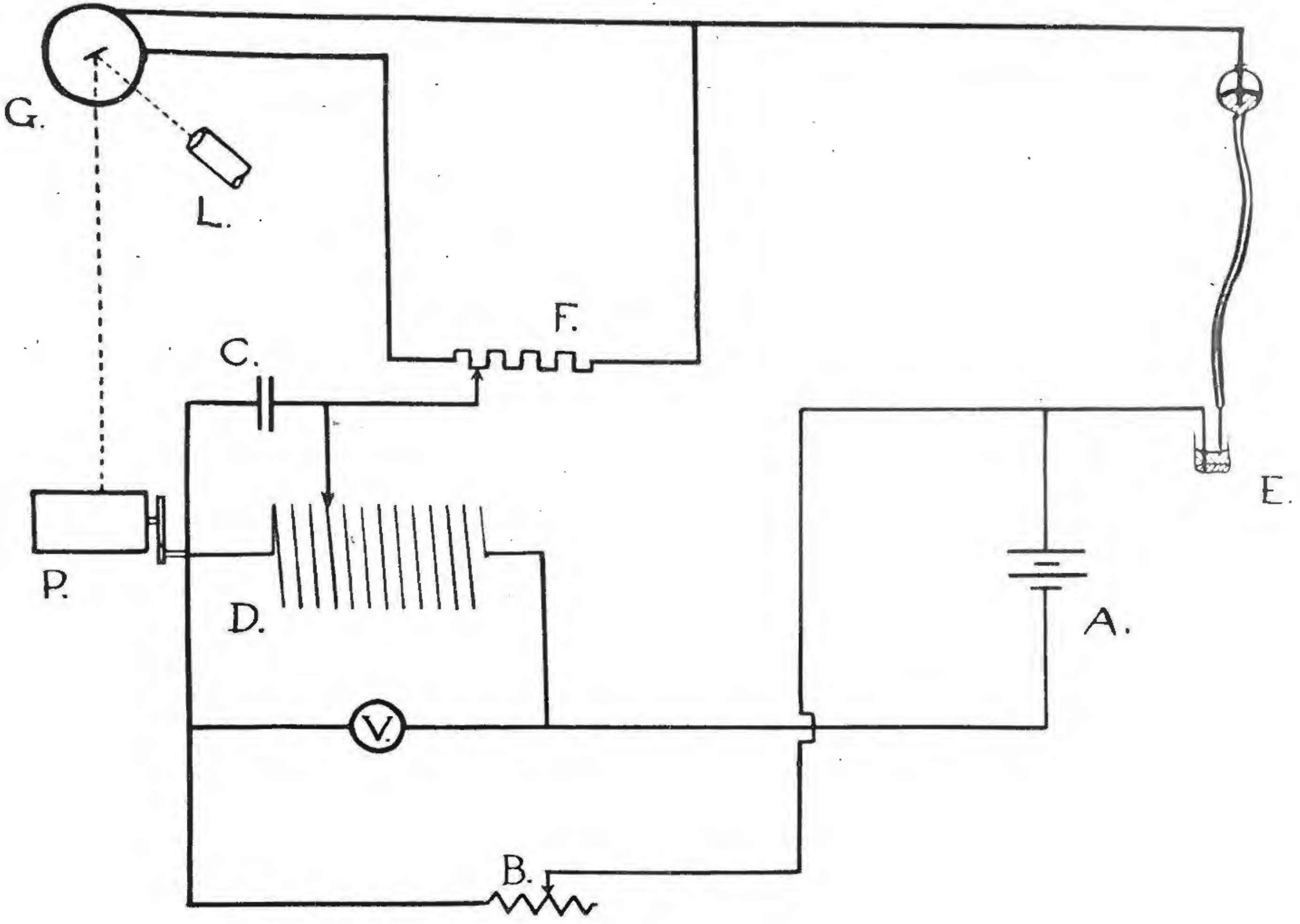


Fig. 4 Simplified Diagram of the Polarograph.

scale, under which is a slit in the casing around a drum, P. on which the photographic paper is held by a spring lever. This recording drum is geared to the resistance drum in such a way that the latter does twenty revolutions while the former does one. Each time the zero mark on the resistance drum passes a pointer on the machine, a contact is actuated which illuminates a small lamp for a fraction of a second, thus giving rise to a series of lines on the graph.parellel to the axis of rotation. For a complete run over the potentiometer wire, there will thus be 21 such lines, which form the abscissae of the polarogram.

Current for the motor, galvanometer lamp, and abscissa lamp, is supplied from the mains through a transformer attached to the apparatus.

Special attention should be given to the preparation of the electrodes.

(a) The Cathode.

This electrode is formed from a finely drawn capillary of hardly fusible special glass which is remarkably indifferent to the action of acids and alkalies. This is connected with a glass reservoir of about 100 ml. capacity by a length of pressure tubing, which should be steamed out and allowed to dry perfectly before use. Chemically pure mercury is now introduced into the reservoir, which is raised until drops of mercury are forced through the capillary. The length of the capillary is gradually reduced until the interval between successive drops is as required, with the reservoir, about 70 cm. above the bottom of the capillary. The drop rate is usually adjusted to four seconds, with the capillary dipping in distilled water.

A piece of copper wire is soldered to the negative lead, and dipped into mercury in a glass tube in which has been fused a short piece of platinum wire. Due to the amalgamation of copper with the mercury in the tube, excellent contact is made. This terminal passes through the cork of the reservoir.

It is recommended that the capillary be cut with a good glass knife so as to give a smooth and horizontal fracture.

(b) The Anode.

A layer of pure mercury on the bottom of the electrolysis vessel serves as anode, care being taken to ensure good contact. The mode of connection with the source of potential depends on the type of electrolysis vessel used, as illustrated in Fig. 5.

If the removal of dissolved oxygen is unnecessary, a glass weighing bottle 5 cm. high, and 2.5 cm. diameter has been found convenient, and economical in the use of mercury. In this case, contact is made as for the cathode, and as illustrated in the first diagram of Fig. 5.

A special vessel for saturation with any gas is supplied by the makers, and, as shown in the second diagram, consists of a conical vessel with a side tube for admitting the gas, and a sealed-in piece of platinum wire for making contact with mercury in the side-arm on the right.

Fig. 2 shows the casing in which is housed the motor and the Kohlrausch drum. The voltmeter is visible through a glass panel let in the top of the machine. The controls on the left hand panel are as follows:

<u>Top row:</u> <u>left to right.</u>

(a) The sensitive voltage regulator.
(b) The accumulator switch.
(c) A switch for re-connecting the motor after an automatic cut-off has operated (see below).

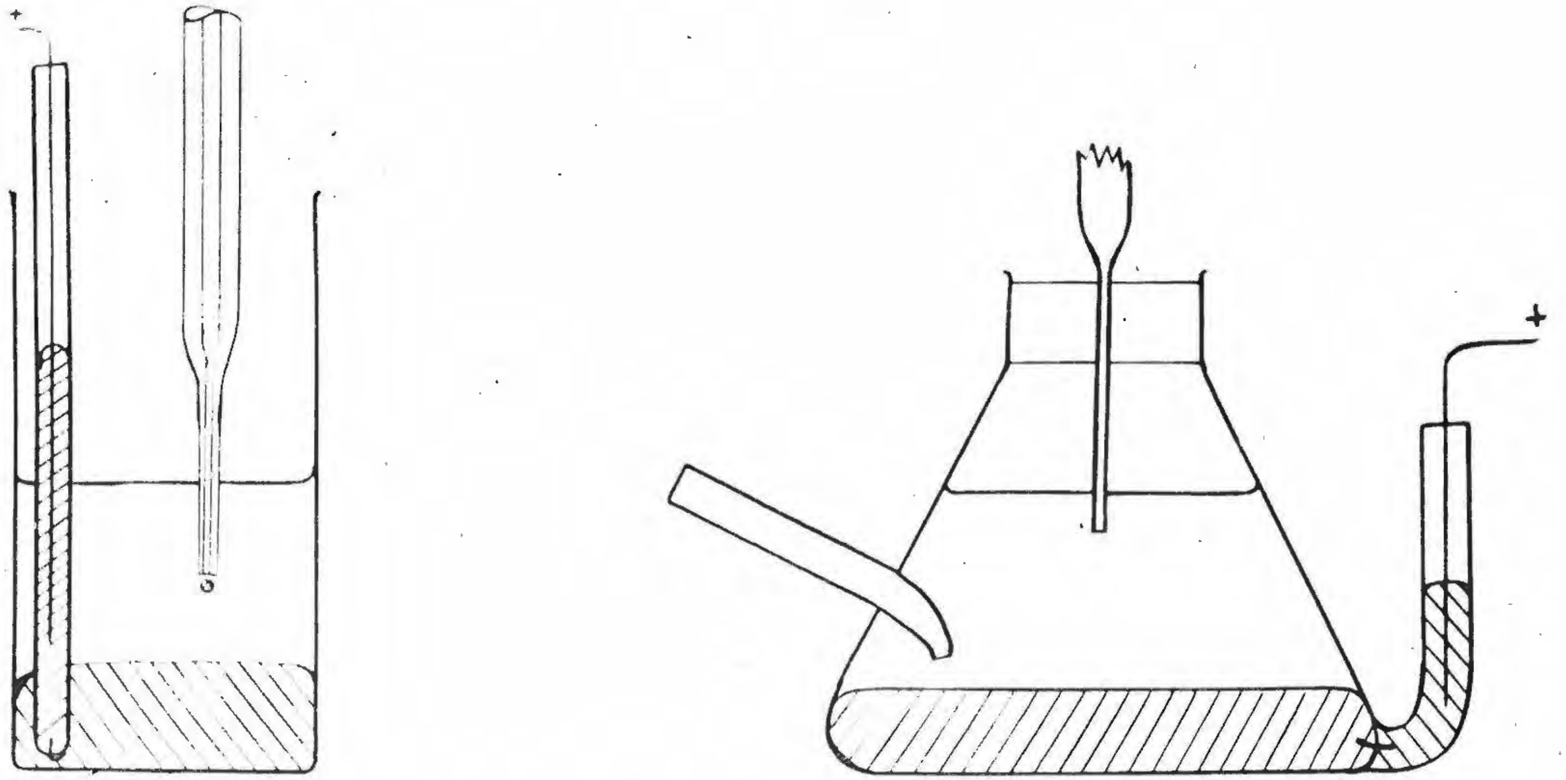


Fig. 5 Electrolysis Arrangements.

Lower row: left to right.

(d) The abscissa lamp switch.
(e) The motor switch: Forward, off or Reverse.
(f) The galvanometer lamp switch.

In the left hand lower corner can be noticed a lever for clamping the machine in position, and a knurled wheel for moving the instrument along the rails so as to get the light ray in the correct position on the scale.

On the right hand panel are the various sensitivity sockets, ranging from 1/10,000 up to full sensitivity. Below these may be seen a wheel for rotating the resistance drum by hand, so that the throw of the galvanometer may be noted on the scale, and the correct sensitivity chosen before exposing the paper.

Fig. 3 shows the photodrum casing in position, and the scale above it. At the left end of the drum is a lever for opening and closing the slit in the casing as required. At the other end may be seen the freely revolving graduated ring which is coupled to the photodrum but not to the casing. By means of this a number of curves may be taken on one sheet of paper, and may be suitably placed with reference to the abscissa lines.

Above the photodrum may be seen the knob for coupling the resistance drum to the recording mechanism. By means of the wheel above this, the "contact potential" is set i.e. the potential at which electrolysis is started. This is very useful, as it is frequently unnecessary for the applied voltage to begin at zero. Incorporated with this is the device which automatically switches off the motor when a desired potential is reached. When this has operated, the restoring button must be pressed to restore the circuit, as mentioned above.

The paper which is graduated in cm. and mm. squares, is removed from the drum in red light, developed in 1:3 metol-Hydroquinone developer to the desired intensity(for about 2 minutes), rinsed and fixed in an acid hyposulphite bath. After washing and drying, the polarogram is numbered, pressed and kept for evaluation.

The following details are recorded at the time of the experiment for subsequent evaluation purposes.

<u>Polarogram No. 38.</u>

Solution: 2 ml. N/500 Kcl + 1 ml.Quaternary Base.
Air removed: No.
Accumulator Voltage: 3.
Sensitivity: 1/20.
Photodrum reading: 0
Galvanometer light: 2
Contact potential: 1.8 volts
Anode potential: + .214 volts
Drop rate: 4 secs. in distilled water.
Temperature: 21.2° C.

In all experiments, conductivity water was employed, prepared by the distillation of CO_2- free water in a copper vessel and condenser, so arranged that the first and last fractions are rejected.

