"A study of the electrochemical reduction of some nickel salts in the presence of organic additives".

A thesis submitted to the University of London for the Degree of Doctor of Philosophy.

by

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June 1961
Acknowledgements.

The work described in this thesis was carried out in the laboratories of the Chemistry Department, Battersea College of Technology, under the supervision of the Head of Department, Dr. J.E. Salmon, and the direction of Dr. V.S. Griffiths, Reader and Head of the Spectroscopy Department.

The author wishes to express his sincere appreciation of the help and encouragement he has received from Dr. Griffiths during the course of this work.

Grateful thanks are also due to the technical staff for their assistance.

The award of a scholarship by Messrs. Wilmot-Breeden Ltd. is also gratefully acknowledged.
Abstract

The work describes the influence of coumarin on the polarography of the nickel ion at the dropping mercury electrode under the influence of a direct current. It was found that the nickel polarograms were distorted by adsorption of the coumarin on the surface of the electrode. The extent of the adsorption was a function of the coumarin concentration in the bulk of the solution, and also of the cathode potential. As the cathode potential was gradually made more negative the coumarin was eventually desorbed. The potential at which the nickel was reduced was coincident with that at which the desorption occurred. Studies on the influence of coumarin and some of its derivatives on the mercury electrocapillary curve indicated that they were adsorbed with the plane of the molecule parallel to the mercury surface.

Coumarin is also reducible at the dropping electrode, the reduction requiring one electron per molecule of coumarin. The reduction products have been reported in the literature as the meso and racemic forms of tetrahydrodi-4,4'-coumarinyl. In the presence of excess nickel the apparent height of the coumarin wave is reduced to one-half its value in nickel-free solutions. For this, an explanation is offered which requires that the products of the reduction of four coumarin molecules react with each nickel ion, in the diffusion layer surrounding a mercury drop, in such a way that reduction of the nickel ion can no longer take place. Evidence is given in favour of the
suggestion that, in unbuffered solutions, cathodic reduction of coumarin produces hydroxide ions, which consequently cause removal of nickel ions from the diffusion layer by precipitation of nickel hydroxide.

Further experimental evidence indicates that the phenomena controlling the electrochemical reduction of the nickel ion are confined to the boundary region between an electrolyte solution and the electrode surface.
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Section I - Introduction

A brief survey of plating from bright nickel solutions.
(i). **Bright nickel plating.**

A nickel plating solution commonly used at the present time, and one on which most of the organic bright solutions are based, is the Watts type of electrolyte. This solution basically contains the following ingredients:

- Nickel sulphate, \( \text{NiSO}_4 \cdot 7\text{H}_2\text{O} \) 250 gm./litre
- Nickel chloride, \( \text{NiCl}_2 \cdot 6\text{H}_2\text{O} \) 37.5gm./litre
- Boric acid, \( \text{H}_3\text{BO}_3 \) 25 gm./litre

The quantities may be varied to suit different requirements.

This solution produces a soft, dull deposit; but one which is capable of taking a high lustre by polishing and before the advent of fully bright solutions it was from this type of electrolyte that most of the nickel was deposited for decorative purposes.

Two main types of bright solution are currently in operation, one depending on the addition, among other things, of small amounts of cobalt salts, and the other depending on the addition of one or more complex organic compounds. The organic baths are normally preferred today on account of the lower cost of the brightening agents used in them. These solutions contain levelling agents which not only improve the lustre of the deposit but also allow a reduction of the initial polishing.

Two main classes of organic additive exist. Additives in the first class cause a levelling of the nickel deposit and by virtue of the levelling or smoothing action they
enhance the brightness of the deposit, although the deposit is never fully bright, unless subsequent mechanical polishing is given. Additives in the second class greatly increase the lustre of the deposit and are known as brighteners. Brighteners usually have little or no levelling properties.

Although empirically it is possible to obtain almost any type of deposit, from rough or dull to smooth or fully bright, the mechanisms of the levelling and brightening processes are not understood. Theories which have been suggested usually depend upon the preferential adsorption of the additive on the surface to be plated.

The function of the constituents of the Watts solution requires some discussion. The nickel sulphate supplies the bulk of the nickel for the electrodeposition. It is necessary also to have nickel chloride present in the electrolyte as chloride ions are necessary to assist anode corrosion. In absence of chloride ions a nickel anode becomes passive, resulting in anion discharge. It is now more usual to use depolarised nickel anodes containing small quantities of substances which depolarise them and eliminate passivity. This depolarisation is further aided by the addition of chloride to the electrolyte, thus aiding solution of the anode as noted above.

It is stated in text books on nickel plating technology that boric acid acts as a "buffer" in maintaining the pH of the solution at a desired value. Variation in pH has a
marked effect on the nature of the deposit obtained and so its control is very important. However, no original references are ever given to support this statement and so it is supposed that the information has evolved in the light of plating experience. The operating pH of a Watts solution is usually about pH 5 and so the buffering action at this pH cannot be due to boric acid alone, since boric acid behaves as a weak, monobasic acid with a dissociation constant of $6 \times 10^{-10}$. This topic is discussed at a later stage.

At pH values lower than 5 the cathode efficiency decreases and there is a greater tendency to pitting of the cathode, presumably due to evolution of hydrogen. In a Watts solution the cathode efficiency is about 95 per cent so that side reactions, such as hydrogen evolution, are reduced to a minimum.

When a plating bath has been in operation for some time the quality of the nickel deposit deteriorates, due to breakdown of the addition agents into materials which have harmful effects on the nickel plate. That this is indeed the case, is shown by the fact that the deposit is not improved simply by replenishing the additive. It is necessary to remove all organic material by digesting the whole solution with activated carbon for several hours.

Many organic substances have been reported in the literature to have been used as addition agents in nickel plating baths. The present work is mainly concerned with the
electrochemical reduction of some nickel salts in the presence of coumarin. A study of the reduction products of coumarin has also been made. For the bulk of the work a polarographic technique, using a dropping mercury electrode was employed. The nature of the plating solutions was also studied by means of absorption spectrophotometric, ion-exchange and pH titration techniques. A few derivatives of coumarin have also been briefly investigated.

(ii). Reduction of coumarin.

As the working life of a plating solution containing coumarin increases so the concentration of the coumarin in the bulk of the solution decreases. At the same time the quality of the nickel deposit deteriorates. Some of the coumarin is doubtless incorporated in the nickel plate, either as coumarin itself, or as a breakdown product, but some, if not most, of the coumarin is decomposed by the passage of the current, i.e. by an electrochemical reaction at either the cathode or the anode. However, the major part of the work in this thesis employs a polarographic technique using a dropping mercury electrode, at which it is not possible to study the oxidation of coumarin, and so attention has been confined to possible reduction products.

In the literature coumarin has been reported to be reduced in several ways.

Fries and Fickewirth (1) reduced coumarin by means of
zinc dust in alkaline solution and obtained, in addition to melilotic acid, \( C_6H_4(OH)CH_2CH_2CO_2H \), two tetrahydrodicoumaric acids, \( C_{18}H_{18}O_6 \), m. 280-282 and 158°C, giving rise to the anhydrides, \( C_{18}H_{14}O_4 \), m. 284 and 256°C respectively.

Zwenger (2) found that coumarin on reduction by sodium amalgam in aqueous solution gave melilotic acid, and in alcoholic solution gave a tetrahydrodicoumaric acid, \( C_{18}H_{18}O_6 \) which, however, was different from either of the acids obtained by Fries and Fickewirth, since, on heating it lost two molecules of water to give an anhydride, \( C_{18}H_{14}O_4 \), m. 223°C.

Dyson (3) also studied various reductions involving the coumarin nucleus. By condensing two molecules of salicylaldehyde with one molecule of succinic acid he obtained dicoumarin, which could be reduced by stages with sodium amalgam to tetrahydrodicoumaric acid, which on heating above 100°C gave tetrahydrodicoumarin, \( C_{18}H_{14}O_4 \), m. 222-4°C. The reactions involved are given in the following sequence:
-13-

\[
\begin{align*}
\text{tetrahydrodicoumaric acid} & \quad \text{dihydrodicoumaric acid} \\
C_{18}H_{18}O_6 & \quad C_{18}H_{12}O_4
\end{align*}
\]

Heat above 100°:

\[
\begin{align*}
\text{tetrahydrodicoumarin} & \quad \text{dihydridicoumarin} \\
\text{m. } 222-4^\circ & \quad \text{m. } 256^\circ
\end{align*}
\]
The tetrahydrodicoumarin obtained by Dyson possesses two similar asymmetric carbon atoms and so should give rise to a dl-form and a meso-form. Asahina and Fujita (4) repeated the reduction of Dyson's dicoumarin and were able to isolate two tetrahydrodicoumarins m. 243, 248° which, when mixed melted at 222-4°.

Fries and Fickewirth designated to their tetrahydrodicoumaric acids the Dyson formulae shown above, in spite of the difference in melting point. They found that Dyson's tetrahydrodicoumarin on reduction gave derivatives of succinic acid CO₂H.CH₇CHR.CH₇.CO₂H, whereas coumarin, on direct reduction, gave β,γ-disubstituted adipic acids, CO₂H.CH₂CHR.CH₂.CO₂H. Thus, neither of the tetrahydrodicoumarins of Fries and Fickewirth are identical with those of Dyson. The formulae for the isomers obtained by Fries and Fickewirth are thus

\[
C_{18}H_{14}O_4, \text{ meso- and racemic } m. 256, 284°
\]

A substituted coumarin has also been reduced in acid solution by means of zinc and acetic acid, by Smith and Denyes (5) giving monomolecular and dimolecular reduction products. They claim that the monomolecular product is a substituted dihydrocoumarin and the dimolecular product is almost certainly linked in the 4,4' structure.
Although not reported in the literature it seems possible that coumarin may be reduced to dihydrocoumarin $C_9H_8O_2$, especially at a cathode at which hydrogen is being evolved. It has been reported (6,7) that coumarin and related compounds can be hydrogenated to dihydrocoumarin over Raney nickel. Whether dihydrocoumarin is stable in neutral or slightly acid solutions is uncertain, as there seems to be a possibility that the hetero ring can be hydrolysed irreversibly to melilotic acid:

$$\text{dihydrocoumarin} + \text{H}_2\text{O} \rightarrow \text{melilotic acid}$$

Zwenger has already reported melilotic acid as a reduction product in the case of reduction by sodium amalgam in aqueous solution.

Coumarin is reducible polarographically. Harle and Lyons (8) were able to obtain a reduction product on a large enough scale to recrystallise it into two compounds, m. 247, 284°. They claim that these products were the meso- and racemic forms of tetrahydrodicoumarin, linked in the 4,4' position, obtained by Fries and Pickewirth. Patzak and Neugebauer (9) were able to reduce coumarin polarographically in alcoholic tetraethylammonium bromide, in two steps, the second of these presumably corresponding to reduction to dihydrocoumarin. This topic however, is discussed more fully
Thus, a wide range of reduction products is possible:

in section III(i).

-16-

-CH

H	CH

\( \text{Na/Hg EtOH} \) \( \text{Na/Hg H}_2\text{O} \) \( \text{hydrogenation} \) \( \text{Zn/acid} \) \( \text{alkaline Zn H}_2\text{O} \) \( \text{polarographic} \)

\( \text{tetrahydrodicoumaric acids} \)

\( -\text{H}_2\text{O} \)

\( \text{electrolytic reduction?} \)

\( \text{tetrahydrodi-3,3'-coumarinyl, meso and racemic forms} \)

\( \text{melilotic acid} \) \( \text{distil} \)

\( \text{tetrahydrodi-4,4'-coumarinyl, meso and racemic forms} \)

\( \text{m. 243,248°} \)

\( \text{m. 82-84°} \)

\( \text{m. 256,284°} \)
However, not all of these reduction products are likely to appear in an electrolysis in which the pH is maintained at about 5. According to Harle and Lyons, who studied the polarographic behaviour and absorption spectra at various pH values, coumarin exists entirely in the lactone form at pH values less than 6.8 and entirely as coumarinic acid at pH values greater than 11.2. At intermediate pH values both forms are present. This result has been confirmed by Mattoo (10) who calculated the equilibrium constant for the hydrolysis of the lactone ring. He obtained the value $pK^\text{thermodynamic}_a = 9.56$ (at 25$^\circ$).

Harle and Lyons found that the dimolecular reduction product was insoluble in sodium carbonate solution but soluble in hot, concentrated sodium hydroxide. On acidification of this solution a precipitate was obtained. In view of these results it seems unlikely that the tetrhydrodicoumaric acids would be found in a plating bath.

(iii) Possible mechanisms of levelling.

It has been stated previously that the mechanisms of levelling and brightening are not understood. However, it is found that organic compounds which have a levelling action on plating solutions also have a considerable effect on the cathode potential. This is possibly due to the adsorption of the additive on to the surface of the electrode. Work has been reported by Frumkin (11) on the adsorption of organic
compounds at a metal-electrolyte interface in which it appears that the degree of adsorption on an electrode is closely related to the potential applied to it. This subject is dealt with in later sections.

The relationship between the degree of adsorption of an organic compound at an electrode-electrolyte interface with applied potential is likely to depend on the nature of various constituent groups contained in the molecule. Additives used in nickel plating baths often have very high dipole moments. Examples are thiourea, for which $\mu = 4.89$ D (12) or 7.6 D (13) (both determinations in dioxane), and coumarin, for which $\mu = \text{ca. } 4.5$ D (14,15) (both determinations in benzene). Thus, in section IV the dipole moments of some coumarin derivatives have been measured and attempts have been made to correlate these results with the degree of adsorption of the derivative at a mercury electrode.

A possibility which has not so far been considered is that of complex ion formation between the organic additive and nickel ions. It is possible that such a complex ion, once formed, is reduced electrolytically by a different mechanism from that of a simple nickel ion. Indeed, it has been found by Aten and Boerlage (16) that a finer grained deposit was obtained by decreasing the effective metal ion concentration in the solution adjacent to the cathode by a number of methods, including that of complex ion formation. Thus, the possibility of the formation of a nickel-coumarin complex was investigated.
Section II

A review on the polarographic method.
Foreword.

Some aspects of the polarographic method have been well treated in text-books on polarography. An outstanding example is the case in which a state of extreme concentration polarization exists at the surface of the microelectrode. Under such conditions the current obtained is governed by the rate of diffusion of material to the electrode surface. The treatment of such diffusion-controlled currents is well-known, as is also the method of treatment of "reversible" polarographic waves. However, the method of treatment of "irreversible" polarographic waves is not so widely known and a comprehensive survey is difficult to obtain from a single source. An adequate survey of the treatment of irreversible polarographic waves is given in this section as the results have been made use of in the experimental sections of this thesis. For completeness, and also for easy reference purposes, the fundamental theory is also included, and it is hoped that the advantages to be gained in clarity more than offset the disadvantages suffered by the increase in volume.
(i). General principles of polarography.

**Introduction** - The polarographic method of chemical analysis is based on the observations of Professor Heyrovsky of Prague University. The development of the subject up to the present time is due in large part to his efforts and to those of his colleagues. The method is based on the interpretation of the current-voltage curves that are obtained when solutions of electroreducible or electro-oxidisable substances are electrolysed in a cell in which one electrode consists of mercury falling dropwise from a very fine bore glass capillary tube. The easily polarized droplets of mercury emerge regularly from the capillary tube, and are continuously exposing a fresh mercury surface to the electrolyte, thus preventing the accumulation of any products of electrolysis at the electrode. The other electrode is a large unpolarized pool of mercury. From the unique characteristics of such current-voltage curves both the species and concentration of the electroreducible or electro-oxidisable substances present in the solution can be determined.

In 1925 Heyrovsky and Shikata (17) invented an instrument with which dropping electrode current-voltage curves could be obtained automatically and recorded photographically. The name"polarograph" was coined by Heyrovsky to indicate that this instrument graphically records current-voltage curves obtained with polarized electrodes. The automatically recorded curves are called"polarograms".
The term "polarography" and the various terms derived from it have found general use although the term "voltammetry" has sometimes been used.

**General principles.** - A typical arrangement for obtaining current-voltage curves with the dropping mercury electrode is shown schematically in figure 1. The solution to be analysed is placed in a suitable cell A, through the neck of which the dropping mercury electrode B is introduced so that the lower end of the capillary is immersed in the solution. This electrode consists of a mercury reservoir joined to a piece of fine glass capillary tubing. The height of the reservoir above the lower end of the capillary is adjusted until the mercury falls freely into the solution at the rate of one drop in a time interval of about two to six seconds. The mercury pool C is at the bottom of the electrolysis cell and is joined via the sliding contact D of the rheostat E to the positive side of the battery F. (This is the more usual arrangement where the d.m.e. functions as the cathode. In
certain electrolyses the d.m.e. can function as the anode). The negative pole of the battery is connected through the sensitive mirror galvanometer G to the reservoir of the dropping electrode. The galvanometer records currents flowing in the circuit and a very wide range of currents is measurable by using an Ayrton shunt in conjunction with it. By adjusting D, the voltage applied across the cell can be varied from zero up to the maximum e.m.f. of battery F, and for each voltage the corresponding current is indicated by the galvanometer. The galvanometer readings oscillate between a maximum and minimum value owing to the periodic change in area as each drop grows and falls. The value of the average current at each applied voltage is required and is readily determined by employing a galvanometer with a relatively long period. The technique therefore is to apply a gradually increasing voltage, starting from zero applied voltage by altering the position of D, and to read the galvanometer deflection corresponding to each setting of D. A current-voltage graph is then constructed from the results by plotting the average galvanometer deflections converted to microamperes along a vertical axis against the applied potential, in volts, along a horizontal axis.

A typical current-voltage curve is shown in figure 2, which illustrates the result of electrolysing an air-free solution of lead ions in a suitable potassium chloride solution. (Potassium chloride is necessary to prevent
electrical migration). At first only a very small current, the "residual current" flows through the cell until the decomposition potential is reached. When the decomposition potential is exceeded electrolysis begins, consisting of the discharge of lead ions at the dropping mercury cathode to form an extremely dilute lead amalgam, and the anodic dissolution of mercury, with the subsequent formation of calomel, at the large, quiet anode. The reactions are represented thus:-

\[ Zn^{++} + 2e + Hg \rightarrow Zn(Hg) \quad \text{(dropping electrode)} \]

\[ 2Hg + 2Cl^- \rightarrow 2e + Hg_2Cl_2 \quad \text{(quiet electrode)} \]

As the applied e.m.f. is increased further the current does not increase indefinitely, but gradually approaches a limiting value and finally becomes constant (apart from a slight increase due to the residual current) and independent of further increases in the applied e.m.f. Other factors remaining constant, this limiting current is directly proportional to the concentration of lead ions in the solution. This fact is the basis of quantitative polarographic analysis.

The conditions leading to the production of this
limiting current are explained as follows. As the lead ions are discharged at the cathode their concentration in the immediate neighbourhood of the mercury is reduced and this loss is compensated by the diffusion of fresh lead ions from the bulk of the solution. The rate of this diffusion is governed by the difference in concentration between the lead ions in the cathode layer and in the remainder of the solution. As the applied voltage is slowly increased above the decomposition potential, more current flows because more lead ions are being discharged at the cathode and so the rate of diffusion increases. Eventually, on increasing the applied voltage still further, a condition is reached when the lead ions are discharged so rapidly that the lead ion concentration in the cathode layer is virtually zero. The difference in concentration between the cathode layer and the rest of the solution is then simply equal to the concentration of lead in the bulk of the solution. Under these circumstances a steady rate of diffusion is set up giving rise to a steady "diffusion current" which is practically unaffected by further increases in the applied voltage. The magnitude of the diffusion current depends on a number of factors and these will be discussed in a later section.

The potential of the point on the current-voltage curve at which the diffusion current is one-half of its limiting value is known as the half-wave potential (E_{1/2}). This potential is of great significance since it is independent of the
concentration of the reacting ions in the solution, the size of the mercury drops, and of the galvanometer sensitivity. The half-wave potential is characteristic of the kind of ion being deposited from a given base electrolyte and due to its invariance it is preferable to quote the half-wave potential rather than the decomposition potential of a reducible ion since the latter varies with concentration of the reducible ion. The theory of the half-wave potential is discussed at a later stage. The characterisation of the half-wave potentials in "unknown" solutions forms the basis of qualitative polarographic analysis.

The necessary conditions that must be fulfilled in order to obtain a limiting current are that at least one electrode of the cell is very small, and that the concentration of the reducible substance is not too large. That is, conditions must be such as to favour the attainment of an extreme state of concentration polarization. Limiting currents are therefore not peculiar to the dropping mercury electrode, but may be also obtained with small solid electrodes, such as a platinum microelectrode, or with a small quiet mercury electrode. In the present work, attention has been confined to the dropping mercury electrode which has certain advantages over the other types. The current observed with the dropping mercury electrode becomes steady immediately at each new setting of the applied e.m.f. and is independent of the time of electrolysis. This favourable behaviour is due to the fact that a fresh mercury
surface is continuously being exposed by the growing drops; the phenomena at a given drop are exactly duplicated at its successor. Thus the dropping electrode is easily prepared, gives reproducible results, and, as will be shown later, results obtained with one capillary can be directly compared with results obtained with another capillary.

The dropping electrode is generally employed as cathode (electroreduction) but it is also possible to employ it as anode in the study of certain electro-oxidation reactions. However, the use of the dropping electrode as anode is limited to those reactions whose oxidation potential is smaller than the potential at which the mercury itself is oxidised (+0.4 volt vs. the S.C.E.).

The reason for using a relatively large, quiet pool of mercury as the second electrode of the cell is that such an electrode remains practically depolarized when the solution contains halide or other ions which form insoluble salts with mercury. It thus retains a practically constant potential independent of the applied e.m.f., and only the dropping electrode becomes polarized. Thus, in solutions of chlorides the quiet electrode acquires a potential equal to the potential of a calomel electrode at the same chloride ion activity.

A supporting electrolyte should be incorporated in the solution under test to prevent electrical migration of ions to the cathode; that is, to ensure that the limiting current is entirely a diffusion current. To ensure complete
elimination of the migration current the supporting electrolyte
congcentration should be at least fifty times larger than that
of the reducible substance. The essential requirements of a
base electrolyte are as follows:-

(1). The decomposition potential of its cation should
be appreciably more negative than that of the substance to be
determined.

(2). The ions being studied should exist in the base
electrolyte in one definite form, either as simple hydrated
ions or stable complexes.

(3). The anion of the base electrolyte should depolarize
the anode, so that it remains at a constant potential at
various values of the applied e.m.f.

(4). If more than one reducible substance is present in
solution the base electrolyte should give well-defined and
well-separated steps for all constituents.

(5). It should not cause any of the substances under
determination to be precipitated.

A large number of supporting electrolytes are available.
Simple salts of the alkali and alkaline earth metals can be
used for determination of the baser metals. The mineral acids
are also widely used. Tetra-alkylammonium ions have the very
negative reduction potential of about -2.6 volts versus the
saturated calomel electrode (S.C.E.), and can thus be used
for the determination of the alkali and alkaline earth metals.
Throughout the present work the supporting electrolyte has
been chosen with respect to the properties required of it.
The current-voltage curves do not always have the ideal shapes shown in figure 2. Sometimes the diffusion current rises to a very high peak, subsequently falling to its steady limiting value, instead of proceeding directly to this limiting value. Peaks on current-voltage curves are known as "maxima" and they must be suppressed for accurate quantitative work. In many cases these maxima can be removed by means of colloids or other adsorbable substances, but even small amounts of these substances may appreciably change the magnitude of the normal diffusion current of an ion and so precautions must be taken in their use.

Oxygen is reducible at the dropping mercury electrode giving two waves. The first, corresponding to a reduction to hydrogen peroxide, is fairly steep, having a half-wave potential of about -0.15 volts vs. the S.C.E. The second, corresponding to a reduction of the peroxide to hydroxide ions, is very ill-defined and extends over an appreciable voltage range. Its half-wave potential is -0.94 volts vs. the S.C.E. Since these steps interfere with the determination of other reducible substances oxygen should be removed from the test solutions before diffusion currents are recorded. This is conveniently done by passing pure nitrogen or hydrogen through the test solution in the polarograph cell for about ten minutes before recording polarograms. The extent to which the oxygen has been removed can readily be determined polarographically. The last traces of oxygen are not readily
removed by this method. From neutral or alkaline solutions oxygen can be removed by the addition of small amounts of sodium sulphite.

**Scope, accuracy and limitations of polarographic analysis.** - Since so many diverse types of substances are subject to electrolytic reduction or oxidation, the scope of the polarographic method is potentially very great. In the field of inorganic analysis it has been applied to the determination of practically all of the common metals and other reducible ions. A large variety of organic substances are reducible at the dropping electrode and yield well-defined waves. Not all organic compounds do give well-defined waves. Applications of the polarographic method to organic analysis are somewhat limited as related compounds generally reduce at similar potentials, so that it is impossible to distinguish them polarographically.

Under ordinary conditions the accuracy of the polarographic method is of the order of ±2 per cent in the concentration range from about $10^{-4}$ to $10^{-2}$ molar, and about ±5 per cent between $10^{-5}$ and $10^{-4}$ molar. This compares favourably with the accuracy of other microanalytical methods.

* * * * * * *
(ii). Theoretical principles - the diffusion current.

Introduction. - The phenomenon of the limiting current obtained with the dropping electrode is caused by the extreme state of concentration polarization which results from the depletion of the concentration of the electroreducible or electro-oxidisable substance at the electrode surface by the electrode reaction. In the most general case reducible or oxidisable ions are supplied to the depleted region at the electrode surface by two forces: (1) a diffusive force, proportional to the concentration gradient at the electrode surface, and (2) an electrical force, proportional to the electrical potential difference between the surface and the solution. Thus, the limiting current can be regarded as the sum of a "diffusion current" and a "migration current", the latter being due to the electrical forces.

When a large excess of an indifferent salt (i.e. a salt whose ions do not participate in the electrode reaction) is added to a solution containing a relatively small concentration of the reducible or oxidisable ions, the current through the solution will be carried practically entirely by the large excess of indifferent ions, i.e. the transference number of the reacting ions is reduced practically to zero. Under these conditions the electrical forces on the reducible ions are nullified, the migration component of the limiting current is practically completely eliminated, and the limiting current becomes solely a diffusion current.
In the case of uncharged substances diffusion usually plays the major role in governing the limiting current, even when the ionic concentration of the solution is small. However, in the case of dipolar uncharged molecules there will be a certain amount of electrical migration unless the solution contains a relatively large concentration of an indifferent salt.

For the evaluation of diffusion currents it is convenient to discuss the theory of diffusion to plane and spherical solid microelectrodes before proceeding to the more complicated theory of diffusion to the dropping mercury electrode and the calculation of diffusion currents thereat.