Preparation of the Mercury used.

The necessity for the use of mercury of the highest possible degree of purity is stressed in the literature, and all the mercury employed was purified electrolytically by the method of Newbery and Naude (29). Fig. 6 illustrates the type of apparatus used. The bottoms of two large glass bottles of different sizes are cut off, and the necks sealed together as shewn. Crude mercury forms the anode, although it is advisable to purify this as much as is rapidly possible, to avoid early fouling of the electrodes. If no pure mercury is available to start the cathode, a stainless iron sheet or platinum may be used at the commencement. The electrolyte is prepared by dissolving 20 gm. mercuric oxide in 20 ml. of 75 per cent perchloric acid diluted with 80 ml. water. A slight excess of free acid is advantageous. The mercuric salt thus produced is completely reduced to the mercurous condition by the action of the current before any mercury is deposited. The mercurous perchlorate electrolyte has the advantage that all the metallic perchlorates are

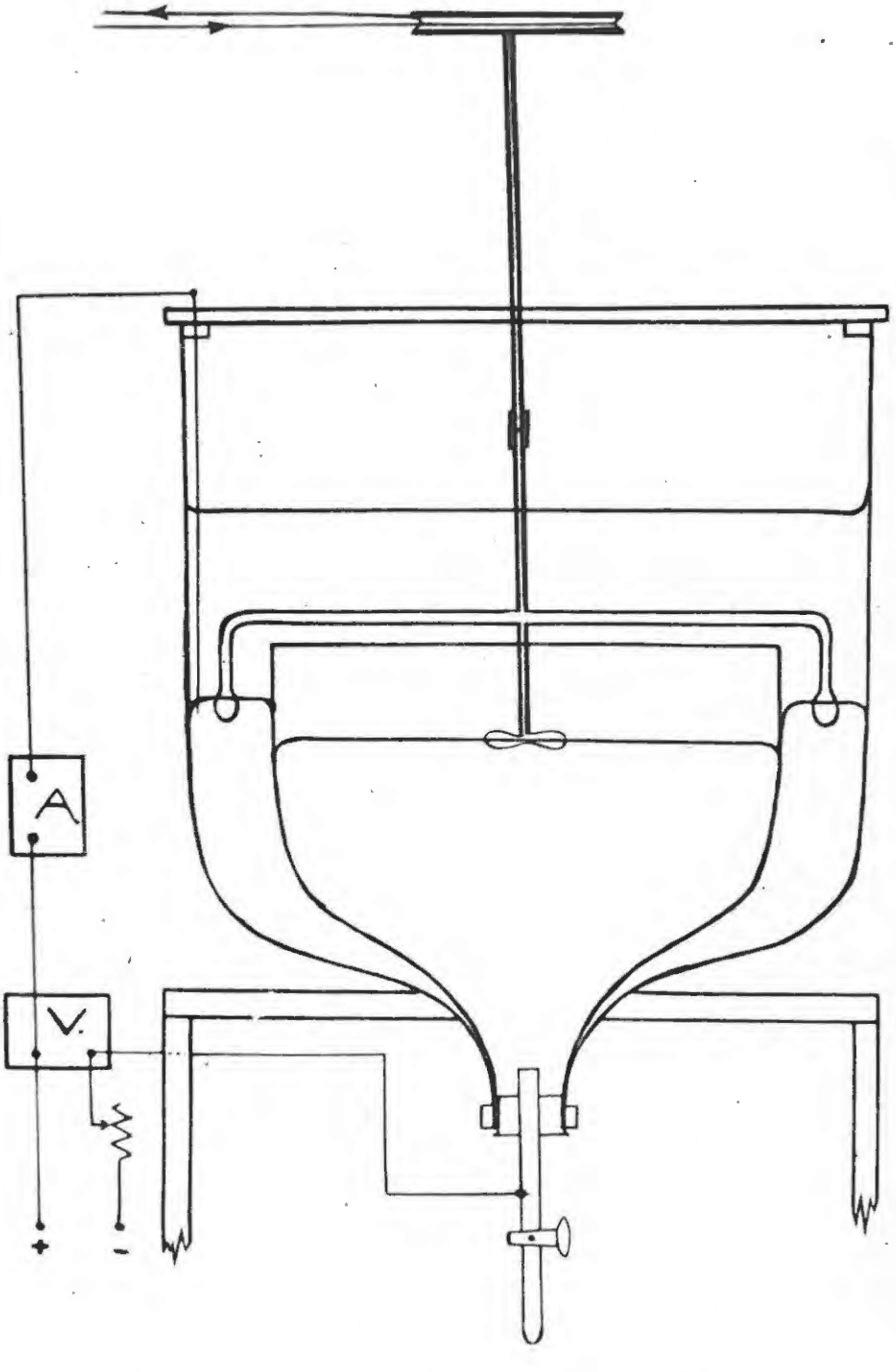


Fig. 6 Diagram of Mercury Refiner.

soluble in water (potassium being one of the least soluble) and consequently metals less noble than mercury will be dissolved from the anode, and kept in solution. Any metals more noble than mercury, if present, will not be dissolved if the current density is kept low.

Stirring is provided by glass rods bent as shewn, rotated by an electric motor, with the speed suitably reduced by a system of pulleys. A current of 1 amp. at 0.5 volts is maintained. Occasionally it is advisable to withdraw the electrolyte and crystallise out the mercurous perchlorate. Contact at both electrodes is made by platinum wire fused in glass.

After what appears to be thorough examination, the authors conclude that the normal product of the process is spectroscopically pure mercury.

D. The Effect of Experimental Conditions on the results.

The basis of quantitative work on the polarograph is the accurate measurement of a very small current representation, and it is understandable that small variations in experimental conditions may have appreciable effects on the results. These factors will now be briefly discussed.

(i) The Cathode Surface.

The limiting currents observed with different capillaries are not identical, due mainly to a variation in the cathode surface. Kemula found as an empiric rule, that capillaries, which show the same rate of flow of mercury, give in the same solution limiting currents of the same height (quoted from ref. 12). It would appear that this holds when this rate is measured in weight per unit time, for if two capillaries were providing the same number of drops in unit time, the wider one would give larger drops with a greater surface area. This in turn would lead to an increased rate of arrival of cations at the cathode surface, and hence an increased current.

Ilkovic (30) states that small variations in the number of drops falling per unit time cannot have any marked effect on the limiting current, and even if two values differed by 100%, the corresponding difference in the current would be 12%, for capillaries in normal use.

In practice, a dropping rate of four seconds per drop has been adopted in this laboratory, and this is regulated by adjusting the height of the mercury reservoir until the rate is correct over a period of forty seconds, according to a stop-clock. The standardisation is carried out with the capillary dipping in distilled water, without the application of potential. It has been found important to see that the distilled water does not collect electrolytes from the electrodes during electrolysis of solutions, as otherwise a quite erroneous dropping rate may be recorded.

(ii) <u>Diffusion Coefficient.</u>

Ilkovic (loc. cit.) calculates this from the formula

$$D = \frac{u.\ R.T.}{n\ F^2} \quad \ldots \quad (13)$$

where u = mobility of the cation being reduced

n = the number of electric charges involved

R, T, and F have the usual thermodynamic significance.

Enough has been said under the theoretical section to indicate the effect on the limiting current of the rate of diffusion. From mathematical considerations, Ilkovic (loc.cit.) has deduced that the current i is proportional to $D^{\frac{1}{2}}$. It may be pointed out that the viscosity of the solution is included in the above expression by Walden's relationship.

$$\text{Equivalent conductivity at infinite dilution} = \frac{11.15}{e \times M^{\frac{1}{2}}} \quad \ldots(14)$$

where e = viscosity of the solvent

M = molecular weight of the salt.

In Section III, the effect of alcohol in increasing viscosity of the solution, and lowering the limiting current is noted. Also, in the same section, some discrepancies in results are noted which may possibly be traced to the viscosity effect of the indifferent electrolyte.

(iii) Temperature.

The manufacturers' typewritten instructions accompanying the apparatus state that a variation of a few degrees in temperature is not serious, whereas Hohn (31) observes that a change of 1° causes an error of about 2.5%. As a rule, a variation of more than 0.6 or 0.7 degrees over a series of curves was not observed, although a variation of 1.5° has been recorded. In the later experiments described in this thesis it was customary to record on each polarogram about seven curves, including a standard curve for comparison, and since the observed wave heights were compared against this standard, temperature variations should not cause an error of more than about 3%.

Hohn (loc.cit.) advises an initial determination of the temperature error, as per cent, per degree, and when the stage of precise results is reached, this should be carried out.

(iv) Effect of other ions.

The effect of other ions on the limiting current has been dealt with from the point of view of general theory under Section I.B. but there remains a practical consideration. The concentration of other ions may influence the activity of the reducible cations, and Hohn (loc.cit.) reports that the wave-height becomes several per cent smaller when the "foreign ion" concentration is raised from N/1000 to N/100, or N/100 to N/10. A change from IN to 2N, however, has a scarcely appreciable result. Hohn recommends the elimination of this possible error by having at hand a Basic Solution (Grundlösung) for the supply of the "indifferent electrolyte". By adding equal volumes of test and standard solutions to definite volumes of Basis Solution, the influence of the foreign ions is kept constant, and thus eliminated. He further recommends that the concentration of the indifferent electrolyte should be at least ten times as great as that of the ion to be estimated. He includes a comprehensive list of suitable Basic Solutions for various determinations (32).

(v) Importance of good contacts.

A bad contact in the measuring circuit may, through the added resistance, cause an incorrect registration of the current. This may lead to faulty results and incorrect reduction potentials. It is therefore advisable to check over the terminal connections outside the machine periodically, as the wires are liable to break on account of flexing. The platinum contact wires should be clean and dry. The leads should contact with the platinum contacts through copper wires dipping into mercury. To ensure good contact at the anode, the mercury layer has been put into the electrolysis vessel, the anode terminal is cleaned, dried and inserted, and then the test solution is introduced into the vessel.

Eucken (33) has put forward the equation

$$i = k.\ T.\ C_A.\ O.\ f(C_B.\ C_C.....) \quad ...(15)$$

where k = a proportionality constant.

T = temperature.

C_A = concn. of ion under test.

O = cathode surface.

$f(C_B..)$ = function of concns. of other ions.

It will be seen from this that when T, O and f are constant, $i = k_1.\ C_A$.

Ilkovic (34) has mathematically deduced that

$$i = 0.63.\ n.\ F.C.D^{\frac{1}{2}}.\ m^{2/3}.\ t^{1/6} \quad ... (16)$$

where n = number of electric charges involved.

F = Faraday.

C = concentration of ion under test.

D = diffusion constant.

m = amount of mercury flowing out of the capillary in unit time.

t = the drop time.

Although at one stage in his calculations he neglects the decrease in the diffusion layer due to the increase in size of the mercury drop, his results agree well with experimental data.

E. Absolute Determination of Results.

(a) Quantitative.

It must be borne in mind that we are hot concerned with the measurement of the actual limiting current, but with the comparison of the heights of two waves which are representative of current strength. According to Hohn (35) there are three available methods of determining this wave-height, depending on the precise form of the curve. These may be termed the Intersection, Tangential and Complete Determination Methods, and are illustrated in Fig. 7.

In the Intersection method (Fig. 7 A), straight lines are drawn through the straight portions of the curve before and after the ascent, and also through the steep ascending part of the wave. The distance between the two points of intersection, is defined as the wave-height.

The wave-height may also be regarded as the vertical distance between the two points of contact of parallel tangents at the beginning and end of the wave. Heyrovsky suggested tangents at 45° (36), but it has been shewn mathematically that the point of greatest curvature of the exponential curve is at the

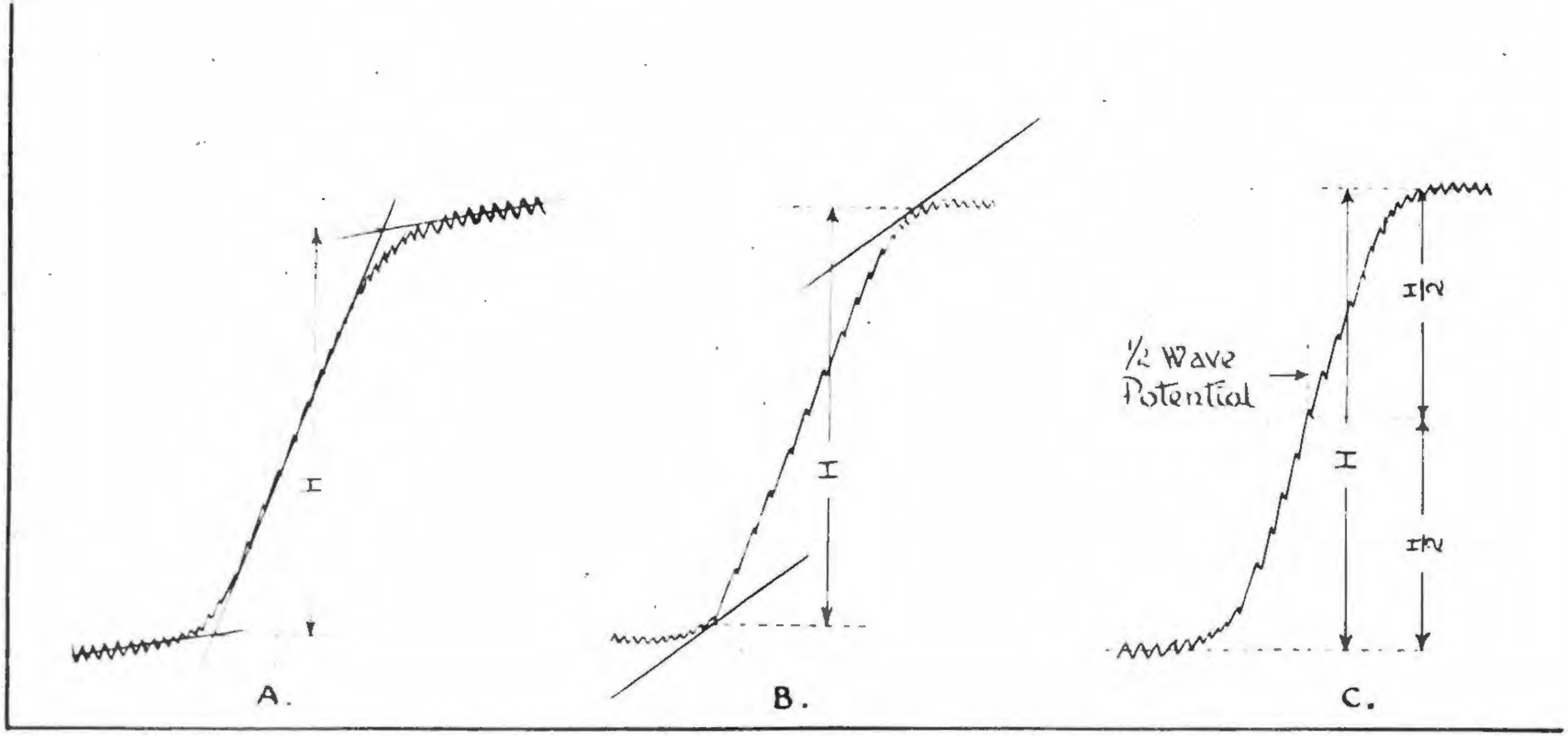


Fig. 7 Determination of Wave Height.

point of contact of the 35° 16' tangent, so that the use of these tangents has been suggested by Semerano (37). The method is illustrated in Fig. 7 B.

The full height of the completely built-up wave may be determined as in Fig 7 c by drawing parallel lines through the horizontal portions of the curve before and after the wave, and determining the distance between them. Where practicable, this method is easily the most satisfactory, as it is rapid, convenient, and generally more accurate than the tangential method as on account of the normally greater height obtained, errors in reading become of slightly less importance.

The method adopted here was to prick the centre of the curve at its highest and lowest points, using a magnifying glass to assist in locating the positions as accurately as possible. The vertical distance between these two points was read off on the graduations marked on the paper, and noted as the wave height. These graduations are not quite accurate, as the photographic paper appears to shrink somewhat during processing. The error, however, is only of the order 0.5%, and since we are dealing with comparative measurements, may be neglected altogether.

It will be noted that the three modes of wave determination outlined will give different heights, but as long as the same method is used for standard and test solutions, the comparison should lead to satisfactory results.

It has already been noted that the current intensity depends on the cathode surface area, and we should expect a continual current fluctuation due to the formation and falling of successive drops. This is observed in practice, but if the galvanometer is damped to a period of about five seconds, the instrument is unable to respond to the continual change, and very small oscillations result. Hohn(31) recommends that the middle of the oscillations should be taken as representing the curve. It must be emphasised that we are measuring relative concentrations, and hence the electrolysis vessels must be dry, and known volumes of indifferent electrolyte must be added to known volumes of solution.

Suppose that under similar conditions, the standard solution, of concentration C, and the test solution of concentration C, give wave heights of H at sensitivity S, and h at sensitivity s, respectively.

Now since the current is proportional to the concentration,

$$\frac{H}{C \times S} = \frac{h}{c \times s}$$

$$\text{whence} \quad c = \frac{h \times S}{H \times s} \times C \quad \ldots \quad (17)$$

(b) Qualitative.

The equation for the reduction

$$E_c = -E_0 + \frac{RT}{nF} \ln C \quad \ldots \ (18)$$

indicates that the actual reduction potential, E_c, depends on the concentration, and becomes more positive with increasing concentration. Polarographically, this signifies that the kink in the curve will appear earlier in the case of larger concentrations. However, since in the reversible process, the kink after the ascent will be moved a similar amount in the opposite direction, the middle point of the curve should undergo no change in position with concentration variations. The potential at this middle point has been termed by Heyrovsky and Ilkovic the "Halfwave potential" (38), and it is this potential which characterises the cathode process.

That the Halfwave potential is at the point of inflexion of the curve, and is independent of concentration, dropping rate, or galvanometer sensitivity may be shewn mathotically as follows: (39)

The potential of the polarised drop is governed by

$$P = - \frac{RT}{nF} \log \frac{k.C_{M_e}}{C_o} \quad \ldots \quad (19)$$

where C_{M_e} = concn. of the amalgam at the drop surface

C_o = concn. of the reducible cations close to the drop surface.

Under the conditions of the dropping mercury cathode, the rate of diffusion of reducible cations to the drop, and therefore also the current intensity depends on the difference $C - C_o$, where C is the concentration of the cations in the bulk of the solution.

We have thus -

$$i = k_1 (C - C_o) \quad \ldots \quad (20)$$

In addition, we know that the concentration of amalgam is proportional to the current i.e.

$$i = k_2 C_{M_e} \quad \ldots \quad (21)$$

Combining equations (20) and (21), we have that

$$\frac{C_{M_e}}{C_o} = \frac{i/k_2}{(K_1 c - I)/k_1}$$

so that the potential becomes

$$P = -\frac{RT}{nF} \log \frac{k1/k2}{c - i/k_1} \qquad \ldots \qquad (22)$$

By a rather laborious double differentiation, and equating $\frac{d^2 P}{di^2}$ to zero (the condition for inflexion) we find that

$$i_{infl.} = \frac{k1\ C}{2} \qquad \ldots \qquad (23)$$

and the potential at inflexion is

$$P_{infl.} = -\frac{RT}{nF} \cdot \log k. \, {}^{k1}/_{k2} \qquad \ldots \qquad (24)$$

where k represents the "solution tension" of the amalgamated atom, and $k1/_{k2}$ from the nature of the constants in equations (20) and (21), is seen to be independent of the dropping rate or of the concentration. We thus have that the potential at the point of inflexion has a characteristic value which is unaffected by the concentration of the reducible ion, or of the rate of flow of the mercury.

Now once the diffusion current i_d has been established, it follows from the theory that the C_o of eqn. 20 becomes vanishingly small, so that

$$i_d = k_1 C$$

Then from equation (23)

$$i_{infl} = \frac{i_d}{2} \qquad \ldots \qquad (24)$$

Thus the potential at the halfwave height is that of the inflexion point.

It is of interest to note that since

$C_o = C - 1/k_1$,

$C_o = C - C/2$ at the inflexion point

$= C/2$

i.e. when the inflexion point has been reached, the concentration of the reducible cations close to the drop surface has been reduced to exactly one-half of that prevailing in the body of the solution.

For the practical determination, the wave height is first determined as described, and half the result is added to the lower limit of the wave. The potential of the curve at this height is read off in terms of the recorded abscissa, and from the potential at which contact was made, and the relationship between the applied voltage and the scale divisions, we may calculate the potential applied to the cathode at this point.

As an example, suppose the halfwave point occurs 2.80 abscissa units after contact was made, and 3 volts are applied across the drum. The 20 abscissa units correspond to the 3 volts, and if contact was made at 1.80 volts, the actual potential applied at the middle point will be

$$1.80 + 2.80 \times 3/20$$

This, however, gives only the potential actually applied, which will be reinforced or opposed by the potential between the anode mercury surface and the solution above it. For the determination of this value, a potentiometric system is employed, using an N/10 calomel half-cell. The applied e.m.f. is supplied from the electrode terminals on the polarograph, the platinum anode contact being dipped into the Hg layer to be tested. The other terminal is connected through a tapping switch to the calomel half-cell, which is connected to the electrolysis vessel through an agar-saturated KCl bridge. The applied voltage is accurately adjusted, conveniently to two volts, and the drum rotated until the point of balance is obtained, and the e.m.f. tapped from the drum is read off. To protect the galvanometer, it is necessary to get the approximate position of the drum at a sensitivity of, say 1/30, and then gradually work up to full sensitivity for the final reading. The circuit should be checked with a standard cell from time to time.

Since the anode potentials are merely relative to some arbitrary standard, it is customary to refer them to a definite zero, and the N calomel cell is used for this purpose. Consequently a correction must be applied to the N/10 calomel cell used.

The method of combining the half-wave and anode potentials to give the final result is apt to be confusing, and the position may be clarified as follows:

In the normal Poggendorff potentiometric arrangement, positive is connected to positive, and vice versa. If, therefore, the Hg anode is connected to the cathode or negative terminal, we know that the anode is more negative than the terminal of the calomel half-cell.

Suppose the balance is obtained at x volts. The potential of Hg against soln. in N/10 calomel half-cell $= + .3358$ volts

at anode $= + .3358 - x$ volts.

The latter against an N calomel half-cell

$= + .2828 - (.3358 - x)$

$= x - .053$ volts.

Now an actual external e.m.f. say $- E$, is applied to the cathode during electrolysis. The anode is already positive with respect to the solution by $x - .053$ volts, and therefore the total potential operating is the difference $- E - (x - .053)$.

Reversing the connections in the anode potential determination simply signifies that x is negative.

Hence to evaluate, add ($- .053$ volts) to the observed value of x, regarding the latter as positive when the Hg anode is connected to the negative terminal, and v.v.

The resultant must then be subtracted from $- E$.

II. Its application to the estimation of Sodium and Potassium.

As mentioned previously, a difference of at least 0.2 volts should exist between adjacent deposition potentials. Heyrovsky (40) gives the half-wave potentials of potassium and sodium as - 2.17 and - 2.15 volts respectively, and hence the two ions together give one wave.

Very little work appears to have been done on the estimation of sodium and potassium. V. Majer(41) has investigated the composite wave due to both sodium and potassium in a solution, and makes the statement that the height of such a wave represents the sum of the heights that would be caused by the constituents separately. It should be remembered that according to Ilkovic's equation (33), i, and therefore the wave height, is proportional to $D^{\frac{1}{2}}$, and since D is proportional to the mobility of the cation, we have the relationship that the wave heights caused by different cations are proportional to the square roots of their mobilities.

If Majer's result is reliable, as from the theory it would appear to be, we should be able to estimate quantitatively the sodium and potassium in solution by

1. determining the wave height due to both constituents.

2. precipitating one alkali metal, and finding the wave height due to the other in solution. By comparison, this will give the concentration of the latter, providing a zero error correction is introduced for a trace of the former not precipitated.

3. subtracting the true wave height of the unprecipitated alkali from the total height, and by comparison, determining the concentration of that alkali metal which had been precipitated.

This type of difficulty may be overcome by

(a) the precipitation of one or more of these constituents successively, and subsequent re-electrolysis e.g. Aluminium as hydroxide, from presence of manganese (42),

(b) the formation of a complex ion of one of the constituents with consequent change in the decomposition potential e.g. use of KCN in simultaneous estimation of Nickel and Cobalt (43),

(c) altering the p H value in cases where the presence of hydrogen ion is necessary for the reduction, thus causing a shift in the Reduction potential e.g. Maleic and fumaric acids (44).

Methods (b) and (c) do not apply in this case, and an attempt has been made to find a suitable precipitant for either Na or K.

K. Abresch (45) has proposed precipitating the K with $H_2(PtCl_6)$ or $HClO_4$ and then estimating the K in the re-dissolved precipitate, polarographically. Three disadvantages in this procedure are apparent.