**Linear diffusion.** The simplest diffusion process is one which takes place in only a single direction, and this is termed linear diffusion. If a linear diffusion cylinder is considered as shown in figure 3, in which diffusion is proceeding upward in the negative x-direction, the number of moles of the diffusing substance that diffuse across a given cross-sectional plane of area $A$ cm$^2$ in the infinitesimal interval of time $dt$ is proportional to the concentration gradient $\partial C/\partial x$ at the plane in question, and
is expressible by
\[ \frac{dN}{dt} = DA \frac{\partial C}{\partial x} \cdot dt \quad \ldots \ldots \ldots \ldots \ldots \ldots \quad (1) \]

The proportionality constant \( D \) is the "diffusion coefficient" and is numerically equal to the number of moles of the substance that diffuse across unit area in unit time when the concentration gradient is unity. This relation was first recognised by Fick (18) and it is usually referred to as Fick's First Law.

It is more convenient for the present purposes to consider the number of moles of substance that diffuse through unit area in unit time, and this is called the unit flow or flux. The flux at a plane at a distance \( x \) from the origin, designated by \( f(x,t) \) is given by
\[ f(x,t) = \frac{dN}{A \cdot dt} = D \frac{\partial C(x,t)}{\partial x} \quad \ldots \ldots \ldots \ldots \ldots \ldots \quad (2) \]

Since the concentration, and the concentration gradient, at a given plane decrease with time as the diffusion proceeds, the flux decreases accordingly. Hence, equation (2) is only valid at a given plane at a given instant (instantaneous flux), and this condition is denoted by the subscripts \( x \) and \( t \).

To calculate the total amount of material that will diffuse across a given plane in a finite interval of time it is necessary to have a knowledge of the change in concentration with time at the plane in question. It is thus necessary to know \( C \) both as a function of time and distance \( x \). The change in concentration with time between two planes separated by the
infinitesimal distance $dx$ is equal to the difference between the flux of substance entering across the plane at $x+dx$ and the flux of substance leaving across the plane at $x$; that is

$$\frac{\partial C(x,t)}{\partial t} = \frac{f(x+dx,t) - f(x,t)}{dx} \quad \ldots \ldots \quad (3)$$

We also have

$$f(x+dx,t) = f(x,t) + \frac{\partial f(x,t)}{\partial x} \ dx \quad \ldots \ldots \quad (4)$$

and since, from equation (2)

$$\frac{\partial f(x,t)}{\partial x} = D \frac{\partial^2 C(x,t)}{\partial x^2} \quad \ldots \ldots \quad (5)$$

it is found that the change in concentration with time at a given plane at a given instant is given by

$$\frac{\partial C(x,t)}{\partial t} = D \frac{\partial^2 C(x,t)}{\partial x^2} \quad \ldots \ldots \quad (6)$$

This is the fundamental equation for linear diffusion, and it is sometimes referred to as Fick's Second Law.

**Symmetrical spherical diffusion.** — In symmetrical spherical diffusion the diffusing substance diffuses toward the centre of a sphere along its radii. The diffusion field in this case is a spherical shell surrounding the electrode, as shown in figure 4. The radius of the electrode is designated by $r_0$ and the distance of the diffusion shell by $r$. It is assumed that the

![Diagram of symmetrical spherical diffusion to a solid spherical microelectrode.](image)
The area of the spherical surface is equal to $4\pi r^2$, and the number of moles $dN(r,t)$ that diffuse across this surface in the time $dt$ is given by the following expression, analogous to Fick's First Law,

$$dN(r,t) = 4\pi r^2 D \frac{\partial C(r,t)}{\partial r} dt \quad \ldots \ldots \quad (7)$$

and the flux at $r$ is

$$f(r,t) = \frac{dN(r,t)}{4\pi r^2 dt} = D \frac{\partial C(r,t)}{\partial r} \quad \ldots \ldots \quad (8)$$

In order to calculate the total amount of material that will diffuse across a given shell in a finite interval of time it is necessary to have a knowledge of the change in concentration with time at the shell in question; that is, it is necessary to know $C$ both as a function of time and distance $r$. The change in concentration in the spherical shell of thickness $dr$ in the time $dt$ is evidently equal to the difference between the number of moles which enter the shell at $r+dr$ and the number which leave at $r$, divided by the volume of the shell which is $4\pi r^2 dr$; that is

$$dC(r,t) = \frac{dN(r+dr,t) - dN(r,t)}{4\pi r^2 dr} \quad \ldots \ldots \quad (9)$$

Therefore, the rate of change of the concentration with time at a given value of $r$ and a given time $t$ is

$$\frac{\partial C(r,t)}{\partial t} = \frac{dN(r+dr,t) - dN(r,t)}{4\pi r^2 dr \cdot dt} \quad \ldots \ldots \quad (10)$$
It is now necessary to find an expression for the value of \(dN(r+dr,t)\) since \(dN(r,t)\) is given by equation (7). This may be done in the following way:

The area of the spherical surface at \(r+dr\) is \(4\pi(r+dr)^2\), and the number of moles that diffuse across this surface in the time \(dt\) is

\[
dN(r+dr,t) = 4\pi(r+dr)^2 D \frac{\partial C(r+dr,t)}{\partial r} \, dt \quad \cdots \quad (11)
\]

Now, the concentration gradient at \(r+dr\) is related to that at \(r\) by

\[
\frac{\partial C(r+dr,t)}{\partial r} = \frac{\partial C(r,t)}{\partial r} + \frac{\partial}{\partial r}\left(\frac{\partial C(r,t)}{\partial r}\right)dr \quad \cdots \quad (12)
\]

and hence equation (11) may be written as

\[
dN(r+dr,t) = 4\pi(r+dr)^2 D \, dt\left\{\frac{\partial C(r,t)}{\partial r} + \frac{\partial^2 C(r,t)}{\partial r^2} \, dr\right\} \quad \cdots \quad (13)
\]

or, in the expanded form

\[
dN(r+dr,t) = 4\pi D \, dt\left\{r^2 \frac{\partial C(r,t)}{\partial r} + 2r \frac{\partial C(r,t)}{\partial r} \, dr + r^2 \frac{\partial^2 C(r,t)}{\partial r^2} \, dr\right\} \quad \cdots \quad (14)
\]

in which two terms containing infinitesimals of the second and third orders have been neglected. By substituting the relations expressed by equations (7) and (14) into equation (10), and simplifying, we obtain

\[
\frac{\partial C(r,t)}{\partial t} = D\left\{\frac{\partial^2 C(r,t)}{\partial r^2} + \frac{2}{r} \frac{\partial C(r,t)}{\partial r}\right\} \quad \cdots \quad (15)
\]

This is the fundamental differential equation describing symmetrical spherical diffusion up to a stationary spherical electrode. Since the concentration at any point in the
diffusion shell decreases continually with time $\frac{\partial C(r,t)}{\partial t}$ is a negative quantity.

**Diffusion at the dropping mercury electrode and the Ilkovic equation for the diffusion current.** - Diffusion at a dropping mercury electrode is spherically symmetrical, but due to the periodic growth and fall of the mercury drops the area of the diffusion field changes continuously during the life of a drop. In the case of the dropping electrode the diffusion takes place in a medium that is moving with respect to the centre of the drop, in a direction opposite to the direction of diffusion.

Ilkovic (19) was the first to solve the complex problem of diffusion to the dropping electrode, and to derive an equation for the resulting current. He derived it by regarding the thickness of the diffusion layer as being small compared to the radius of the drop, which justified his use of the equation for linear diffusion. The Ilkovic equation has been derived in a more exact way by MacGillavry and Rideal (20), who obtained the same final expression for the diffusion current. The following treatment is based mainly on that of MacGillavry and Rideal.

It has been shown that the fundamental differential equation for symmetrical spherical diffusion is given by equation (15), namely

$$\frac{\partial C(r,t)}{\partial t} = D\left(\frac{\partial^2 C(r,t)}{\partial r^2} + \frac{2}{r} \frac{\partial C(r,t)}{\partial r}\right) \ldots \ldots \ldots \ldots (15)$$

in which $r$ is a radial distance measured on a fixed
coordinate system whose origin is at the centre of the spherical electrode. In order to apply this equation to diffusion at the dropping electrode the fixed coordinate $r$ must be replaced by a moving coordinate, $\rho$, to take into account the increase in area of the diffusion field during the growth of the mercury drops. MacGillavry and Rideal defined the moving coordinate $\rho$ as the radius of a hypothetical sphere whose volume is the same as the volume enclosed between the surface of the growing mercury drop and a spherical surface of radius slightly larger than the radius of the drop. That is

$$\Delta V = \frac{4}{3}\pi r^3 - \frac{4}{3}\pi r_0^3 = \frac{4}{3}\pi \rho^3$$

Figure 5. Diffusion to the dropping electrode and definition of $\rho$. (Drawn to scale)

where $r$ is the radial distance from a point in the solution to the centre of the drop, and $r_0$ is the radius of the drop at any instant. This definition of $\rho$ is represented pictorially in figure 5 which has been drawn to correct scale.

If it is assumed that the drop is truly spherical then its volume at any time $t$ measured from the beginning of its formation is
where \( m \) is the weight of mercury flowing from the capillary per second, and \( d \) is the density of mercury. Hence \( \alpha \) is the volume of mercury flowing from the capillary per second. This has assumed that with a given capillary, and a constant pressure on the dropping mercury, \( m \) and \( \alpha \) are constant. The justification of this statement will be given later. Thus, the volume of the drop is directly proportional to its age, but its radius increases with the cube root of its age; that is

\[ r_0^3 = \frac{2\alpha t}{4\pi} = \gamma t \quad \ldots \ldots \ldots . \quad (19) \]

Hence from equation (17), \( \rho \) can be expressed as a function of the age of the drop by

\[ \rho^3 = r^3 - \gamma t \quad \ldots \ldots \ldots \ldots . \quad (20) \]

The flux of the diffusing substance at a given instant and a given value of \( r \) is

\[ f(r, t) = \frac{\partial C(r, t)}{\partial r} = \frac{\partial C(r, t)}{\partial \rho} \frac{\partial \rho}{\partial r} \quad \ldots \ldots \ldots \ldots . \quad (21) \]

From equation (20), for a given value of \( t \), then

\[ \frac{\partial \rho}{\partial r} = \frac{r^2}{\rho^2} \quad \ldots \ldots \ldots \ldots \ldots \ldots . \quad (22) \]

and hence equation (21) becomes

\[ f(r, t) = D \frac{r^2}{\rho^2} \frac{\partial C(r, t)}{\partial \rho} = \frac{\partial N(r, t)}{\partial \rho} \frac{\partial \rho}{\partial r} \quad \ldots \ldots \ldots \ldots . \quad (23) \]

where \( A(r, t) \) is the area of the diffusion field at \( r \), at any instant, and \( dN(r, t) \) is the number of moles that diffuse through \( A(r, t) \) in the time \( dt \). By differentiating equation (23) we obtain
Now in terms of the flux of the diffusing substance equation (15) may be written

\[
\frac{\partial f(r,t)}{\partial r} = D \left[ \frac{r^2}{\varepsilon^2} \frac{\partial^2 c(r,t)}{\partial \varepsilon^2} + \frac{\partial c(r,t)}{\partial \varepsilon} \left( \frac{2r}{\varepsilon^2} - \frac{2r^2}{\varepsilon^4} \right) \right] \ldots \ (24)
\]

and by substituting the foregoing relations for \( f(r,t) \) and \( \frac{\partial f(r,t)}{\partial r} \) into this equation, and simplifying, we obtain

\[
\frac{\partial c(r,t)}{\partial t} = \frac{D}{\varepsilon^5} \left[ \varepsilon \frac{\partial^2 c(r,t)}{\partial \varepsilon^2} + \frac{2(\varepsilon^3 - \gamma t)}{(\varepsilon^3 + \gamma t)} \frac{\partial c(r,t)}{\partial \varepsilon} \right] \ldots \ (26)
\]

This is the fundamental differential equation for diffusion to the dropping mercury electrode.

This equation can be simplified because, in the present circumstances, the region involved is confined to a distance very close to the surface of the dropping electrode. Hence \( r \) is only very slightly greater than \( r_0 \) so that \( \varepsilon^3 \) is very much smaller than \( \gamma t \). Thus, when \( \varepsilon^3 \ll \gamma t \)

\[
\frac{\varepsilon^3}{\varepsilon^3 + \gamma t} \approx -1 \quad \text{and} \quad r^4 = (\gamma t)^{4/3}
\]

Thus, equation (26) becomes

\[
\frac{\partial c(r,t)}{\partial t} = \frac{D(\gamma t)^{4/3}}{\varepsilon^5} \left[ \varepsilon \frac{\partial^2 c(r,t)}{\partial \varepsilon^2} - 2 \frac{\partial c(r,t)}{\partial \varepsilon} \right] \ldots \ldots \ (27)
\]

Since the diffusion current is governed by the flux at the electrode surface the problem at hand is to obtain an expression for the concentration gradient at any instant at \( r = r_0 \), from which, by means of equation (2), the flux, and hence the current can be calculated. In order to obtain an expression for \( c(r,t) \) as a function of \( \varepsilon \) and \( t \) it is necessary
to integrate this equation, and the integration requires a specification of the initial and boundary conditions; that is, the concentration in the surface layer at zero time, the method of establishing the diffusion layer, and the restrictions imposed by the geometry of the diffusion field.

In this case the solution is homogeneous before electrolysis, and the concentration \( C(r,0) \) is then equal to the bulk concentration \( C \). After the electrolysis is started \( (t>0) \), the rate of the electrochemical reaction is so high that the concentration of reducible substance at the electrode surface is equal to zero and this boundary condition is denoted by writing \( C(r_0,t) = 0 \) for \( t>0 \). It is also assumed that \( C(r,t) \) approaches \( C \) when \( r \) tends to infinity.