(a) The processes of filtration, careful washing, and dissolution of the precipitate are introduced, when, theoretically, it should be possible to precipitate one element, centrifuge and pour the centrifugate straight into the electrolysis vessel.

(b) Not inconsiderable errors may be introduced into the analysis by his procedure, on account of the very small amounts involved.

(c) The precipitate has to be dissolved in some non-aqueous solvent, such as alcohol or acetone, which will materially affect the wave height - (see under experimental section).

Winkel and Maas (46) also mention the possibility of re-dissolving the potassium, precipitated by magnesium dipicrylaminate, in acetone or alcohol and electrolysing. This method is open to similar objections.

A search has consequently been made for a reagent which will make possible the precipitation of either sodium or potassium without affecting the subsequent polarographic analysis of the centrifugate.

This search has been complicated mainly by three factors:

(1) Many reagents for potassium contain sodium, and vice versa.

(2) Alcohol may be required to aid precipitation.

(3) The reagent itself may cause polarographic phenomena which will interfere with the estimation.

Objection 1. This rules out such reagents as Sodium cobaltinitrite and Potassium pyroantimonate. The possibility of adding a measured excess of reagent, and determining the unprecipitated alkali originally in solution by difference, has been suggested. However, the reagents used in practice are relatively so concentrated that the effect of the alkali originally present is lost, at the sensitivity which would be necessary for recording the electrolysis.

It might be argued that dilution subsequent to precipitation would overcome this, but the concentration relationships would still be such as to make the experimental errors of the method of considerable magnitude when referred to the amount of original alkali.

Objection 2. Alcohol has been shewn to have a depressant effect on the diffusion current, the magnitude of this effect depending on the proportion of alcohol in the solvent (see experimental section). This does not of necessity exclude the presence of this or other organic solvents, but it would mean that considerable care would have to be taken to ensure that the proportion of alcohol in both the standard and test solutions is exactly the same.

Objection 3. The use of ammonium bitartarate, for instance, would be impracticable owing to the combination of waves due to NH_4^+ and Na^+ (halfwave potential of NH_4^+ is - 2.09 volts (40). Work on Zinc Uranyl acetates carried out in this department (47) has shewn this reagent to be unsuited, as the deposition of Zinc before that of the alkalies gives a wave which makes it necessary to work at very low sensitivites.

Magnesium uranyl acetate was also tried out by the same worker (47), and this seemed more promising, but consistent values of the product Height/concentration x sensitivity could not be obtained. It has been suggested that this is due to the carrying down of some potassium in the presence of a large excess of sodium. No attention was given to the possibility of error due to volume changes produced by precipitation. Although this inconsistency is noted in the series containing equal amounts of sodium in equal volumes of water, and varying amounts of potassium, it is possible that the quaternary base employed as indifferent electrolyte may have produced a precipitate with varying quantities of reagent. A visual estimation showed that on precipitation of 1 c.c. + - N/10 magnesium dipicrylaminate from 12 ml. of solution, the precipitate after centrifuging occupied about 0.35 ml. whereas the increase in total volume was about 0.25 ml. In this case the error introduced is less than 1%

No details are available of the work, and it is also possible that a zero error due to incomplete precipitation of the Potassium was not included in the calculations.

III. Experimental Section.

NOTE. It has not been thought necessary to reproduce the few hundred curves recorded, and only such as are illustrative of the description have been included. Reproduction was effected by going over the image on the polarogram with India ink, and photographing the result. A new copy of the curve in India Ink on white board would give better photographic results, but the process would be time-consuming and scarcely as accurate.

(a) The effect of alcohol.

No reference could be found in the literature as to the effect of non-aqueous precipitants on the polarographic wave, so a simple experiment was carried out to see if the predicted result would be observed.

According to International Critical Tables, the viscosity of water at 20°c is 9.84 millipoises, whereas that of ethyl alcohol at 20°c is 17.16 millipoises.

Walden's equation, quoted previously shows that Equivalent conductivity at infinite dilution

$$= \frac{11.15}{e \times M^{\frac{1}{2}}} \qquad \ldots (14)$$

where e = viscosity of the solvent.

Also the wave height is proportional to the square root of the mobility of the cation, so we should expect the wave height to decrease as the viscosity of the solution increases.

Six solutions, made up as follows, were electrolysed:

A. 2 ml. $^{N}/_{100}$ NaCl + 2 ml. $^{N}/_{4}$ Q.B.* + 4 ml. water

B. do. + do + 2 ml. water + 2 ml. alcohol absolute.

C. do. + do + 4 ml. alcohol absolute

D. 2 ml. $\frac{N}{250}$ NaCl + do + 4 ml. water

E. do + do + 2 ml. water + 2 ml. alcohol absolute

F. do + do + 4 ml. alcohol absolute.

A. B. and C. were electrolysed at a sensitivity of $^{1}/_{50}$ and D. E. and F. at $\frac{1}{20}$. The decrease in current with increasing viscosity is clearly shown in the result, Fig. 8. The consequence of this phenomenon was discussed in Section II.

* Q. B. is a convenient abbreviation for the qua~~r~~ternary base, tetramethyl ammonium hydroxide. This is prepared by the action of moist silver oxide on a sample of tetramethyl ammonium iodide which has

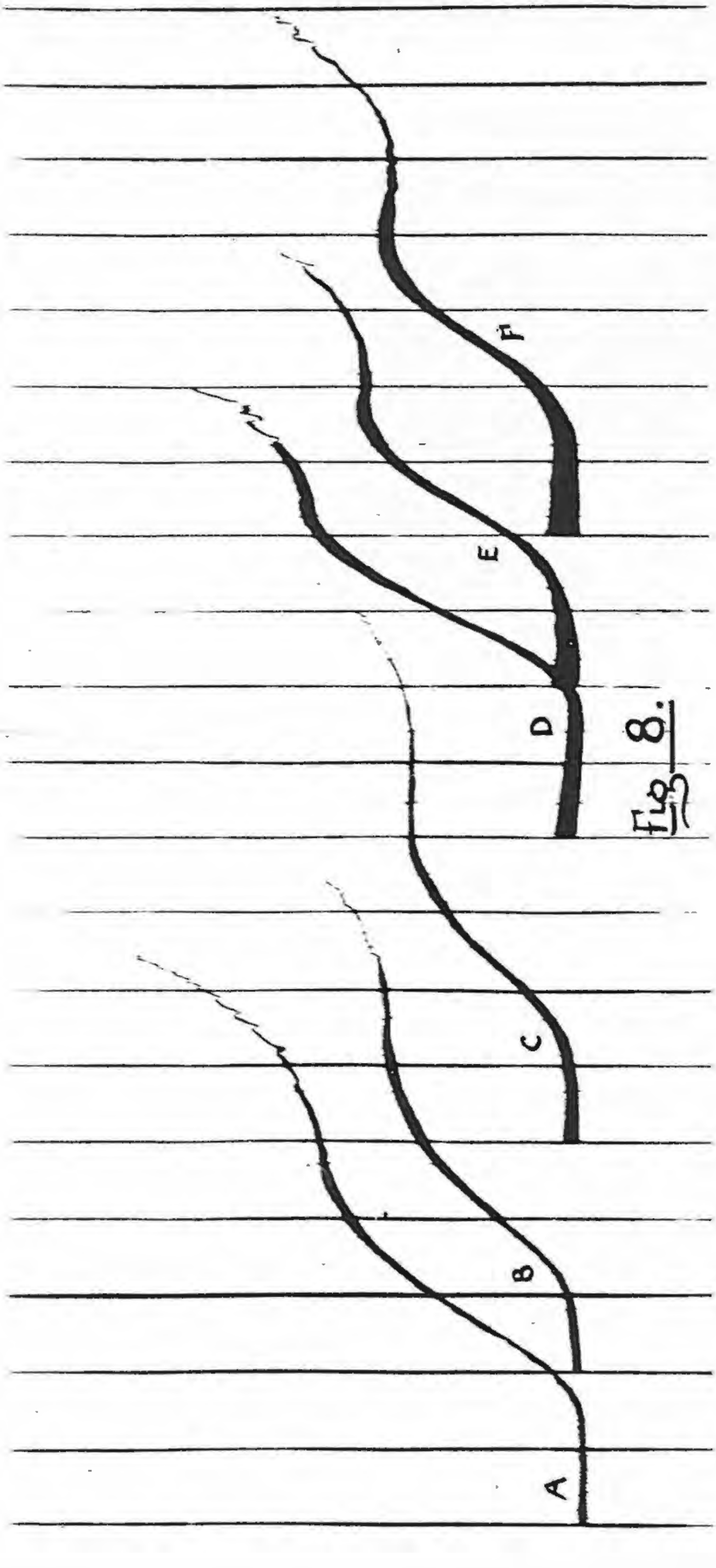


Fig 8.

undergone several recrystallisations. The halfwave potential of the substitute ammonium ion is - 2.8 volts.

(b) The effect of phosphomolybdic acid.

The use of this substance as a quantitative reagent for potassium was reported by Illingworth and Santos (48) but unfortunately optimum conditions for precipitation were not recorded. It was found that unless the reagent is very concentrated, precipitation is by no means complete, hence the solid was shaken up with cold water until no more dissolved. It was noted that of the Merck's G. R. preparation used some was in the form of crystals which were excessively soluble, and some existed as a practically insoluble powder, the latter being discarded.

It was found that any sodium present was completely masked by a large maximum, not suppressible by methylene blue (see Fig. 9A, where sensitivity was 1/3,000). The reagent itself, when poured onto a mercury surface went a blue-green colour, and from the work of Merrill and Russell (49), this would seem to be due to the formation of molybdenum molybdate. Their research on the deposition of

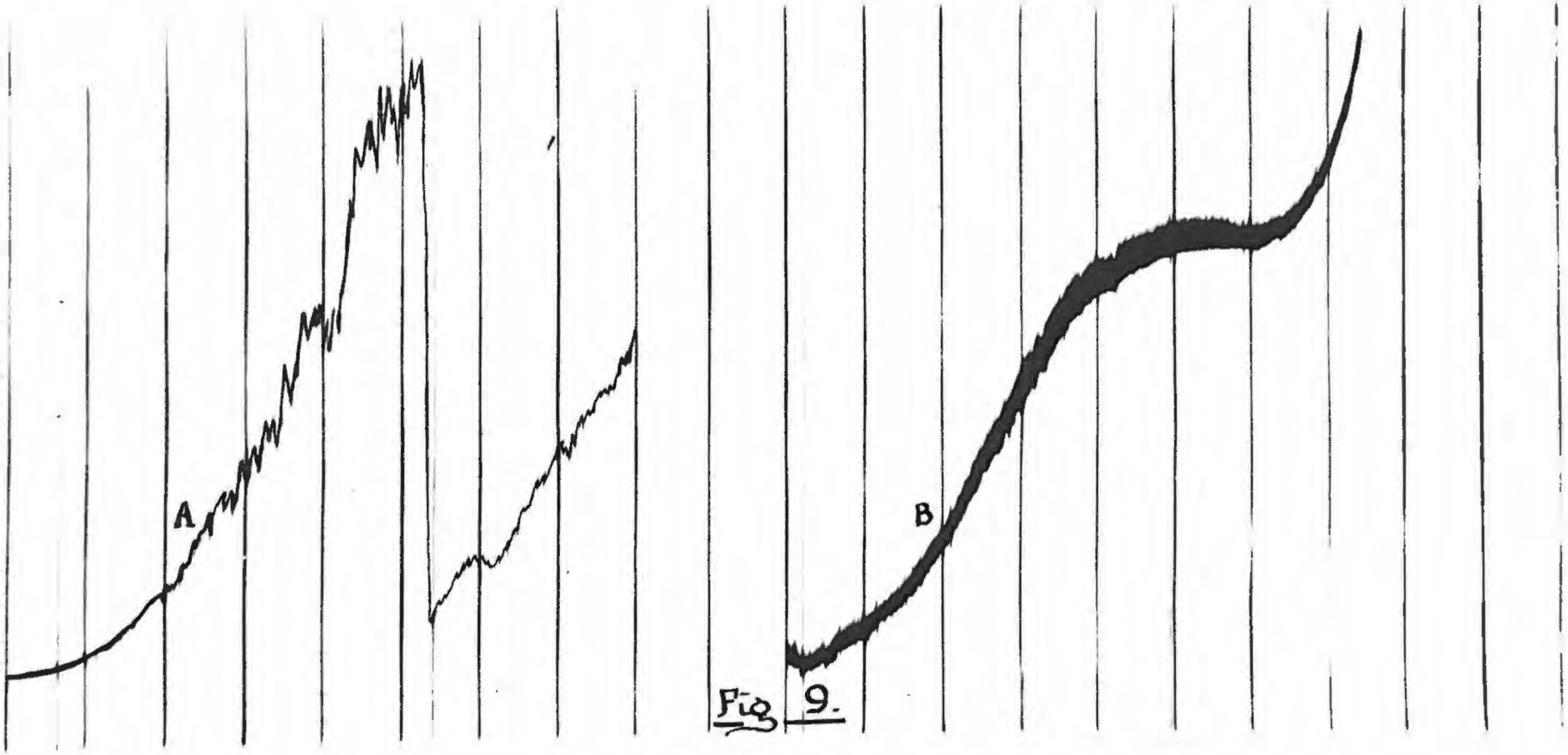


Fig 9.

molybdenum at a stationary mercury cathode also reveals a green colour due to tervalent Mo, and a brown due "to a stage of valency between four and five".

It was decided to attempt to remove excess reagent after the precipitation of K, by adding one of the other ions giving insoluble salts e.g. NH_4, Rb, Cs, Ag, thallous or mercurous ions. NH_4 is unsuitable because of its deposition potential, so mercurous and silver nitrate were tried out. Both tetramethyl ammonium iodide and hydrochloric acid were used for precipitating the excess mercurous mercury. But in neither case was a successful result obtained. Fig. 9b shows a result after precipitating Hg_2^{++} with HCl and although the wave is fairly normal, its height is about four times that theoretically due to the sodium present, and also the wave starts too soon for sodium alone.

A result of using $AgNO_3$ to precipitate excess acid, and then removing excess Ag with quaternary iodide is shown in Fig. 10a, the electrolysis being carried out after diluting the resulting solution 1:100. The halfwave potential of the wave observed does not correspond to sodium, but a very small kink was noticed as marked by the arrow

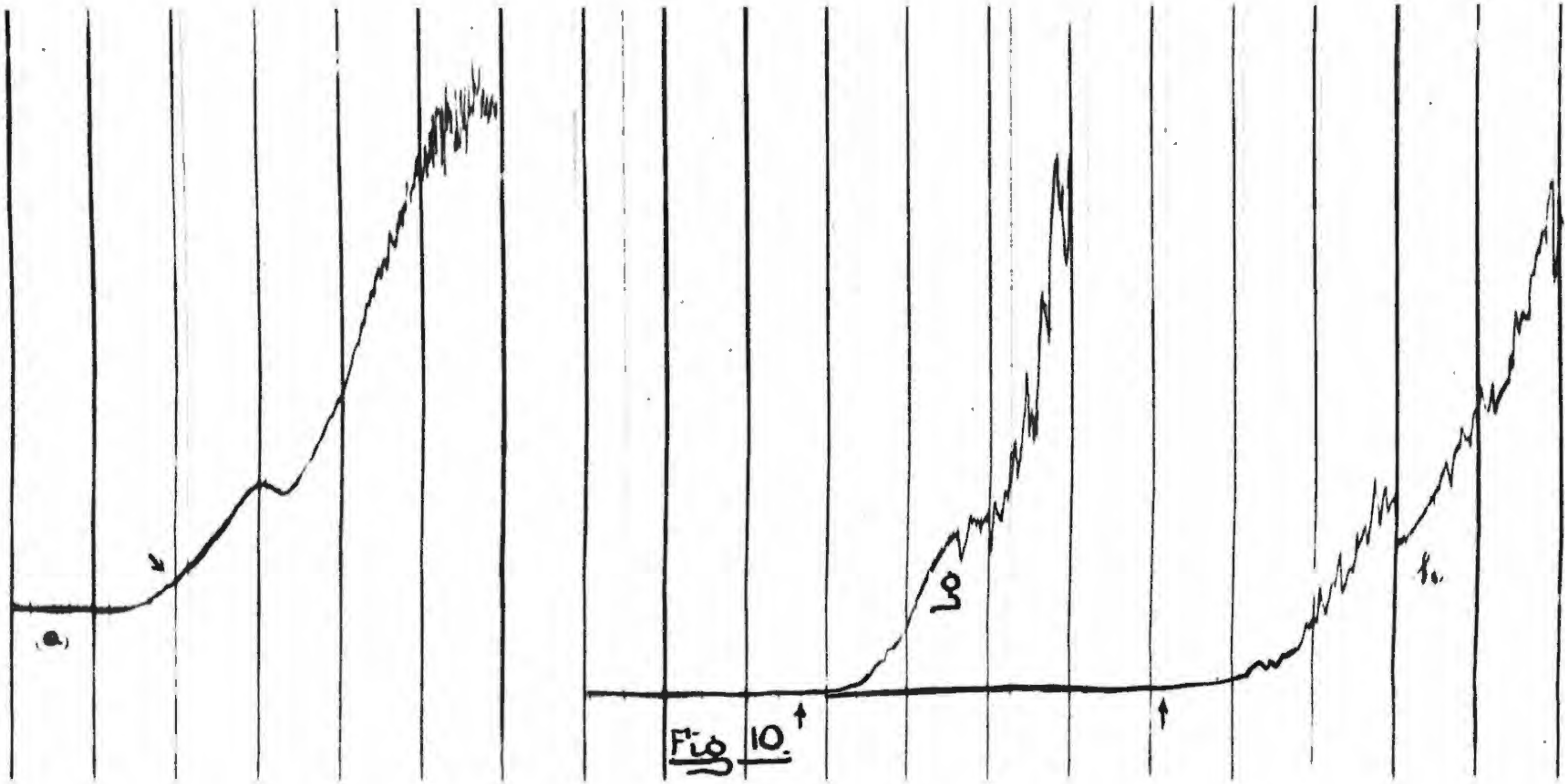


Fig 10.

and if this is regarded as the end of a first wave a halfwave potential of -2.165 volts is obtained. However, the result was certainly not clear enough for any definite statement to be made.

Fig. 10 g and h show the result of electrolysing the reagent plus quaternary iodide and base respectively, contact being made at potential 1.2 volts, the accumulator voltage being 3. Fig. 11A, B, C. shows results of the procedure suggested in the last paragraph without dilution, also at a contact potential of 1.2 volts. Even in the most promising result, 10g, the first rise in current, as indicated by the arrow, occurs at -1.96 volts whereas an N/2000 solution of KCl showed its first increase at -2.02 volts, so that these results would indicate the method to be useless, as the observed wave extends far beyond that of sodium or potassium.

(c) <u>The Oxygen Exaltation Method.</u>

The method is described by Heyrovsky and Bures (50), a summary of their paper being given below, together with some criticisms and experimental observations.

The general principle is to take two

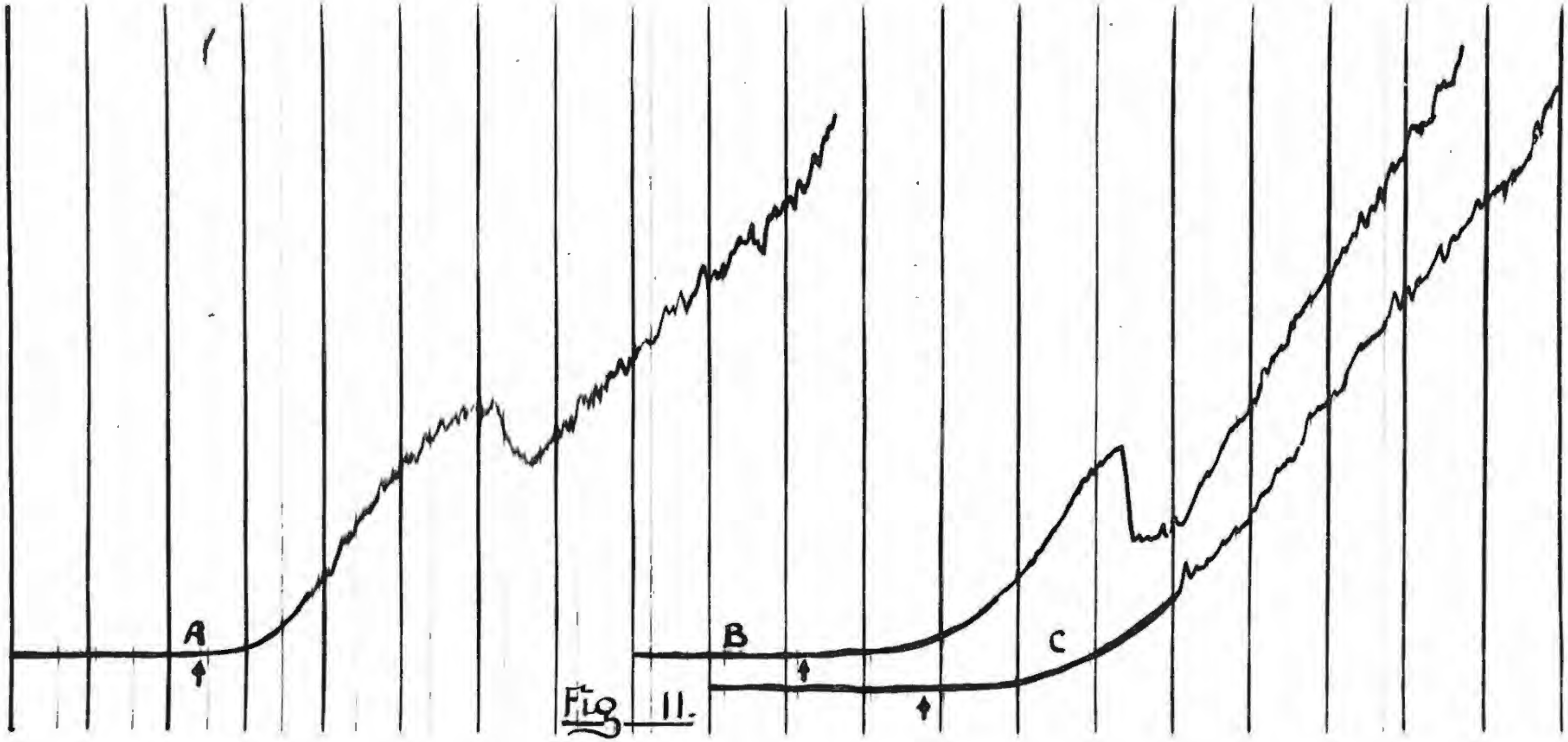


Fig 11.

polarograms of the solution, one with all oxygen removed by the passing of H_2 or N_2 and another where the solution is saturated with oxygen. Fig. 12 is a reproduction of their diagram and shows the electrolysis of an N/1000 NaCl solution at a sensitivity 1/20. The theory of the treatment is as dealt with Section I B (c).

For curve 1.

$i_{Na} = i_m + i_d$ Now $i_d = i_{Na} \frac{v}{u + v}$

$\therefore i_{Na} = i_d \frac{u + v}{v}$ (Ref. to this theory of
(exaltation c.c.c.c. 6.1934.446.

For curve 3.