The solution of this equation for the given boundary conditions is given in Appendix II. The solution is

\[
C(r_0,t) = C \text{ erf}(s) \quad \cdots \quad (28)
\]

where

\[
s = \frac{1}{6} \left( \frac{\varepsilon^2}{(R_D)^2} \right)^{1/3} \quad \cdots \quad (29)
\]

The notation \( \text{erf}(z) \) represents the "error integral" defined by the formula

\[
\text{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z \exp(-y^2) \, dy \quad \cdots \quad (30)
\]

and its value depends only on that of \( z \). Values of this function have been given in the literature, e.g. \((21,22,23)\), and are given for various values of \( z \) in Table 1. It is noted that the value of the function rapidly approaches unity as a
Table 1

Values of the function $\frac{2}{\sqrt{\pi}} \int_0^z e^{-y^2} dy$ for various values of $z$

<table>
<thead>
<tr>
<th>$z$</th>
<th>$\text{erf}(z)$</th>
<th>$z$</th>
<th>$\text{erf}(z)$</th>
</tr>
</thead>
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<tr>
<td>0</td>
<td>0</td>
<td>1.3</td>
<td>0.93401</td>
</tr>
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<td>0.1</td>
<td>0.11246</td>
<td>1.4</td>
<td>0.95229</td>
</tr>
<tr>
<td>0.2</td>
<td>0.22270</td>
<td>1.5</td>
<td>0.96611</td>
</tr>
<tr>
<td>0.3</td>
<td>0.32863</td>
<td>1.6</td>
<td>0.97635</td>
</tr>
<tr>
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<td>0.42839</td>
<td>1.7</td>
<td>0.98379</td>
</tr>
<tr>
<td>0.5</td>
<td>0.52050</td>
<td>1.8</td>
<td>0.98909</td>
</tr>
<tr>
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<td>1.9</td>
<td>0.99279</td>
</tr>
<tr>
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<td>0.99532</td>
</tr>
<tr>
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<td>2.2</td>
<td>0.99814</td>
</tr>
<tr>
<td>0.9</td>
<td>0.79691</td>
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</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td>1.0</td>
</tr>
</tbody>
</table>
limit as \( z \) becomes large.

The resulting current at any instant during the life of a drop is governed by the flux of the diffusing substance at the surface of the drop \( (\mathcal{L} = 0) \) and is given by

\[
i = A n F f(r, t) \mathcal{L} = 0 \quad \ldots \ldots \ldots \ldots \ldots \ldots (31)\]

where \( A \) is the surface area of the drop, \( n \) is the number of electrons involved in the electrode reaction per ion or molecule, and \( F \) is the Faraday, expressed in coulombs. The current is then given in amperes.

We have

\[
f(r, t) = \frac{Dr^2}{\mathcal{L}^2} \frac{\partial C(r, t)}{\partial \mathcal{L}} \quad \ldots \ldots \ldots \ldots (23)\]

Thus, it is now necessary to differentiate equation (28) with respect to \( \mathcal{L} \),

\[
\frac{\partial C(r, t)}{\partial \mathcal{L}} = \frac{2C}{\pi^2} \frac{\partial s}{\partial \mathcal{L}} \left( \int_0^s \exp(-y^2)dy \right) \quad \ldots \ldots (32)\]

From equation (29)

\[
\frac{\partial s}{\partial \mathcal{L}} = \frac{1}{6(3\pi)^\frac{1}{2}} \cdot \frac{3C^2}{(st)^\frac{7}{6}} \quad \ldots \ldots \ldots \ldots (33)\]

and since

\[
\left. \frac{\partial}{\partial s} \left( \int_0^s \exp(-y^2)dy \right) \right|_0^s = \exp(-s^2) \quad \ldots \ldots (34)\]

then

\[
\frac{\partial C(r, t)}{\partial \mathcal{L}} = \frac{C \exp(-s^2)(3\pi)^\frac{1}{2}}{\pi^\frac{1}{2}} \cdot \frac{C^2}{(st)^\frac{7}{6}} \quad \ldots \ldots (35)\]

Therefore,

\[
f(r, t) = \frac{Dr^2}{\mathcal{L}^2} \frac{\partial C(r, t)}{\partial \mathcal{L}} = \frac{DCr^2}{(st)^\frac{7}{6}} \left( \frac{3\pi^\frac{1}{2}}{\pi^\frac{1}{2}} \right)^{\frac{1}{2}} \exp(-s^2) \quad \ldots \ldots (36)\]
When \( s = 0 \), \( s' = 0 \)

Thus \( \exp(-s^2) = \exp(0) = 1 \), and \( r = r_o = (\delta t)^{1/3} \)

Hence, from equation (36), the flux at the surface of the drops is given by

\[
f(r, t)|_{\xi=0} = \frac{DC}{(\delta t)^{1/2}} \cdot \left( \frac{Z}{3\pi \rho} \right)^{1/2} = \frac{\gamma^2 \rho}{(\delta t)^{1/2}} \cdot \left( \frac{Z}{3\pi} \right)^{1/2} \ldots \ldots \ldots (37)\]

Hence, from equation (31), the expression for the current becomes

\[
i = nAFD^{1/2} \rho t^{-1/2} \cdot \left( \frac{Z}{3\pi} \right)^{1/2} \ldots \ldots \ldots \ldots \ldots \ldots (38)\]

The surface area of the drop, \( 4\pi r_o^2 \), using equation (19), is given by \( 4\pi(\delta t)^{2/3} \).

Hence,

\[
i = 4 \left( \frac{Z}{3\pi} \right)^{1/2} nAFD^{1/2} \rho t^{2/3} t^{1/6} \ldots \ldots \ldots (39)\]

This equation gives the current at any instant during the life of a mercury drop. The equation predicts that the current should increase with the sixth root of the age of the drop, and hence the current-time curve for an individual drop should be a sixth order parabola.

With an ordinary D'Arsonal galvanometer, which is the type usually used to measure current in

---

**Figure 6.** Theoretical current-time curve, according to the Ilkovic equation, during the formation of an individual mercury drop at the dropping electrode.
polarographic work, the complete current-time curves of the individual drops are not observable, because the inertia of the moving coil is so large that it is unable to follow the complete periodic change in the current. Thus it is necessary to find an expression for the average current during the life of a drop. This is defined as the hypothetical constant current which, flowing for a length of time equal to the drop time would produce the same quantity of electricity as the quantity actually associated with the drop. Mathematically, the average current is defined by

\[ I = \frac{1}{\tau} \int_0^\tau i \, dt \]  

(40)

where \( \tau \) is the drop time.

Thus, from equation (39)

\[ I = 4 \left( \frac{3\pi}{2} \right)^{1/2} \eta \varphi \theta^{2/3} \frac{1}{\tau} \int_0^\tau t^{1/6} dt \]  

(41)

Now,

\[ \frac{1}{\tau} \int_0^\tau t^{1/6} dt = \frac{6}{7} \tau^{1/6} \]  

(42)

and since, from equation (19), \( \gamma = 3\alpha/4\pi = 3m/4\pi d \), where \( m \) is the weight of mercury flowing from the capillary per second and \( d \) is the density of mercury, equation (41) becomes

\[ I = \frac{24}{7} \left( \frac{7\pi}{3} \right)^{1/2} \left( \frac{3\pi}{4\pi} \right)^{2/3} \eta \varphi \theta^{2/3} \frac{1}{\tau} \int_0^\tau t^{1/6} dt \]  

(43)

If \( m \) is expressed in mg./second, the concentration in millimole/litre and the current in microamperes, then equation (43) with numerical constants and the numerical values of \( F \) (96,500
coulombs) and d (13.6 g/m/cc.) inserted becomes

$$I_d = 607nD^{2/3}c^{2/3}t^{1/6} \text{ microamperes} \ldots \ldots (44)$$

where $I_d$ is the average diffusion current over the life of the drop and $t$ is now the drop time. (In future, $t$ will be used to represent the drop time, unless it is specifically wished to distinguish between the drop time and the age of the drop. In this latter case $\tau$ will be used for the drop time and $t$ for the age of the drop). Equation (44) is the equation for the average current which is usually referred to as the "Ilkovic equation".

It is evident from this equation that the average current is directly proportional to the concentration of the electroreducible or electro-oxidisable substance in the body of the solution. In practical work the average of the galvanometer oscillations is measured, and it is tacitly assumed that the average of the oscillations is equal to the true average current. With a D'Arsonval galvanometer of relatively long period the magnitude of the oscillations is usually only a few per cent of the average value. With such an instrument, the average of the oscillations doubtless does correspond very closely to the true average current.

The diffusion currents obtained with the dropping mercury electrode are perfectly reproducible. Antweiler (24) showed that the thickness of the normal diffusion layer (maxima eliminated) was only of the order of 0.05 mm. The diffusion layer is thus so thin that there is no appreciable
stirring effect due to density gradients, which accounts for the perfect reproducibility of the dropping electrode current.

The experiments of numerous investigators have amply confirmed the essential correctness of the Ilkovic equation. This equation is of paramount importance, and the very foundation of quantitative polarographic analysis, since it predicts quantitatively the factors which govern the diffusion current.

Corrections for non-ideal behaviour of the dropping mercury electrode. – The Ilkovic equation, as derived by Ilkovic himself, had as its basis the fundamental equation of linear diffusion. The derivation, just given, of MacGillavry and Rideal was based on the equation of spherically symmetrical diffusion. To do this certain approximations were necessary, such as the assumption that the thickness of the diffusion layer was small compared with the radius of the drop. The shielding effect of the capillary was also neglected. The final equation obtained was identical with that of Ilkovic. This makes it appear likely that the approximations made had converted the original differential equation based on spherically symmetrical diffusion, to one based on linear diffusion.

The fact that the Ilkovic equation assumes linear diffusion is important since careful work (25–29) has shown that this equation does not accurately express the dependence of the diffusion current on the capillary characteristics m
and t. From the Ilkovic equation, equation (44), we have

\[
\frac{I_d}{Cm^{2/3}t^{1/6}} = 607nD^{1/2} = I \quad \ldots \ldots \ldots \ldots (45)
\]

where I should be constant for any particular ion in a given supporting electrolyte at constant temperature. The results of these authors indicate that I is not independent of m and t.

In order to explain this fact Lingane and Loveridge (27) suggested a modification of the Ilkovic equation based on an analogy with the difference between the equations for linear and spherical diffusion. The modified version is

\[
I_d = 607nD^{1/2}Cm^{2/3}t^{1/6}(1 + 39D_m^{-1/3}t^{1/6}) \quad \ldots \ldots (46)
\]

The theoretical aspect of the problem has been more fully investigated by Strehlow and von Stackelberg (30) who developed the differential equation of MacGillavry and Rideal retaining some of the terms originally neglected by them, and obtained an expression similar to equation (46). They also adapted von Stackelberg's derivation (31) of the Ilkovic equation to apply to spherical diffusion. They obtained the result

\[
I_d = 607nD^{1/2}Cm^{2/3}t^{1/6}(1 + 17D_m^{-1/3}t^{1/6}) \quad \ldots \ldots (47)
\]

or

\[
I = 607nD^{1/2}(1 + 17D_m^{-1/3}t^{1/6}) \quad \ldots \ldots \ldots (48)
\]

Both equations (46) and (48) correspond to a linear relation between I and \(m^{-1/3}t^{1/6}\).

Strehlow, Mährich and von Stackelberg (29) claim good agreement between equation (48) and their experimental
results, provided that values of the diffusion coefficient somewhat smaller than those calculated from ionic conductivities (which give values of diffusion coefficients at infinite dilution) are used. They give the value of the numerical constant in the correction term as 17±3. On the other hand, Meites and Meites (28) dispute the validity of the Strehlow-Stackelberg equation on the basis of a decrease in I which they find at higher values of $m^{-1/3}t^{1/6}$ and the question, as yet, remains undecided.

The correction term itself is not large, but is not negligible in accurate work. For normal capillaries $m^{-1/3}t^{1/6}$ may vary between 0.5 and 1.2 mg. $^{-1/3}$ sec$^{1/2}$, which, for $D = 1 \times 10^{-5}$ cm$^2$ sec$^{-1}$ makes the correction term vary from about 3 to 6 per cent. As a first approximation, however, I may be regarded as constant, especially in view of the uncertainties as to its exact value and so $I_d/m^{2/3}t^{1/6}$ may be taken as proportional to the concentration C. Thus, from equation (45), $I = 607nD^{1/2}$ provided that the value of $D^{1/2}$ is calculated from polarographic diffusion currents, by means of the unmodified Ilkovic equation, that is, from

$$I_d = 607nD^{1/2}Cm^{2/3}t^{1/6} = ICm^{2/3}t^{1/6} \quad \ldots \quad (45a)$$

Diffusion current constants calculated by means of this equation should not vary by more than about 3 per cent with variation of $m$ and $t$. 

*****
(iii). Theoretical principles - current-voltage curves.

Equilibrium electrode potentials. - In the last section the magnitude of the current was discussed for the case in which all ions or molecules of the reacting species which encountered the electrode surface underwent reaction, i.e. the condition of complete concentration polarization. Whether or not this condition exists depends on the potential of the electrode, and so it is necessary to consider the relationships existing between current and electrode potential.