Now $i = i_{Na} + i_{O_2}$

Again $i_{Na} = i_m + i_d$ and $i_m = i . \frac{u}{u + v}$

$= (i^1_{Na} + i_{O_2}) \frac{u}{u + v}$

i.e. $i^1_{Na} = i_d \frac{u + v}{v} + i_{O_2} \frac{u}{v}$

+ Exaltation $E = i^1_{Na} - i_{Na} = i_{O_2} \frac{u}{v}$

i.e. as conc. $\rightarrow 0$ + $\therefore$ $i_d \rightarrow 0$, $i^1_{Na} = i_{O_2} \frac{u}{v}$

This seems paradoxical that the wave height of a vanishingly small amount of electrolyte should be independent of further dilution, and also about

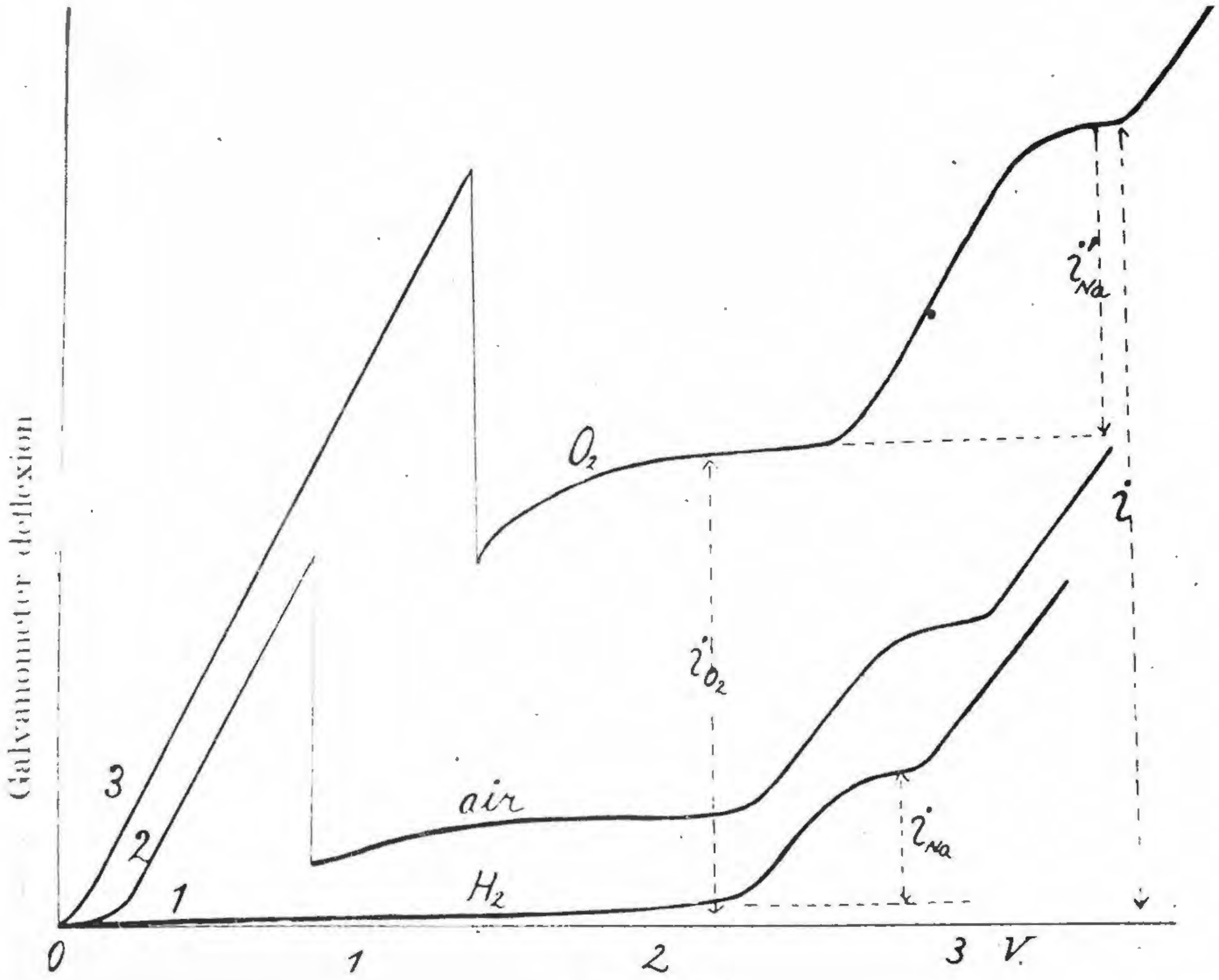


Fig. 12

equal to i_d due to the electro reduction of O_2. Actually the large potential gradient (= i x r which in very dilute solutions may reach several volts), causes the great migration current of the alkalis. thus concentration can no longer be deduced from the wave height, but may be obtained from the product i x r.

Now the shift in the halfwave potential $P_{\frac{1}{2}}$ is equal to i x r ∴ i x r can be measured ∴ r is known from which the concentration of the one electrolyte could be calculated. Note that here $P_{\frac{1}{2}}$ is used as a measure of the quantity of electrolyte.

<u>Personal Notes.</u>

(1) <u>N.B.</u> The limitation that only one electrolyte can be present.

(2) The greatest care would be needed to see that in each reading the distance between anode and cathode, and their sizes were uniform, as otherwise the "cell constant" in each case would be different.

Another method of determining concentration is to deduce the resistance of the soln. from the slope of the linear adsorption current leading to the maximum of O_2. This slope is given by $\frac{E.M.F}{i}$ and is thus equal to i x r (51).

Personal Notes.

(3) All the results quoted in the paper are for solns. of $\frac{N}{1000}$ or more dilute at a sensitivity of $\frac{1}{20}$ or $\frac{1}{25}$. In my experiments using $\frac{N}{100}$ solns. at sensitivities $\frac{1}{300}$ or $\frac{1}{500}$ no such O_2 maximum was observed. In our laboratory it is impossible at present to confirm these experiments as at the higher potentials necessary for more dilute solns. the drum windings become endangered due to warming up. The authors used a specially wound drum of high resistance wire.

Qualitative Aspect.

As deduced above $E = i_{O_2} \frac{u}{v}$. for K^+ at 18°

$\frac{E}{I_{O_2}} = 0.985$

from Cl' soln.

for Na^+ at 18° $\frac{E}{I_{O_2}} = 0.661$

and thus we can distinguish. Furthermore the composition of a mixture of Na^+ and K^+ with a common anion, say Cl' can be determined from this ratio.

If x is the molar fraction of K^+

$$\frac{u}{v} = \frac{C.x.64.4 + C(1-x).43.2}{C.\ 65.4}$$ where C = molar concn. cancels.

A table is given of $\frac{u}{v}$ for values of x from 0 to 1 by 5%. The highest possible accuracy for the ratio would be 5%. Experimental results quoted seem to justify the conclusion.

Cations of other base metals e.g. Ba and Mn shew the same effect. In place of O_2, any other easily reducible non-electrolyte may be used e.g. Quinone or hydroquinone, though it is advisable not to have too great a concn., due to the formation of maxima which take some time to fall.

<u>Personal Notes</u> (4) At the higher potentials applied (nl. above about 3 v) a fairly vigorous evolution of gas was observed, with slight fouling of the electrode, and this led to an oscillation of the galvanometer which made any extremely accurate estimation of wave height out of the question (Fig. 13c). It is surprising that the authors have not mentioned these phenomena.

(5) Criticism of the method for application to soil analysis.

The method holds possibilities only if all other non-

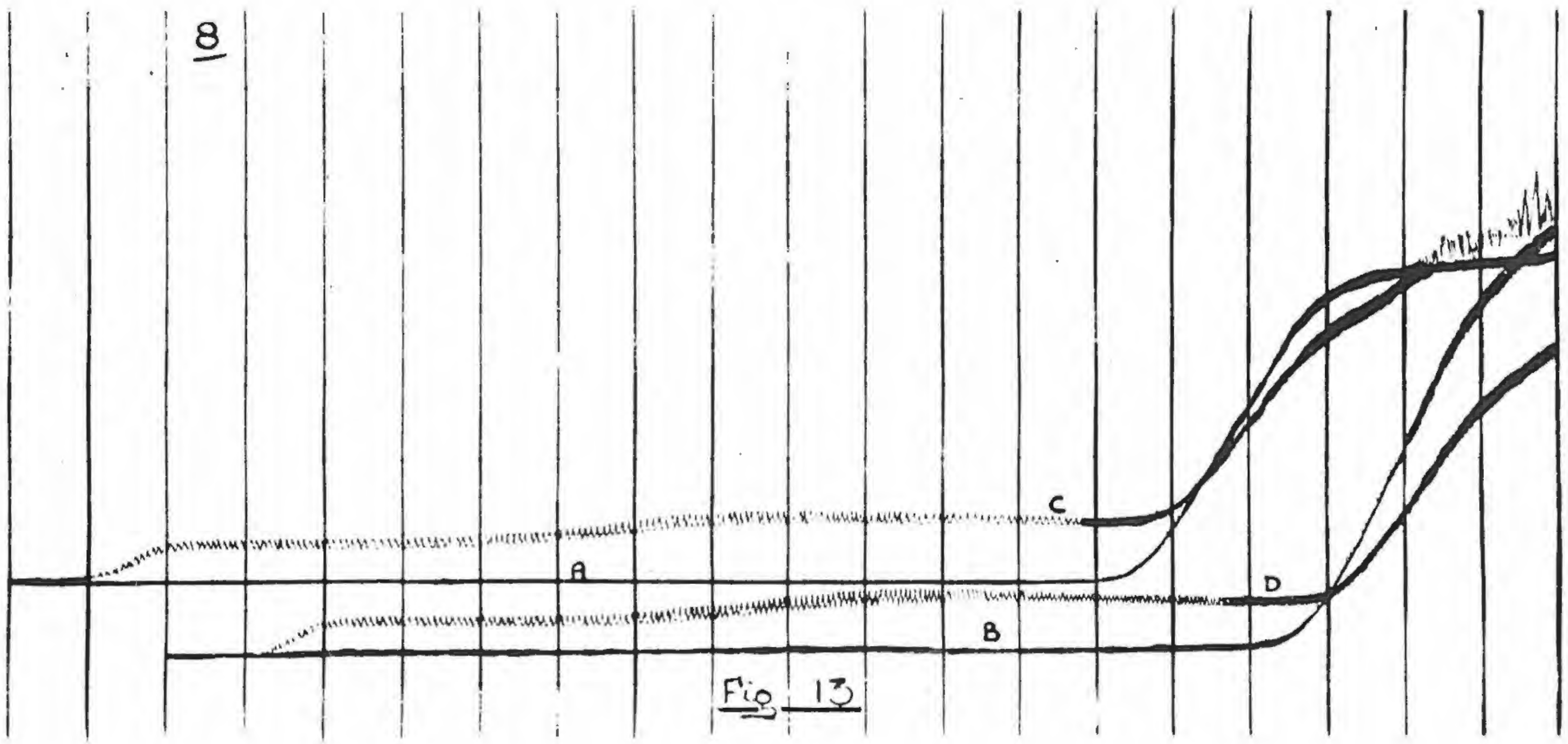


Fig 13

volatile ions are removed from the soln, and alkali metals are evaporated down as total chlorides, being then made up to a soln not less than N/100 with respect to (alkali metal)$^+$. Even then the method gives a very approximate measure of the relative amounts of Na$^+$ and K+ in the soln. To get actual amounts, we should have to adopt one of two methods:

(a) work from resistances calculated from i x r, the shift in $P_{\frac{1}{2}}$ (bearing in mind that $P_{\frac{1}{2}}$ would vary for different proportions of the alkali metals), this again leading to the "cell-constant" difficulty mentioned above. <u>or</u>

(b) repeat the polarogram in the presence of excess indifferent electrolyte, when the total wave height due to Na$^+$ and K+ could be measured. Knowing the relative proportions Na+ and K+ we could hence calculate their actual concn.

The latter method (b) is certainly practicable, but of course the reliability of the results are dependent on those obtained in the first section of the experiment.

The paper is of theoretical value, but from the practical point of view it would appear advisable to concentrate on polarographic estimation of wave height due to the alkalis and then estimate one after precipitation of the other.

Fig. 15 records the electrolysis of N/100 NaCl and KCl solutions, the respective curves being A and B with oxygen removed by the passage of electrolytic hydrogen and C and D after saturation with electrolytic oxygen. If this method became practicable it would be advisable to obtain the O_2 from a purer source than the potassium hydroxide solution electrolysed with nickel electrodes.

Other polarograms showing the complete curves up to a potential of four volts, reveal to an even greater extent the oscillations due to gas evolution.

(d) Silver Cobaltinitrite Reagent.

The possibility of using the Periodic Table to discover some compound similar to sodium cobaltinitrite but not containing sodium, was conceived. The search was stimulated by the report on a Silver cobaltinitrite reagent (52), but as in this case, a silver nitrate solution is added to a solution containing 25 gm. sodium cobaltinitrite in 150 ml. the objection to the ordinary sodium reagent is not removed.

A good deal of time was spent in an attempt to prepare the silver co-ordination compound per se according to the reaction

$$Co\ (NO_3)_2\ +\ 5\ Ag\ NO_2\ +\ 2\ HNO_2\ \ (from\ 2\ Ag\ NO_2\ +\ 2\ HNO_3)\ =\ Ag_3\ Co(NO_2)6\ +\ 2\ Ag\ NO_3\ +\ NO\ +\ H_2O$$

Normally acetic acid is used as the acidifying agent, but trouble due to silver acetate precipitation was expected, and nitric acid was used. Cobaltous nitrate was dissolved in the nitric acid in the correct proportions, and solid $Ag\ NO_2$ was added. Solution was accompanied by evolution of brown fumes. A portion of filtrate, after standing with $K\ NO_3$ for 2 days, produced a slight precipitate. Trials with HCl showed that the silver is ionisable, but the wrong complex has been formed, supporting a suggestion that the nitric acid has caused replacement of the nitrito groups by nitrato.

The slight precipitate noticed may have been due to the fact that a very small amount of the true complex remains in solution, so the reagent was electrolysed after the addition of quaternary base, with the result as shown in Fig. 14. A was taken at a sensitivity of $^1/30$ and B at $^1/300$. It will

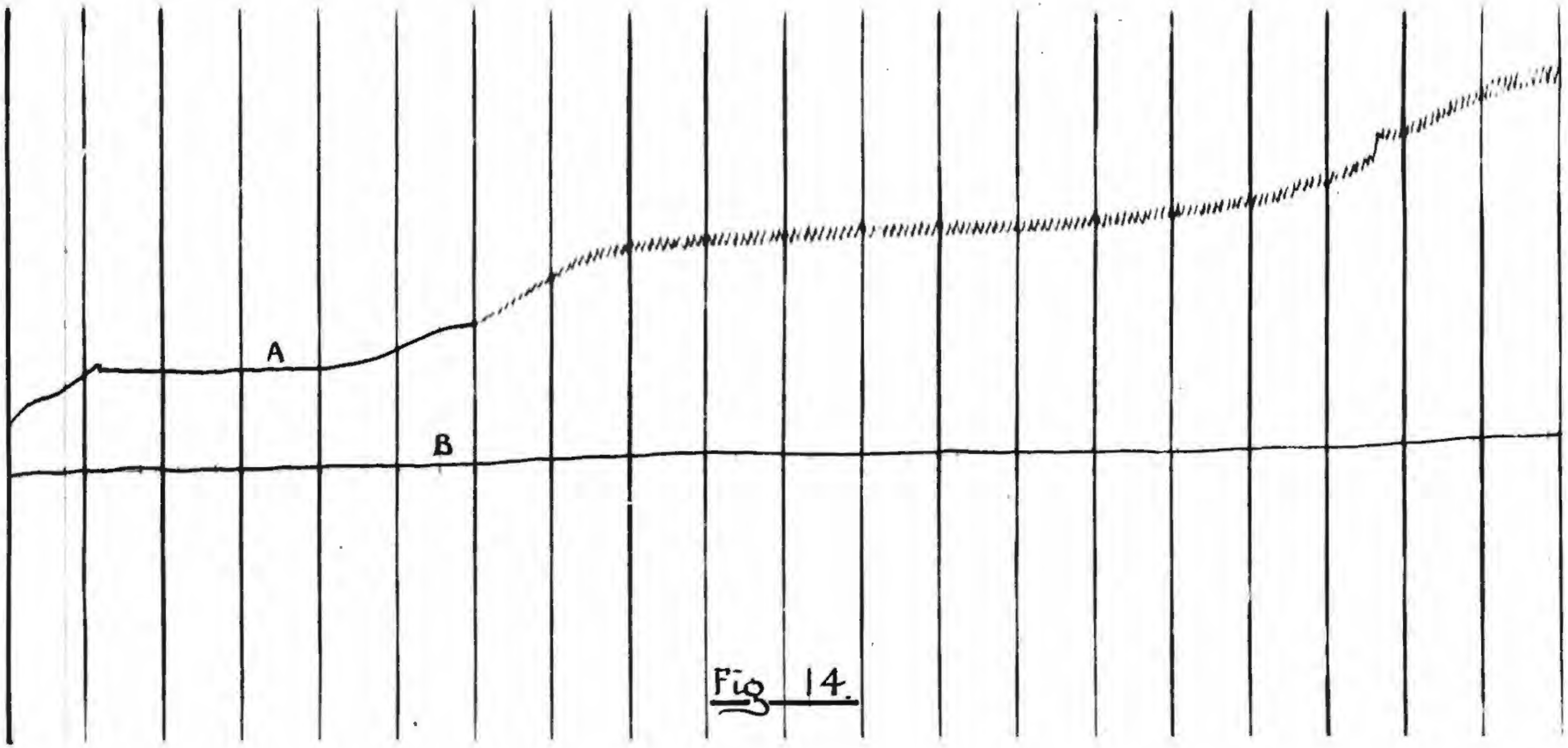


Fig 14.

be noticed that there is no complicating rise around the deposition potentials of Na or K. nl. about abscissae 14 to 16. Attempts to prepare more reagent with no complicating action around the sodium deposition potential were unsuccessful. It should be placed on record that when trying to solve this problem, it was noticed that even Schering-Kahlbaum's reagent nitric acid, sp. gr. 1.40, made up with conductivity water gave a sharp maximum in the presence of sufficient tetramethyl ammonium hydroxide to ensure alkalinity. This maximum was similar to that interfering in the second lot of reagent. Although the bubbling through of air removed the maximum in the case of the acid, this had no effect on the reagent maximum. It was thought that the non-appearance of this phenomenon in Fig. 14 was due to either the mechanical stirring employed in dissolving the $AgNO_3$, or to evaporation on the waterbath to increase the concentration, but repetition of these conditions failed to yield positive results.

However, since it was obvious that at the most only a very small proportion of the potassium was being precipitated the search was abandoned in in favour of trying out dipicrylamine. Any further investigation of the above problem might include trying the preparation with acetic acid instead of nitric, making the reagent as concentrated as is permitted by the solubility of silver acetate.

(e) Reproducibility of results.

Before the final series of experiments on dipicrylamine, it was decided to try out the constancy of results obtained from NaCl solutions of different concentrations at different sensitivities. The following results were obtained and recorded on Fig.15.

Other values obtained for the same constant at different times are 978, 1048, 1065, 1027. Results A and B seem to belong to a different group and the only explanation that can be advanced is that in the other cases, the Q.B. is a good deal more concentrated and the increased viscosity effect depresses the value of H. This is further borne out by the fact that from results C to D there is a further drop in the constant, with an increase in viscosity. In results D and E where the viscosities are practically identical a variation of about 8%

Solution.	Wave height	Sensitivity	H/c x S. x 10^{-3}
A. 5 ml. N/1000 NaCl + 1 ml. n/4 Q.B.	54.0mm.	1/20	1296
B. 5 ml. N/500 NaCl + 1 ml. Q.B.	66.2mm.	1/30	1192
C. 2 ml. N/250 NaCl + 1 ml. Q.B.	53.9mm.	1/50	1010
D. 2 ml. N/100 NaCl + 2 ml. Q.B.	63.7mm.	1/75	955
E. 2 ml. N/50 NaCl + 2 ml. Q.B.	74.3mm.	1/75	975

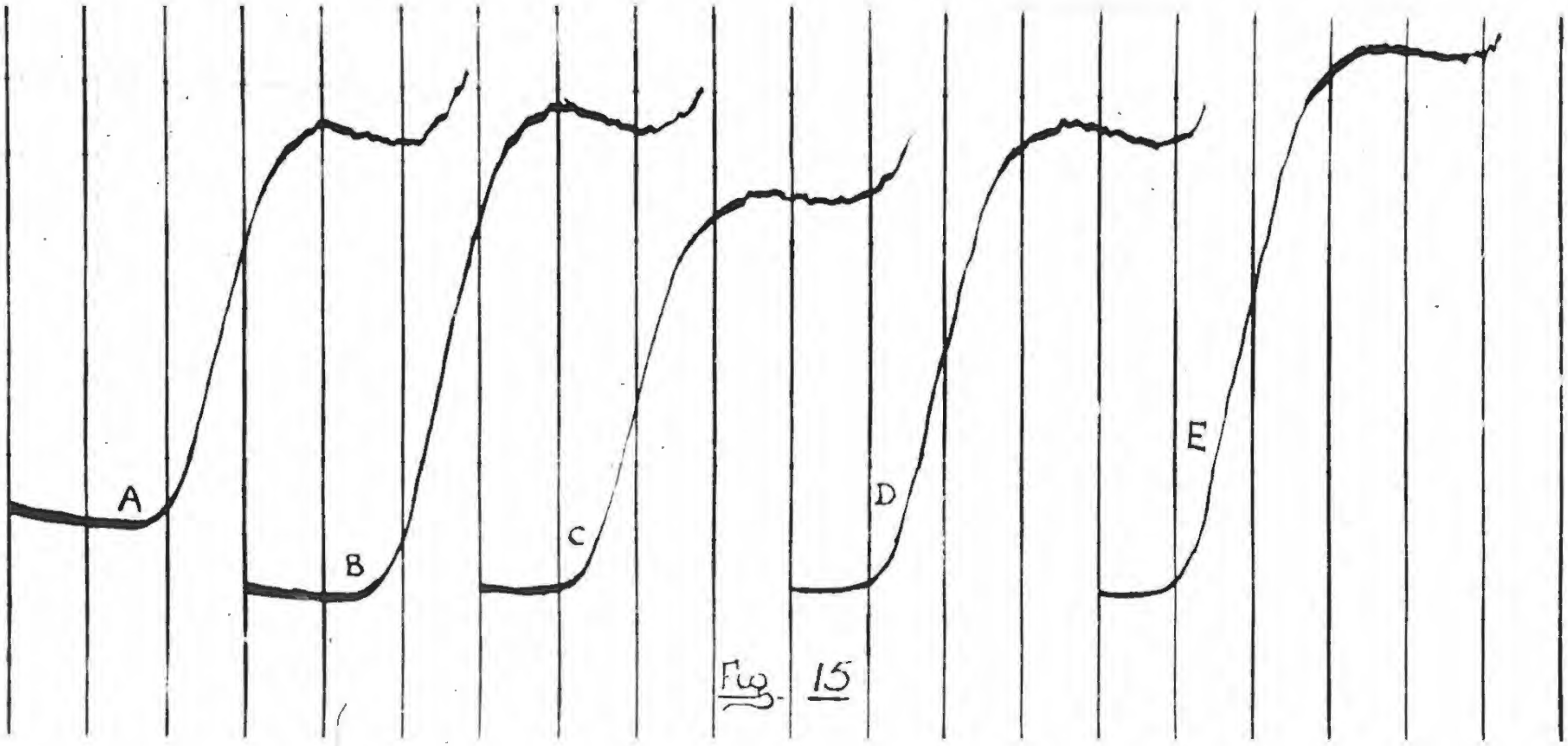


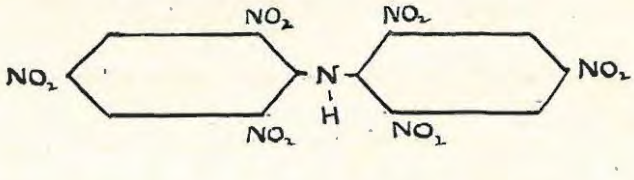
Fig. 15

is obtained, which is within the limit of accuracy claimed. The direction of the difference between D and E is possibly explained qualitatively by the fact that the concentration of Q.B. relative to that of NaCl is twice as great in D and E and consequently a greater depressing effect on the activity of Na^+ might be expected. It must also be noted that a possible source of error in the machine itself is excluded here, as both D. and E were taken at sensitivity 1/75.

It is to be regretted that time was not available for further study of similar experiments, as it is unsafe to draw definite conclusions from so few results. However, it would seem that under strictly comparable conditions the machine gives reliable results.

(f) The effect of Magnesium Dipicrylaminate.

The standardisation of the quantitative estimation of potassium with dipicrylamine (or hexanitrodiphenylamine)



has been described by Winkel and Maas (46). The substance, which functions as an acid on account of the accumulation of negative groupings, is completely insoluble in water. The K, Rb, and Cs salts are very difficulty soluble, whereas the Na, Li, Mg and Ca salts are soluble. The NH_4 salt is essentially more soluble than the K salt.

The solubility of the K salt is 1 gm/litre and as the K forms about 1/10 its weight, the solubility with respect to potassium is 1:10,000. the normality is then about 2×10^{-3}. However, excess of potassium salts or of alkali dipicrylaminate strongly reduces this figure. The Na salt is about 75 x as soluble as the K salt. The NH_4 salt is easily co-precipitated with potassium. The test solution should not react acid, or dipicrylamine will be precipitated.

To prepare the reagent, the authors dissolve the commercial NH_4 salt in hot water, and precipitate the acid with dilute suplhuric acid. An aqueous suspension of the acid is then treated on the water-bath with magnesium carbonate, and the resulting solution filtered. Concentrated NaCl solution is now added to convert to the Na salt, and if after standing for some days, impurities separate, these are filtered off. The acid is precipitated as before, and then made up with $MgCO_3$, to about n/5 to n/2.

However, the acid was supplied to us and as sodium was to be avoided, the acid was dissolved with $MgCO_3$, later re-precipitated, and redissolved to a concentration of about n/20, as fresh supplies could not have been rapidly obtained, and as dilute solutions of potassium were being investigated.

In the presence of much Na, it is recommended that the reagent be added to the boiling solution. A high concentration of NaCl disturbs the result e.g. in one case they report where the Na^+ concentration is 20 x that of K^+, a result 2.3% high was obtained.