In general, oxidation-reduction reactions occurring at an electrode can be represented by

\[ aA + bB + \ldots + ne = pP + qQ + \ldots \]  \hspace{1cm} (49)

in which A, B, P, Q etc. represent the components of the oxidation-reduction system; and a, b, n, p and q are stoichiometric coefficients. The equation correlating the equilibrium potential to the concentrations of the involved substances was first derived by Kernst in the particular case of a metal-cation equilibrium. A more general form of the electrode potential, and one which corresponds to the reaction given above is

\[ E = E^0 - \frac{RT}{nF} \ln \frac{\prod a_{A}^{p} a_{B}^{q}}{\prod a_{A}^{a} a_{B}^{b}} \]  \hspace{1cm} (50)

in which the a's are the activities of the substances involved, R is the gas constant, T the absolute temperature and F the faraday. The constant \( E^0 \) is the "normal" or "standard potential" for the reaction being considered, i.e. the
potential which is being measured when all the activities are made equal to unity, the conditions being those corresponding to the standard state.

In many polarographic processes the electrode reaction corresponds to

\[ M^{n+} + Hg + ne = M(Hg) \]  \hspace{1cm} \text{(51)}

where \( M^{n+} \) represents a metal cation and \( M(Hg) \) symbolises the amalgam formed at the surface of the mercury drops. In this case the potential of the electrode is given by

\[ E = E^0 - \frac{RT}{nF} \ln \frac{a_{M(Hg)}}{a_{M^{n+}}a_{Hg}} \]  \hspace{1cm} \text{(52)}

Since the amalgams formed at the dropping electrode are very dilute, \( a_{Hg} \) will be virtually the same as the activity of pure mercury, and can be regarded as constant. If \( E^0 \) is replaced by \( E^0_{am} - \frac{RT}{nF} \ln a_{Hg} \), where \( E^0_{am} \) is the standard potential of the amalgam, equation (52) may be written

\[ E = E^0_{am} - \frac{RT}{nF} \ln \frac{a_{M(Hg)}}{a_{M^{n+}}} \]  \hspace{1cm} \text{(53)}

Electrode potentials and the kinetics of the electro-chemical reaction: the relationship between current and potential. - In the last section it was assumed that electrochemical equilibrium was achieved at the electrode whose behaviour was being studied. Under these conditions no current will flow. In polarography the relationships of interest concern the variations in current with change of electrode potential. The simplest type of electrode reaction which is
common in practice is that in which two soluble species are involved. The reaction may be written in the abridged form

\[ O + ne = R \quad \ldots \ldots \ldots \ldots \ldots \ldots \quad (54) \]

and its reverse by

\[ R = O + ne \quad \ldots \ldots \ldots \ldots \ldots \ldots \quad (55) \]

where \( O \) and \( R \) denote oxidant and reductant respectively. If either, or both, of the reactants are insoluble, modifications to the theory can be applied. The following treatment largely follows that of Delahay (33).

If it is assumed that the electrode process is of the first order, the net rate of the reaction, expressed in moles of substance transformed at the electrode surface per unit of time and per unit of area, is

\[ -\frac{\mathrm{d}N_o}{\mathrm{d}t} = \frac{\mathrm{d}N_r}{\mathrm{d}t} = k_f, n C_o - k_b, n C_r \quad \ldots \ldots \ldots \ldots \ldots \ldots \quad (56) \]

where the subscripts \( o \) and \( r \) are used to denote quantities referring to the oxidant and reductant respectively. The \( C \)'s are concentrations and the \( k \)'s are formal rate constants for the forward and backward processes. These \( k \)'s characterise the kinetics of an heterogeneous process and are expressed in \( \text{cm.sec}^{-1} \) whereas conventional rate constants for a first order reaction are in \( \text{sec}^{-1} \). The use of formal rate constants also serves to eliminate activity coefficients from the equations.

In order to interpret the constants \( k_f, n \) and \( k_b, n \) of equation (56) it is necessary to introduce additional kinetic considerations. A substance which undergoes a chemical transformation has to overcome an energy barrier. This
principle is applicable to any type of reaction, but in the case of an electrochemical reaction it is necessary to take into account the effect of the electrical field at the electrode-solution interface. This field favours the electrochemical reaction in one direction and hinders it in the other. If \( E \) is the electrode potential referred to any arbitrary potential scale, a fraction \( \alpha E \) of this potential favours the cathodic reaction; likewise, a fraction \( (1 - \alpha)E \) favours the anodic reaction. The parameter \( \alpha \) introduced in this manner is the transfer coefficient for the electrode process. It has been shown (34–36) that the rate constants in equation (56) can be written

\[
\begin{align*}
    k_f, h &= k_f^0, h \exp \left( -\frac{\alpha n_a E}{RT} \right) \\
    k_b, h &= k_b^0, h \exp \left( \frac{(1 - \alpha)n_a E}{RT} \right)
\end{align*}
\]

where the \( k^0 \)'s are the values of the rate constants for \( E = 0 \), \( n_a \) is the number of electrons involved in the rate determining step of the reaction, and the other notations are conventional.

The current is now simply given by multiplying the rate of the electrode process by the area of the electrode and by the charge involved in the reduction of one mole of substance \( 0 \), and is expressed by

\[
i = nF \left[ C_f^0 k_f, h \exp \left( -\frac{\alpha n_a E}{RT} \right) - C_r k_r^0, h \exp \left( \frac{(1 - \alpha)n_a E}{RT} \right) \right] \cdots (59)
\]
At the equilibrium potential, by definition, the current given by equation (59) is equal to zero, and the following relationship is obtained:

\[
\frac{C_o k_f^o}{C_r k_b^o} = \exp\left(\frac{n_a F}{RT} E_e\right)
\]

(60)

where \( E_e \) is the equilibrium potential. By rearranging the terms in this equation the following relationship results:

\[
E_e = \frac{RT}{nF} \ln \frac{k_f^o}{k_b^o} - \frac{RT}{nF} \ln \frac{C_r}{C_o}
\]

(61)

This expression is the same as the Nernst equation in which the standard potential is expressed in terms of the formal rate constants \( k_f^o \) and \( k_b^o \). The first term on the right-hand side of equation (61) is conveniently represented by \( E_c^o \), which is the equilibrium potential when the concentrations of the reactants are both equal to unity. The value of \( E_c^o \) is generally not very different from the standard potential \( E^o \), and can often be identified with \( E^o \).

Equation (59) can now be written in the following way:

\[
i = nF A \left[ C_o k_s^o h \exp\left(\frac{-n_a F}{RT}(E - E_c^o)\right) - \frac{C_r k_s^o h \exp\left((1-\alpha)n_a F}{RT}(E - E_c^o)\right)}{RT}(E - E_c^o)\right]\]

(62)

The current given by this equation is zero at the potential \( E_c^o \) since equilibrium is achieved at that potential and since the concentrations \( C_o \) and \( C_r \) are equal then \( k_s^o h = k_s^o h \). Hence, the two rate constants may be replaced by
a single rate constant $k_{S,h}$ and the expression for the current now becomes

$$i = nF\alpha k_{S,h} \left[ C_0 \exp \left( -\frac{\alpha n a F}{RT} (E - E^0) \right) - C_r \exp \left( \frac{(1 - \alpha)n a F}{RT} (E - E^0) \right) \right]$$

$$.... (63)$$

It is seen from this equation that the current is now a function of the difference of potential $(E - E^0)$, whereas in equation (39) the current depends on the potential $E$. Therefore, the value of $k_{S,h}$ is truly characteristic of the electrode process whereas the constants $k_{f,h}^0$ and $k_{b,h}^0$ depend on the difference between the potential $E^0$ and the zero of the scale of potentials.

The foregoing treatment was developed for the case in which the species involved in the electrochemical reaction are present in solution, but these considerations are also valid in cases in which the concentration of either the reducible or oxidisable substance is negligible, and equation (63) can thus be simplified accordingly.

**Reversibility of an electrode reaction.** - At the equilibrium potential the current given by equation (63) is equal to zero by definition, but as soon as the potential differs from the equilibrium potential a current is observed. The magnitude of the current corresponding to a departure $\eta$ from the equilibrium potential depends on the rate constant $k_{S,h}$. In the following table values of the overvoltage $\eta$ have been calculated for a current of $10^{-6}$ ampere for various
values of the rate constant $k_{s,h}$ and assuming the following
data: $n = 1$, $A = 1$ sq. cm., $C_0 = C_I = 10^{-6}$ mole/litre, $\alpha = 0.5$,
$T = 298^0K$

Table 2. Variation of the overvoltage with the rate constant at the standard potential.

<table>
<thead>
<tr>
<th>$k_{s,h}$ cm. sec$^{-1}$</th>
<th>$\eta$ volts</th>
</tr>
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<tbody>
<tr>
<td>$10^{-3}$</td>
<td>± 0.0002</td>
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<tr>
<td>$10^{-4}$</td>
<td>± 0.003</td>
</tr>
<tr>
<td>$10^{-5}$</td>
<td>± 0.02</td>
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<td>± 0.59</td>
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<td>± 0.83</td>
</tr>
<tr>
<td>$10^{-14}$</td>
<td>± 1.06</td>
</tr>
</tbody>
</table>

It can be seen that the change of potential needed to
cause the flow of a current of $10^{-6}$ ampere varies tremendously
with the value of the rate constant $k_{s,h}$ at the standard
potential. An electrochemical reaction occurring without
measurable overvoltage is said to be reversible; conversely,
an electrode reaction involving a measurable overvoltage is
irreversible. Even though the distinction between reversible
and irreversible processes is somewhat artificial since the
degree of reversibility depends on the magnitude of the
current involved, the terms are useful in describing the
behaviour of electrode processes.

The overvoltage is thus defined by

\[ \eta = \text{irreversible potential} - \text{reversible potential} \]

Interpretation of current-voltage curves for reversible processes. - In this sub-section a rigorous treatment is outlined for the calculation of currents controlled by the rate of semi-infinite linear diffusion to a stationary, flat, microelectrode. The equation is also in remarkably good agreement with experimental data in the case of the dropping mercury electrode. It has been assumed that the electrochemical process involved is that of reduction of a substance 0 to its reduction product R, R not being originally present in the solution, and that the substance R is soluble either in the solution, or in mercury in the case of the deposition of an amalgam forming metal on a mercury electrode. It has also been assumed that electrochemical equilibrium is achieved at the electrode.

Since the product of the electrode process diffuses into the bulk of the solution (or into mercury) the concentration at a distance \( x \) from the electrode surface, at time \( t \), \( C_r(x,t) \) also obeys the general equation for linear diffusion. Therefore, two functions \( C_q(x,t) \) and \( C_r(x,t) \) have to be determined by solving two partial differential equations of the form of equation (6). It is necessary to prescribe two initial and boundary conditions. The initial conditions are:
\( C_0(x,0) = C^0 \) where \( C^0 \) is the concentration of \( O \) in the bulk of the solution and 
\( C_r(x,0) = 0 \) since it has been assumed that \( R \) is originally absent.

The first boundary condition is given by the Nernst equation. Thus
\[
E = E^0 - \frac{RT}{nF} \ln \frac{f_r C_r(0,t)}{f_o C_o(0,t)}
\]
which can alternatively be expressed
\[
\frac{C_o(0,t)}{C_r(0,t)} = \Theta = \frac{f_r}{f_o} \exp \left( \frac{nF}{RT} \left( E - E^0 \right) \right)
\]
The second boundary condition is given by saying that, at the electrode surface, the flux of \( O \) towards the electrode surface is equal to the flux of \( R \) away from the electrode surface.

Hence
\[
D_o \left( \frac{\partial C_o(x,t)}{\partial x} \right)_{x=0} = -D_r \left( \frac{\partial C_r(x,t)}{\partial x} \right)_{x=0}
\]
A solution of these equations for \( C_o(x,t) \) and \( C_r(x,t) \) has been given by Delahay (37), and at the electrode surface \( (x = 0) \) is as follows:
\[
C_o(0,t) = C^0 \frac{\xi \Theta}{1 + \xi \Theta} \quad \ldots \ldots \ldots (66)
\]
\[
C_r(0,t) = C^0 \frac{\xi}{1 + \xi \Theta} \quad \ldots \ldots \ldots (67)
\]
where \( \xi = \sqrt{D_o/D_r} \). It can subsequently be shown (37) for linear diffusion to a plane microelectrode that
\[
i = \frac{i_d}{1 + \xi \Theta} \quad \text{or} \quad \xi \Theta = \frac{i_d - i}{i} \quad \ldots \ldots \ldots (68)
\]
Thus equations (66) and (67) become
\[ C_o(0,t) = C^0 \frac{i_d - i}{i_d} \] \hspace{1cm} (69)\]
\[ C_r(0,t) = C^0 \sqrt{\frac{D_0}{D_r}} \frac{i}{i_d} \] \hspace{1cm} (70)\]

On substituting for \( C_o(0,t) \) and \( C_r(0,t) \) equation (64) becomes
\[ E = E^0 - \frac{RT}{nF} \ln \left( \frac{f_r}{f_o} \sqrt{\frac{D_o}{D_r}} \right) - \ln \frac{i}{i_d - i} \] \hspace{1cm} (71)\]

Since a relatively large excess of supporting electrolyte is present in the solution the values of the activity coefficients \( f_o \) and \( f_r \) can be regarded as independent of the concentrations of \( O \) and \( R \). Hence, the second term on the right hand side of equation (71) is independent of current and the equation can be simplified to
\[ E = \xi - \ln \frac{i}{i_d - i} \] \hspace{1cm} (72)\]

The half-wave potential, \( E_{1/2} \), is defined as the value of \( E \) at the mid-point of the wave where \( i = \frac{1}{2} i_d \) and equation (72) can now be written:
\[ E = E_{1/2} - \frac{RT}{nF} \ln \frac{i}{i_d - i} \] \hspace{1cm} (73)\]

This equation has been derived for the case of linear diffusion to a plane microelectrode. Heyrovsky and Ilkovic (38) derived the characteristics of the current-potential curve for the dropping mercury electrode by postulating equations (69) and (70). An equation identical to equation (73) was thus obtained. This equation, which is rigorous for semi-
infinite linear diffusion, is in very good agreement with experimental data in the case of the dropping mercury electrode. At 25°C the equation simplifies to

\[ E_{d.e} = E^{1/2} - \frac{0.0591}{n} \log \frac{i}{i_d - i} \quad \ldots \ldots \quad (74) \]

Thus, a plot of \( \log \frac{i}{(i_d - i)} \) vs. \( E_{d.e} \) should give a straight line having a slope of \( -n/0.0591 \), or \( -16.9n \text{ volt}^{-1} \), from which \( n \) may be determined.

**Interpretation of polarographic waves for irreversible processes.** - The first attempt at developing a theory of irreversible waves was made by Eyring and coworkers (39), who formulated the fundamental idea that the characteristics of irreversible waves are determined both by rates of diffusion and electrochemical reaction. A more rigorous treatment was developed independently by several groups of investigators (40-45) who derived the rigorous solution for the boundary value problem corresponding to semi-infinite linear diffusion. The derivation of the shape of the current-voltage curve is quite involved and is only outlined briefly in the following pages. The treatment is based mainly on that of Delahay (33, 41, 45), and Delahay and Strassner (42). As in the case of reversible waves the reaction considered is that of reduction of a substance 0 to its reduction product R in an electrode process involving \( n \) electrons. It is assumed that R is originally absent and is soluble either in the solution or in mercury.
From equation (56) the number of moles of $O$ being consumed per unit of time is given by

$$\frac{dN_O}{dt} = k_f, h C_O(0, t) - k_b, h C_R(0, t) \quad \cdots \quad (75)$$

The first boundary condition is given by equating the rate given by this equation to the flux of the substance at the electrode surface. Thus

$$D_o \left( \frac{\partial C_O(x, t)}{\partial x} \right)_{x=0} = k_f, h C_O(0, t) - k_b, h C_R(0, t) \quad \cdots \quad (76)$$

The second boundary condition is written as expressing that the sum of the fluxes of $O$ and $R$ at the electrode surface is equal to zero. Thus

$$D_o \left( \frac{\partial C_O(x, t)}{\partial x} \right)_{x=0} + D_r \left( \frac{\partial C_R(x, t)}{\partial x} \right)_{x=0} = 0 \quad \cdots \quad (77)$$

The initial conditions are: $C_O(x, 0) = C^0$, and $C_R(x, 0) = 0$, where $C^0$ is the concentration of $O$ in the bulk of the solution. Also, $C_O(x, t)$ approaches $C^0$ for $x \to \infty$, and $C_R(x, t) \to 0$ for $x \to \infty$.

For the case of linear diffusion to a plane micro-electrode the solution was derived independently by Smutek (40), Kambara and Tachi (44) and Delahay (45). The current for the reduction of substance $O$ is

$$i = nFAC^0k_f, h \exp(Q^2t)erfc(Qt^{1/2}) \quad \cdots \quad (78)$$

where

$$Q = \frac{k_f, h}{D_o^{1/2}} + \frac{k_b, h}{D_r^{1/2}} \quad \cdots \quad (79)$$

and the other symbols have their usual meanings.
In principle, the above treatment could be transposed to the case of the dropping mercury electrode by applying the corresponding equations for spherical diffusion. These calculations would be elaborate, as the treatment of MacGillavry and Rideal (20), previously outlined, for the much simpler case of diffusion controlled currents is quite involved. Delahay (41,45) has treated the problem in a much less arduous manner by the following method.

The value of the area of the dropping mercury electrode is calculated in terms of the characteristics m and t of the capillary and the resulting value of A is introduced into equation (78). Furthermore, the rate constants $k_{f,h}$ and $k_{b,h}$ are made equal to infinity and zero respectively, and the resulting equation is compared with the Ilkovic equation. The details are as follows:

The power expansion of $\exp(x^2)\text{erfc}(x)$ for values of $x$ greater than unity is given by

$$\exp(x^2)\text{erfc}(x) = \frac{1}{\sqrt{\pi} x} \left( 1 - \frac{1}{2x^2} + \frac{1.3}{(2x^2)^2} - \frac{1.3.5}{(2x^2)^3} \ldots \right)$$

(80)

The surface area of the mercury drop, $4\pi r_0^2$, using equation (19) is given by $A = 4\pi(\delta t)^{2/3}$, and so for $k_{b,h} = 0$, the right hand side of equation (78) is given by

$$nFAC_0 k_{f,h} \exp\left( \frac{k_{f,h}t}{D_0} \right) \text{erfc}\left( \frac{k_{f,h}D_0^{1/2}}{D_0^{1/2}} \right) = 4\pi nF(\delta t)^{2/3} e^0 \frac{D_0^{1/2}}{\sqrt{\nu} e^{1/2}}$$

for large values of $k_{f,h}$.

(81)
This expression becomes identical to equation (39), the Ilkovic equation, if multiplied by the factor $(7/3)^{1/2}$. A similar conclusion was reached by Ilkovic (19) for the case of a simple diffusion process. Such a derivation is not rigorous. Since, from equations (18) and (19), $\gamma = \frac{3m}{4\pi d}$, the expression for the instantaneous current at the dropping mercury electrode becomes

$$i = \left(\frac{7}{3}\right)^{1/2}\left(\frac{36\pi}{d^2}\right)^{1/3} n m^{2/3} t^{2/3} C_0 k_f h \exp(Q^2 t) \text{erfc}(Q t^{1/2})$$

... (82)

After making numerical transformations the following expression for the current at any instant during the drop life for any point along the wave, is obtained:

$$i = 708 \pi n^{1/2} m^{2/3} t^{2/3} C_0 k_f h \exp(Q^2 t) \text{erfc}(Q t^{1/2})$$

... (83)

When the overvoltage exceeds 0.1 volt the rate of the backward reaction becomes negligible with respect to the forward reaction and the expression then becomes

$$i = 708 \pi n^{1/2} m^{2/3} t^{2/3} C_0 k_f h \exp(k_f h t D^{-1}) \text{erfc}(k_f h t^{1/2} D^{-1/2})$$

... (84)

This is thus the general expression for the current at any time $t$ during the life of a drop for a totally irreversible process.

Unless a fast-recording polarograph, which can record current-time curves over the life of a drop, is available, it is now necessary to obtain an expression for the average current over the life of a drop. Mathematically, for a drop...
time \( \tau \), this is given by

\[
I = 708 \pi \frac{nm^{2/3}C_{0}k_{f,h}}{\tau} \int_{0}^{\tau} \left( \frac{t^{2/3} \exp\left(k_{f,h}^{2}tD_{o}^{-1}\right) \text{erfc}\left(k_{f,h}tD_{o}^{-1/2}\right)}{t} \right) dt
\]

Two simple methods of evaluating equation (85) are available. The first of these is due to Delahay (41), the method being outlined as follows. The function appearing under the integral sign is plotted as a function of \( \tau \) for different values of \( k_{f,h}D_{o}^{-1/2} \) and the ratio \( \gamma \) of the average current to the maximum value is determined by graphic integration for different values of \( \tau \). The average current is then given by

\[
I = 708 \pi \frac{nm^{2/3}C_{0}k_{f,h}}{\tau} \gamma \cdot \ldots \ldots \ldots \ldots (85)
\]

where function \( \gamma \) is defined by

\[
\gamma = \left( \text{erfc}\left(k_{f,h}tD_{o}^{-1/2}\right) \exp\left(k_{f,h}^{2}tD_{o}^{-1}\right) \right) \ldots \ldots (87)
\]

The values of \( \gamma \), obtained by applying this formula for different values of \( k_{f,h}D_{o}^{-1/2} \) are calculated and \( \gamma k_{f,h}D_{o}^{-1/2} \) is then plotted against drop time, for the different values of \( k_{f,h}D_{o}^{-1/2} \).

For large values of \( k_{f,h} \) the current is governed by the Ilkovic equation, and is given by equation (44), namely

\[
I_{d} = 607nD_{o}^{2/3}C_{0}m^{2/3}\tau^{1/6} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (44)
\]

Thus, we have

\[
\frac{I}{I_{d}} = \frac{\gamma}{6} \frac{\pi \frac{nm^{2/3}C_{0}k_{f,h}}{\tau}}{\gamma k_{f,h}D_{o}^{-1/2}} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (88)
\]

The value of \( \gamma k_{f,h}D_{o}^{-1/2} \) is calculated for any point on the wave from the experimental value of \( I/I_{d} \) by application of equation
The point having the drop time as abscissa and \( \beta k_f h D_0^{-\frac{1}{2}} \) as ordinate is located on its diagram and the value of \( k_f h D_0^{-\frac{1}{2}} \) for the curve passing through this point is then determined by interpolation. It is now a trivial matter to find the value of \( k_f h \).

The second method of finding the value of equation (85) is given by Milner (46). Equation (84) can be written

\[ i = 708nm^{2/3} t^{1/6} C_0 \pi^{1/2} h^{1/6} \exp (h^2 t) \text{erfc}(ht^{1/2}) \]  

(89)

where

\[ h = k_f h D_0^{-\frac{1}{2}} \]  

(90)

Values of the function \( \pi^{1/2} h^{1/6} \exp (h^2 t) \text{erfc}(ht^{1/2}) \), which will be denoted by \( \Theta(ht^{1/2}) \) have been calculated by Milner from data given by Carslaw and Jaeger (47). Values of this function are given in Table 3. It is seen that \( \Theta(x) \) has the property of asymptotically approaching unity as \( x \) becomes large.

The average value of the current for constant voltage is thus given by

\[ I = P \frac{1}{z} \int_0^z t^{1/6} \Theta(ht^{1/2})dt \]  

(91)

where \( P \) represents the value of the time independent symbols from equation (89). The value of the integral is a function of both \( z \) and \( h \). If, however, the variables are changed such that \( H = h z^{1/2} \) and \( y = t/z \) equation (91) becomes

\[ I = P z^{1/6} \int_0^1 y^{1/6} \Theta(Hy^{1/2})dy \]  

(92)

For large values of the rate constant \( k_f h \) the value of \( \Theta(Hy^{1/2}) \)
Values of $\Theta(x)$ and $\phi(x)$ for different values of $x$, where $\Theta(x) = \pi^{1/2}x \exp(x^2)\text{erfc}(x)$, and $\phi(x) = \frac{7}{6} \int_0^1 y^{1/6} \phi(xy^{1/2}) dy$

<table>
<thead>
<tr>
<th>$x$</th>
<th>$\Theta(x)$</th>
<th>$\phi(x)$</th>
<th>$x$</th>
<th>$\Theta(x)$</th>
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<td>0.210</td>
<td>4.0</td>
<td>0.971</td>
<td>0.925</td>
</tr>
<tr>
<td>0.3</td>
<td>0.391</td>
<td>0.291</td>
<td>4.5</td>
<td>0.977</td>
<td>0.937</td>
</tr>
<tr>
<td>0.4</td>
<td>0.476</td>
<td>0.361</td>
<td>5.0</td>
<td>0.981</td>
<td>0.945</td>
</tr>
<tr>
<td>0.5</td>
<td>0.546</td>
<td>0.423</td>
<td>6.0</td>
<td>0.987</td>
<td>0.959</td>
</tr>
<tr>
<td>0.6</td>
<td>0.604</td>
<td>0.478</td>
<td>7.0</td>
<td>0.990</td>
<td>0.968</td>
</tr>
<tr>
<td>0.8</td>
<td>0.694</td>
<td>0.564</td>
<td>8.0</td>
<td>0.992</td>
<td>0.973</td>
</tr>
<tr>
<td>1.0</td>
<td>0.758</td>
<td>0.630</td>
<td>10.0</td>
<td>0.995</td>
<td>0.982</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>20.0</td>
<td>0.999</td>
<td>0.995</td>
</tr>
</tbody>
</table>
approaches unity and so we have

\[ I_d = \pi \frac{1}{6} \int_0^1 y^{1/6} dy = \frac{6}{7} \pi \frac{1}{6} \quad \ldots \ldots \quad (93) \]

Thus

\[ \frac{I}{I_d} = \frac{7}{6} \int_0^1 y^{1/6} \Theta(Hy^{1/6}) dy = \phi(H) \quad \ldots \ldots \quad (94) \]

The value of this function depends only on \( H \). Values of \( \phi(H) \) have been computed graphically and tabulated by Milner. The values are reproduced in Table 3. Both \( \Theta(x) \) and \( \phi(x) \) are plotted against \( \log x \) in figure (7). Since \( H = \frac{k_{f,h}^0}{D_0} \frac{1}{2} \) it is now a simple matter to find \( k_{f,h} \).

It has previously been shown that

\[ k_{f,h} = k_{f,h}^0 \exp \left( -\frac{\alpha n_a E}{RT} \right) \quad \ldots \ldots \ldots \quad (57) \]

the symbols being as previously assigned. Thus, a plot of \( \log k_{f,h} \) against potential should give a straight line having a slope of \( -(\alpha n_a F/RT) \log e \), or \( -16.9 \alpha n_a \text{ volt}^{-1} \). The value of \( \alpha n_a \) can then be determined.