The method of testing out the reagent was as follows: First of all, the centrifugate of 1 ml. N/20 R + 1 ml. n/4 Q.B. + 10 ml. water was electrolysed at a sensitivity of $^1/_{10}$ (Fig. 16A.) Curves B and C are of solutions respectively containing

5 ml. N/1000 KCl + 2 ml. N/200 R + 1 ml. Q.B. + 4 ml. H_2O (sens. $^1/_{10}$)

and

5 ml. N/500 KCl + 5 ml. N/20 R + 1 ml. Q.B. + 1 ml. H_2O (sens. 1/20)

It will be noted that the reagent does give a rise similar to that of the potassium, and it is possible that a trace exists in the acid supplied,

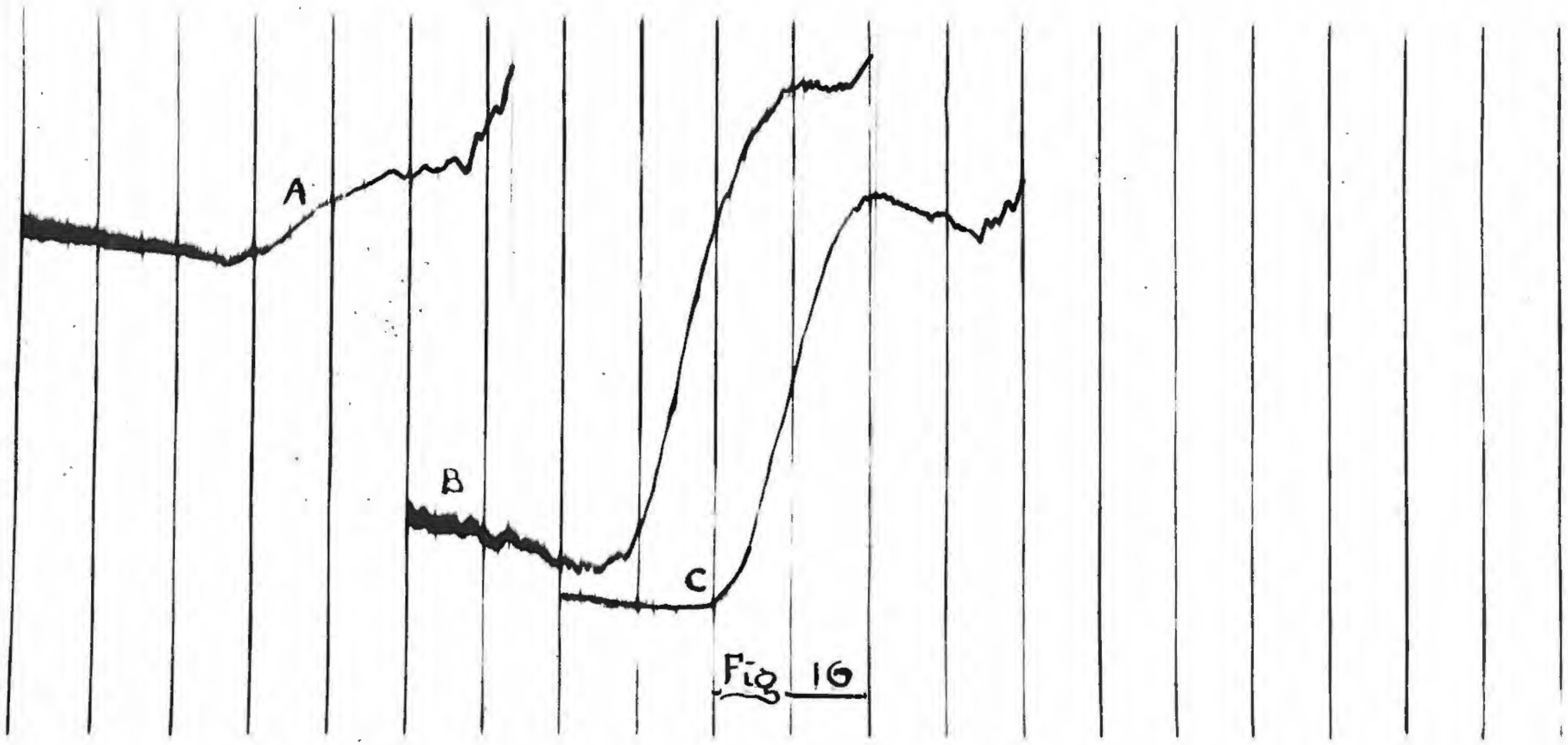


Fig 16

as every care was taken in the preparation of the reagent. However, it is small compared with the height of the waves in B and C, and as a zero error must be introduced on account of the slight solubility of potassium dipicrylaminate, this initial rise need not concern us. An important point revealed by curves B and C is that the form of the curve due to the potassium is not affected. Qualitatively, therefore, this reagent should be suitable for the separation of sodium and potassium.

For the quantitative investigation accurate n/10 solutions of G. R. NaCl and KCl were made up in conductivity water, and diluted down to give solutions of normalities .02, .01, .004, .002 and .001. Two ml. of each dilution of KCl (except .02N) were in turn added to two ml. of each dilution of NaCl, reagent and then quaternary base introduced, and then water was added to make each series up to a definite volume. For each series, two checks were included. One was an NaCl solution for comparison with the observed wave heights, and the other a solution similar to those in the series except that 2 ml. conductivity water replaced the NaCl solution, in order that a zero error might be determined. From

No.	Observed H in mm.	Sens.	H at full S.	Zero at full S.	Resultant Wave.	Na$\overset{\text{Cl}}{\text{ce}}$ Sought.	Na$\overset{\text{Cl}}{\text{ce}}$ found.	Error.
A.	50.6	1/20	1012	670	342	.000333N.	.000349N	+ 5%
B.	58.2	1/30	1746	670	1076	.000666N	.00110N	+ 65%
C.	77.6	1/30	2328	670	1758	.00133N	.00179N	+ 31%
D.	82.1	1/50	4105	670	3435	.00333N	.00350N	+ 5%
E.	82.0	1/100	8200	670	7530	.00667N	.00770N	+ 15%

the observed wave height was subtracted the zero error, and from the result was calculated the concentration of NaCl by comparison with the standard curve.

The results were frankly disappointing. As an example, the calculations for the first series are tabulated:

In the above series 2 ml. N/1000 KCl were mixed with 2 ml. of NaCl solution, 1 ml. of N/20 magnesium dipicrylaminate and 1 ml. Q.B. See Fig. 17.

In the remaining series, the total wave heights, with one exception (which was checked with a duplicate), increased with increasing Na concentrations, but the increases were irregular and the apparent zero error gave results which were completely anomalous, in one case the zero error being greater than the observed wave height.

During these experiments, every care was taken in the adjusting of dropping rate, in the pipetting out of solutions according to a definite method, and in cleaning and drying after steaming out, the electrolysis vessels and centrifuge tubes used. Consequently, other sources of error must be considered. In this connection it is unfortunate that Hohn's excellent and practical book in German (3) arrived only towards the end of the available time, and it is strongly recommended that any further research should be prefaced by a thorough study of such a book.

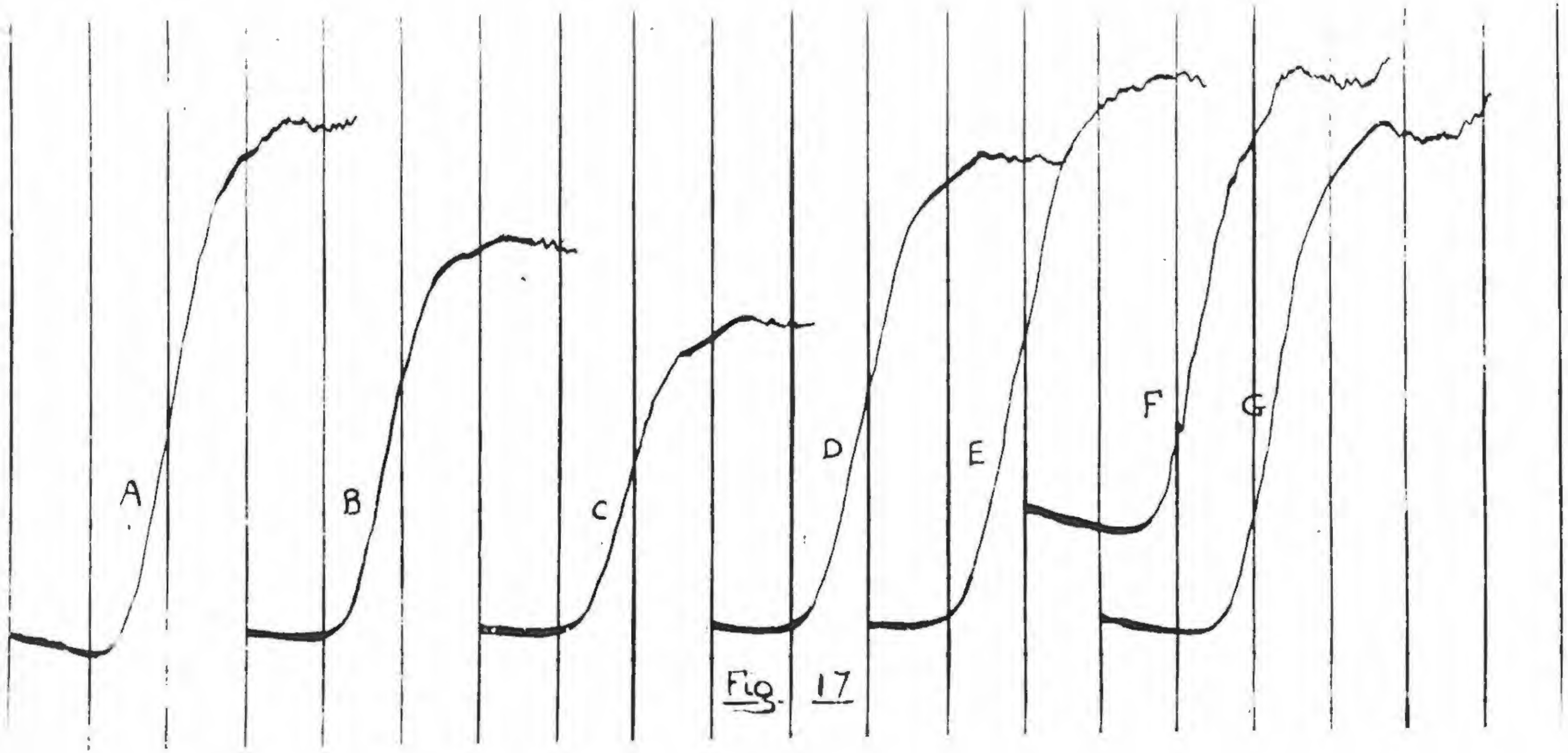


Fig. 17

Possible sources of error.

(i) Proportions of quaternary base used. In the light of the remarks on the reproducibility of results, this would seem to be the most important source of error. It need not be, if the standard curve is taken from a solution with the same percentage of indifferent electrolyte as the test, and also if the concentration is adjusted to, say, from 10 to 25 times the concentration of the ion to be determined.

(ii) Standardisation of zero error. A real difficulty is encountered here, as the solubility of potassium dipicrylaminate is influenced by alkali salt in solution. This signifies that the zero error varies with the concentration of sodium. It may be necessary to adopt a mean error corresponding to an average concentration of sodium or else find a more sensitive reagent for potassium or sodium, as the approximately N/1000 value for potassium dipicrylaminate represents a comparatively high concentration in polarographic analysis.

(iii) Distance of capillary below surface of the solution. Theoretically, this should not appreciably affect the result, and a certain amount of care was exercised to prevent a variation of more than a few mm. in this distance, or in the distance above the anode surface.

(iv) The concentration and use of the reagent. Although the reagent is more dilute than recommended, a much greater excess is added than 25%. However, values of the normality of the K salt from zero error determinations, correspond to from 0.5 to 1 x 10^{-3}N which is less than the reported value. Occasionally the solutions were allowed to stand for different times after adding the precipitant, until the quaternary base was added, but this should be covered by the above results.

SUMMARY and CONCLUSIONS.

The polarographic method has been described, and an attempt made to solve the difficulty of the simultaneous deposition of sodium and potassium. Various methods have been examined, of which precipitation of potassium with magnesium dipicrylaminate seems the most promising. The quantitative results were unsatisfactory, and possible sources of error are discussed.

The method, while very convenient, rapid and labour-saving is not as yet sufficiently standardised to be trustworthy. Careful attention to detail, and development of the technique through practice are important. Every effort should be made to place the method on as reliable a basis as possible, for it should then prove of tremendous value in soil analysis, and in industry generally.

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