Koutecky (48) has given a more rigorous treatment of irreversible polarographic waves by making the same approximation as did Ilkovic (19) in the derivation of a purely diffusion controlled current. The principle of Koutecky's method is as follows. The boundary value problem of the expanding sphere is treated by solving the equivalent problem for linear diffusion at a moving plane boundary. The equations for this latter type of diffusion are given by
Figure 7. The dependence of the functions $\theta(x)$ and $\phi(x)$ on $x$.

Figure 8. Comparison of the Delahay and Koutecky treatments of totally irreversible waves.
with the initial and boundary conditions as given in Delahay's method. The approach is similar to that followed in the case of linear diffusion, but the mathematical difficulties are more serious. Koutecky has calculated the ratio of the instantaneous currents \( i/i_d \) for various points along a polarographic wave. This ratio is given by

\[
\frac{i}{i_d} = F(\chi)
\]

where, expressed in the current terminology

\[
\chi = \left( \frac{12}{7} \right)^{\frac{1}{2}} \left( \frac{k_f h}{D_0} + \frac{k_b h}{D_r} \right) t^{\frac{1}{2}}
\]

The values of \( i/i_d \) for various values of \( \chi \) are given in Table 4.

In terms of the solution of the boundary value problem due to Delahay the ratio of the instantaneous currents \( i/i_d \), for a totally irreversible process, from equations (39) and (84), is given by

\[
\frac{i}{i_d} = \pi^{\frac{1}{2}} k_f h t^{\frac{1}{2}} D_0^{-\frac{1}{2}} \exp \left( k_f h \frac{t}{t_0}^{\frac{1}{2}} \right) \text{erfc} \left( k_f h t^{\frac{1}{2}} D_0^{-\frac{1}{2}} \right) = \Theta(k_f, h t^{\frac{1}{2}} D_0^{-\frac{1}{2}})
\]

As a comparison of the two methods the values of \( F(\chi) \) (for \( k_b, h = 0 \)) and \( \Theta(k_f, h t^{\frac{1}{2}} D_0^{-\frac{1}{2}}) \) are both plotted against \( \log(k_f, h t^{\frac{1}{2}} D_0^{-\frac{1}{2}}) \) in figure (8). It can be seen that, although
Table 4

Values of $i/i_d$ for a totally irreversible wave according to Koutecky.

<table>
<thead>
<tr>
<th>$\chi$</th>
<th>$i/i_d$</th>
<th>$\chi$</th>
<th>$i/i_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.0828</td>
<td>3.0</td>
<td>0.777</td>
</tr>
<tr>
<td>0.2</td>
<td>0.155</td>
<td>3.5</td>
<td>0.803</td>
</tr>
<tr>
<td>0.3</td>
<td>0.219</td>
<td>4.0</td>
<td>0.827</td>
</tr>
<tr>
<td>0.4</td>
<td>0.275</td>
<td>4.5</td>
<td>0.844</td>
</tr>
<tr>
<td>0.5</td>
<td>0.325</td>
<td>5.0</td>
<td>0.858</td>
</tr>
<tr>
<td>0.6</td>
<td>0.369</td>
<td>6</td>
<td>0.880</td>
</tr>
<tr>
<td>0.7</td>
<td>0.409</td>
<td>7</td>
<td>0.895</td>
</tr>
<tr>
<td>0.8</td>
<td>0.444</td>
<td>8</td>
<td>0.909</td>
</tr>
<tr>
<td>0.9</td>
<td>0.476</td>
<td>9</td>
<td>0.919</td>
</tr>
<tr>
<td>1.0</td>
<td>0.505</td>
<td>10</td>
<td>0.927</td>
</tr>
<tr>
<td>1.2</td>
<td>0.555</td>
<td>12</td>
<td>0.939</td>
</tr>
<tr>
<td>1.4</td>
<td>0.597</td>
<td>14</td>
<td>0.946</td>
</tr>
<tr>
<td>1.6</td>
<td>0.632</td>
<td>16</td>
<td>0.953</td>
</tr>
<tr>
<td>1.8</td>
<td>0.662</td>
<td>18</td>
<td>0.958</td>
</tr>
<tr>
<td>2.0</td>
<td>0.690</td>
<td>20</td>
<td>0.963</td>
</tr>
<tr>
<td>2.5</td>
<td>0.740</td>
<td>$\infty$</td>
<td>1.0</td>
</tr>
</tbody>
</table>
the general characteristics of the two curves are the same, there is some measure of disagreement. However, although Koutecky's method is more exact it does not readily lend itself to a treatment based on average currents during drop life. Since the characteristics are the same, no large error should be introduced by the determination of \( \alpha n_a \) by Delahay's method.

For the determination of \( k_{f,h} \), and subsequently \( \alpha n_a \) by making use of equation (57), it is preferable to measure the maximum current during drop life by means of a fast recorder and to compute \( k_{f,h} \) from the values of \( i/i_d \) calculated by Koutecky. However, a fast recording polarograph was not available and so average values, \( \bar{I}/I_d \), were measured and values of \( k_{f,h} \) were calculated from values of \( \bar{I} \), by making use of figure (7). In principle, \( k_{f,h} \) could also be obtained by using Delahay's graphic method, following the example of Delahay and Strassner (42,49), but this method offers no advantages over Milner's method, is less accurate, and requires the preliminary preparation of suitable graphs.

A convenient method of representing polarographic waves is by the "log plot", that is, a plot of the function \( \log i/(i_d - i) \) vs. \( -\bar{E} \). From equation (99) it is seen that the ratio of the instantaneous currents \( i/i_d \), for a totally irreversible process, is given by

\[
\frac{i}{i_d} = \pi^{\frac{1}{2}} X \exp(X^2) \text{erfc}(X) = \Theta(X) \quad \ldots \ldots (100)
\]
where

\[ X = k_{f_i} h^{\frac{n}{2}D_0^{2}} \]  

(101)

From equation (57) it is seen that the variation of \( X \) with potential is given by

\[ \ln X = \ln(k_{f_i} h^{\frac{n}{2}D_0^{2}}) - \frac{\alpha n_{FE}}{RT} \]  

(102)

From equations (100) and (102) it can be shown that

\[ \frac{d}{dE} \log \frac{i}{i_d-1} = -\frac{\alpha n_{FE}}{RT} \left( \frac{1}{1 - \Theta(X)} - \frac{2x^2}{\Theta(X)} \right) \]  

(103)

The derivation of this relationship is given in Appendix II. A similar expression was obtained by Kivalo, Oldham and Laitinen (50).

The term inside the square brackets is variable with potential. However, it rapidly approaches unity as \( X \) becomes small and acquires the value 2 as \( X \) tends to infinity. The proof of this statement is given in Appendix II. Hence, it is to be expected that the "log plot" for an irreversible reduction will be of an hyperbolic form, such that the gradient of the plot in the region corresponding to the head of the wave will be twice that of the lower section. Such a doubling of the log plot slope has been reported in the reduction of the hexaquo-nickel ion in 0.2 molar potassium nitrate by Kivalo, Oldham and Laitinen (loc. cit.), who also showed that experimental current-voltage curves were in close agreement with equation (84).
According to equation (103), at 25°C, we have

\[
\left\{ \frac{d}{dE} \log \frac{I}{I_d-I} \right\} \phi(H) \rightarrow 1 = \frac{2\alpha n_a F}{RT} \log e = 33.8 \alpha n_a \text{ volt}^{-1}
\]

(104)

and

\[
\left\{ \frac{d}{dE} \log \frac{I}{I_d-I} \right\} \phi(H) \rightarrow 0 = \frac{\alpha n_a F}{RT} \log e = 16.9 \alpha n_a \text{ volt}^{-1}
\]

(105)

These relationships also apply in the case of treatments based on the use of average currents during drop life. The justification of this fact is given in Appendix II. In this case we have

\[
\left\{ \frac{d}{dE} \log \frac{I}{I_d-I} \right\} \phi(H) \rightarrow 1 = 33.8 \alpha n_a \text{ volt}^{-1}
\]

(106)

and

\[
\left\{ \frac{d}{dE} \log \frac{I}{I_d-I} \right\} \phi(H) \rightarrow 0 = 16.9 \alpha n_a \text{ volt}^{-1}
\]

(107)

Thus, polarographic waves may conveniently be interpreted either by a plot of \( \log \frac{I}{I_d-I} \) against potential, or by a plot of \( k_{f,h} \) against potential using figure (7) to evaluate \( k_{f,h} \) from values of \( H \) obtained for various values of \( I/I_d \).

* * * * * * *
(iv). Subsidiary processes at the dropping mercury electrode.

The electrocapillary curve of mercury. - The curve which expresses the relation between the potential of mercury and the surface tension at a mercury-electrolyte solution interface is called the electrocapillary curve. Since the surface tension, and therefore the drop time, change with the applied potential, the diffusion current of an electroreducible substance does not remain entirely constant with increasing negative potential. Since the nature of the electrocapillary curve is important in the present work a discussion of this topic follows.

Lippmann (51) found that the surface tension of cathodically polarized mercury first increases, and then decreases again with increasing negative potential, so that the electrocapillary curve has a parabolic shape. In air-free solutions of capillary-inactive electrolytes such as potassium nitrate, the electrocapillary curve has the shape shown in figure (9). The interfacial tension is plotted on the ordinate and the potential of the
mercury, referred to the potential of the \textit{normal} calomel electrode, on the abscissa.

The total surface tension, in general, is due to two effects: (1) attractive van der Waals forces on the surface atoms or molecules which act contractively to decrease the surface area, and (2) an electrical contribution to the surface energy, due to the repulsive coulomb force between fixed surface charges, which acts to increase the surface area, and hence counteracts the van der Waals forces. As a result of this electrical effect the net interfacial tension is decreased.

The change in the total surface tension according to the electrocapillary curve in the absence of capillary-active substances is due entirely to the change in magnitude and sign of the electrical forces with changing applied potential.

At the beginning of the curve (applied potential equal to zero) the mercury has a positive charge which decreases the surface tension. Cathodic polarization of the mercury decreases the positive charge, and the surface tension increases until, at the maximum, the mercury is uncharged. In solutions of capillary-inactive electrolytes this so-called "electrocapillary maximum", or "null point", or "isoelectric point", of mercury is at a potential of \(-0.56\) volts vs. the normal calomel electrode (ca. \(-0.52\) volts vs. the S.C.E.). When the potential of the mercury is made more negative than \(-0.56\) volts the metal acquires a negative charge, and consequently the surface tension decreases. Thus, the mercury
is positively charged to the left of AB (figure 9), uncharged at the electrocapillary maximum, and negatively charged to the right of AB. The part of the electrocapillary curve to the left of AB is called the positive branch, and that to the right of AB is called the negative branch of the curve.

Effect of capillary-active ions on the electrocapillary curve. - Several inorganic anions and many organic anions and cations are capillary-active at a mercury-solution interface. Such ions lower the interfacial tension as a result of their adsorption at the surface of the mercury and change the location of the electrocapillary maximum. This shift of the maximum can be interpreted by a consideration of the change in electrical potential in going from the mercury phase to the other liquid phase, first in the absence of, and then in the presence of capillary-active ions. It is convenient to start at the isoelectric point and assume that the potential, $E$, of the mercury is equal to that of the liquid, $E_0$. Hence, the potential line has the simple shape shown in figure (10), (52).

Figure 10. Potential curve at the isoelectric point in the absence of capillary-active substances.

At the electrocapillary maximum the mercury is uncharged and there is no electrokinetic potential. If capillary-active ions, such as iodide ions, are now added to the solution they are adsorbed onto the face of
the mercury, and simultaneously an equivalent number of potassium ions are dragged along with the iodide ions. The iodide ions accumulate in the adsorbed state very close to the mercury surface, as shown in figure (11). The potassium ions, which are capillary-inactive, do not go as close to the surface as the iodide ions. They are located in the so-called "diffuse double layer". The negatively charged iodide ions give rise to considerable image forces in the mercury phase. However, the interior of the mercury phase is kept constant at -0.56 volts by the external applied e.m.f. Thus, it appears that the surface of the mercury becomes positively charged in the presence of adsorbed iodide or other adsorbed anions, at a potential of -0.56 volts. The electrocapillary maximum can no longer be located at this potential because the positive charge counteracts the surface tension. Consequently, a more negative potential has to be applied to the mercury to remove the positive charge and the electrocapillary maximum is shifted to more negative potentials.

If the potential is made more negative than -0.56 volts it becomes increasingly more difficult for iodide ions to be adsorbed. With increasing negative potential a point is
finally reached where the surface tension has a maximum and where the surface charge has again become equal to zero. At this electrocapillary maximum in the presence of capillary-active anions there are still adsorbed anions, as shown in figure (12). Consequently, the surface tension does not coincide with that on the normal electrocapillary curve at the same potential, but is smaller than the latter. The potential curve is represented in figure (12) and it can be seen that there is still a slight negative electrokinetic potential. As the potential of the mercury is made still more negative a point is finally reached where there is complete desorption of the iodide ions. The electrocapillary curve coincides with the normal one and the potential curve becomes as shown in figure (13). The surface of the mercury is now negatively charged and so the capillary-inactive cations from the solution are drawn close to the surface by the electric field and it is now the
anions which are located in the diffuse double layer.

When the potential of the mercury is made less negative than \(-0.56\) volts the excess of positive charge in the mercury surface will promote the adsorption of iodide ions. The deviation of the new electrocapillary curve from the normal one will become most pronounced at the extreme end of the positive branch of the curve as shown in figure (14) which also shows the effect of other anions in \(1N\) solutions, according to Gouy (53). Bromide, thiocyanate, cyanide, iodide, and sulphide, are increasingly capillary-active in the order given. Chloride is only slightly capillary-active, and nitrate, perchlorate, sulphate, carbonate, hydroxide and phosphate are practically capillary-inactive.

In a similar way it can be shown that capillary-active cations shift the location of the electrocapillary maximum to less negative potentials and produce the most pronounced deviations from the normal curve in the negative branch. Inorganic cations are capillary-inactive but several organic cations (substituted amines, alkaloids) are capillary-active.
Effect of capillary-active non-electrolytes on the electrocapillary curve. - Several inorganic non-electrolytes are capillary-active at a mercury-solution interface, and they lower the surface tension and change the electrocapillary curve. The shape of the curve may be altered in different ways.

(a). The surface tension is lowered but the shape of the curve remains unchanged and the maximum is not shifted.

(b). The adsorbed substances are dipoles which are orientated with the negative side to the mercury. In this case the maximum is shifted to more negative potentials. (Many sulphur-containing compounds, including thiourea (54), fall into this category).

(c). The adsorbed substances are dipoles orientated with the positive side to the mercury. In this case the maximum is shifted to a more negative potential.

All curves coincide with the normal electrocapillary curve at more or less negative potentials, indicating that the capillary-active substances are desorbed at such potentials.

Variation of the drop rate with potential. - It has been shown that the surface tension, and therefore the drop time, changes with the applied potential. Although the precise mechanism by which a drop becomes detached from a mercury thread at the orifice of the capillary is probably somewhat complex, the regularity of the drop fall indicates that it is repeated very exactly. It has been shown (55) that the weight
of the drop which falls is fairly accurately proportional to the surface tension of the mercury, and hence, if the rate of flow of mercury is constant, the drop time will be directly proportional to the surface tension. From the Poiseuille equation

\[ V = \frac{\pi r^4 P t}{8 \ell \eta} \]  

where \( V \) is the volume of liquid that flows in \( t \) seconds from a capillary tube of radius \( r \) and length \( \ell \), \( \eta \) is the viscosity coefficient of the liquid, and \( P \) is the difference in hydrostatic pressure between the two ends of the tube, it can be seen that the rate of flow of the mercury is proportional to the effective pressure forcing it through the capillary. This effective pressure is equal to the applied pressure due to the head of mercury minus a back pressure due to the surface tension of the mercury drop. For normal capillaries the back pressure can be calculated to be 2 to 3 cm. of mercury (see section III(ii)). Thus, even a forty per cent change in the surface tension represents only 1 to 2 per cent change in the effective head of mercury if the total head is about 70 cm. of mercury. Thus, there is very little change in the rate of flow of mercury due to the change in its surface tension, and so the drop time is very nearly proportional to the surface tension. This fact provides a very simple means of following the electrocapillary curve in various solutions, and use has been made of this in the experimental sections.

From the Ilkovic equation it is seen that the value of
the diffusion current is proportional to $m^{2/3}t^{1/6}$. The effect on the diffusion current of variations in potential is thus largely due to variations in the value of $t^{1/6}$, since $m$ is very nearly constant. Hence, when measuring diffusion currents and applying the Ilkovic equation the value of $t$ should be measured at the potential of the electrode.

Dissolved oxygen is capillary-active. Although, in a polarographic analysis oxygen is normally removed by the passage of nitrogen or hydrogen through the solution, the last traces are difficult to remove, and it has been found (56) that the electrocapillary maximum occurs at $-0.4$ to $-0.45$ volt in $0.1M$ potassium chloride deoxygenated by nitrogen or hydrogen.

The condenser current and the residual current. The potential of a mercury electrode relative to a solution of an indifferent electrolyte with which it is in contact may be varied considerably without appreciable reaction occurring at the electrode. The only change which occurs is a change in the charge density in the electrical double layer at the mercury-solution interface. There is no transfer of charge across it such as occurs in an electrochemical reaction. The interface thus behaves as an electrical condenser, the charge of which depends on the potential of the electrode. As can be seen from the section on the electrocapillary curve there is no charge on either side of the double layer when the potential of the electrode is at the electrocapillary maximum or null potential.
When, however, a dropping mercury electrode immersed in an electrolyte solution is held at a potential different from its null potential, a current must flow through the external circuit. This is required in order to provide the charge on the two sides of the interface of each drop. This current is called the "condenser current" and can be calculated to have a magnitude of approximately 0.15 microamperes per volt under normal polarographic conditions.

The existence of a residual current in typical current-voltage curves has already been noted in section II(i) - figure (2). In ordinary practical work the residual current, $i_r$, is the sum of two contributions; that is, $i_r = i_c + i_f$, where $i_c$ is the condenser current just discussed. The residual current also includes a slight "faradaic" current, $i_f$, due to the reduction of traces of reducible impurities in the solution, especially oxygen, the last traces of which are very difficult to remove. Since the residual current often amounts to several tenths of a microampere a correction must be applied when determining diffusion currents.

**Polarographic maxima.** - One of the general characteristics of the current-voltage curves obtained with the dropping mercury electrode is the more or less pronounced maximum which is often present unless special measures are taken to prevent its occurrence. By this, it is meant that instead of the normal increase of current up to a steady average diffusion current as the potential of the electrode
is changed, the current increases almost linearly with change of applied potential up to a value many times that of the true diffusion current, and then quite suddenly falls to a steady normal diffusion current.

In figure 15 a typical "spike" maximum is shown. It can be seen that the height of the maximum is greatly dependent on the concentration of the reducible substance. It also depends on the concentration of the base electrolyte. In general, reducible metal ions in dilute alkali chloride solutions usually do not yield maxima when the concentration of the metal ion is very small, but maxima appear and become more and more pronounced as the metal ion concentration is increased. As a rule there is no simple relation between the height of a maximum and the concentration of reducible substance. In the electrolysis of nickel chloride solutions without any foreign salt present, Emilianova and Heyrovsky (58) found that the ratio of $i_{\text{max}}/i_d$ was equal to 1:1 in a 0.0005N solution, to 2.7:1 in a 0.0025N solution, to 6.1:1 in a 0.0062N solution, and to 6.5:1 in a 0.01N solution. The magnitudes of the maxima also depend on the drop time,
becoming smaller the longer the drop time (59).

Lingane (60) has shown that there is little or no polarization of the dropping electrode while the maximum is developing, but that polarization sets in more or less suddenly when the peak has been reached. This suggests that the supply of the reducible ion to the dropping electrode during the maximum must be abnormally high.

Two explanations of this type of polarographic maximum have been given, the first by Heyrovsky (59,61) and Ilkovic (62), and the second by Antweiler (24) and by von Stackelberg (63,31). A detailed discussion of these explanations is beyond the scope of the present work but a brief comparison of the two theories is given. Heyrovsky attributes the increased supply of the reducible ion to adsorption on the mercury drop due to the condenser current mentioned in the previous section. This view has been opposed on both theoretical and practical grounds (64,65). On the other hand Antweiler has conclusively demonstrated, by microphotographs of the mercury drop, that during a "maximum" the diffusion layer close to the mercury surface flowed rapidly round the mercury drop. In Antweiler's view, due to the shielding effect of the capillary, the current density is greater at the bottom of the drop than at the top, and so causes a potential difference between the top and bottom of the drop, and also a difference of interfacial tension. Electrical double layers can migrate under the influence of a potential gradient and hence cause streaming of
the diffusion layer. This streaming could provide a mechanism for allowing an increased supply of the reducible ion to reach the mercury drop.

If Antweiler's explanation of maxima is correct, then it is to be expected that if the half-wave potential of a polarographic reduction is close to the null point of mercury then no maximum can occur. This is in fact the case for cadmium for which \( E_{1/2} = -0.60 \) volt.

In general, maxima can be suppressed by addition to the aqueous solution of a small concentration of surface-active substance. The function of any such maximum suppressor is to form an adsorbed layer on the aqueous side of the mercury-solution interface which prevents streaming of the diffusion layer. Care is needed in this method as even quite small concentrations of the maximum suppressor can markedly alter the shape of the polarographic wave and the value of the diffusion current (66). Large numbers of different substances have been recommended, two of the commonest being gelatin and methyl red.

Maxima of the "Second Kind". - It has been shown (25, 26, 67, 28) that the diffusion current constant for a given reduction is markedly enhanced at short drop times. This was attributed by Krjukowa (68) to stirring effects within the mercury drop, due to an increased rate of flow of mercury from the capillary.

* * * * * * *
Section III

Polarography of nickel-coumarin solutions.
(i). Literature survey.

**Polarography of nickel.** - In aqueous solution the reduction of the nickel ion at the dropping mercury electrode from non-complex forming supporting electrolytes is irreversible. This is shown by the fact that the half-wave potential (about $-1.1$ volts vs. the S.C.E. in alkali perchlorates or nitrates) is more than 0.5 volt more negative than one would predict from the reversible potential of the Ni$^{++}$-Ni system (about $-0.50$ volt vs. the S.C.E.). Furthermore, the slope of the nickel wave is abnormally small, especially in the presence of gelatin (69).

Pavlik (70) found that the addition of a large concentration of chloride to a nickel salt solution shifted the reduction potential to a more positive potential. In the presence of a high concentration of chloride the wave also had a more nearly normal slope, and the temperature coefficient of the reduction potential was considerably smaller. These effects were attributed to the formation of complex ions between the chloride and nickel ions, which apparently are reduced more reversibly than the hexaquonickel ion. This view is supported by Pavlik's spectroscopic investigations (71). He found that high chloride concentrations in nickel solutions increased absorption in the blue and slightly decreased absorption in the red. The changes corresponded to changes in the polarographic
behaviour. He attributed the results to the formation of ions of the type $[\text{NiCl}_n]^{(n-2)-}$.

With increasing temperature the reduction potential of the hexaquo nickel ion is shifted markedly to a more positive value (70). Lingane and Kerlinger (72) measured the shift of the half-wave potential of the hexaquo-nickel ion with temperature in 0.1M ammonium perchlorate as supporting electrolyte, and found that $dE_h/dt$ was equal to $+3.3$ mv. per degree, whereas the theoretical value if the reaction were irreversible would be $-0.6$ mv. per degree. The fact that the observed temperature coefficient is five times larger than, and of opposite sign to, the theoretical value, indicates that the reduction of the hexaquo-nickel ion involves a large activation energy at the dropping electrode.

In the absence of a maximum suppressor, without any foreign salt present, maxima occur. The relationship between the relative heights of the maxima and the concentration has been given in the previous section, (58).

Strassner and Delahay (49) in their studies on irreversible polarographic waves studied the effect of gelatin on the kinetics of irreversible electrode processes, and in particular the reduction of the hexaquo-nickel ion in molar potassium nitrate. They found that there was a large variation of $\alpha n_a$ with gelatin concentration. For a nickel ion concentration of 0.001M the following values of $\alpha n_a$ were obtained: 0.56 at 0.001 per cent, 0.45 at 0.005 per cent, and
0.32 at 0.01 per cent, concentrations of gelatin.

Kivalo, Oldham and Laitinen (50) studied the polarographic reduction of the nickel ion in a supporting electrolyte of 0.2M potassium nitrate at a gelatin concentration of 0.005 per cent. They found values for $\alpha_n$ equal to 0.37 and 0.32 at the foot, and at the head, of the wave respectively.

Polarography of coumarin. - The literature on the reduction of coumarin at the dropping mercury electrode is contradictory. According to Capka (73), the reduction of coumarin from Britton-Robinson buffers gives a wave, the half-wave potential of which varies with pH. Values obtained for $E_{1/2}$ were -1.61 to -1.68 volt vs. the S.C.E. at pH's 4.8 to 7.8; -1.65 volt at pH's above 7.5. The height of the wave corresponded to a two-electron reduction.

On the other hand, Harle and Lyons (8) state that coumarin gives a single wave with a half-wave potential independent of pH. Values obtained for $E_{1/2}$ were -1.523 to -1.551 volts at pH's 6.82 to 9.89. The wave height varied with pH, decreasing rapidly between pH 9.3 and 10.3. A marked change also occurs in the character of the adsorption spectrum at these pH values. Both the polarographic behaviour and the spectroscopic results are explicable by assuming the pH variable interchange

\[
\begin{align*}
\text{cis-coumarinic acid} \\
\text{CH} = \text{CH} \\
\text{OH} \\
\text{CO}_2\text{H}
\end{align*}
\]
Harle and Lyons deduced that the lactone form is reducible over the range of potentials studied but that the acid is not.

At the top of the wave at pH 6.45 the current is diffusion controlled. It is hence possible to use these conditions for analysis. In general, maxima are absent but appear above 0.005M.

From measurements on the height of the polarographic wave the number of electrons concerned in the diffusion process was deduced to be one. This result was supported by the fact that the value of the reciprocal slope for the plot of \( \log \frac{i}{(i_d - i)} \) vs. \(-E\) was in agreement with the value to be expected for a reversible one-electron reduction. The independence of \( E^{1/2} \) from pH means that at least the potential determining step in the reduction is free of \( H^+ \) participation, and so the step must consist in the addition of a single electron to a neutral molecule.

Harle and Lyons were able to obtain the product of the reduction and separate it into two isomers which they identified as the meso- and racemic forms of tetrahydrodi-4,4'-coumarinyl (m.247,280°), although there remains some doubt about this.

\[
\begin{align*}
\text{tetrahydrodi-4,4'-coumarinyl} \\
\text{meso- and racemic forms}
\end{align*}
\]
The following reaction mechanism was proposed:

\[
R + e \rightarrow R^- \quad \cdots \quad (1)
\]

\[
R^- (+ H^+) \rightarrow RH \quad \cdots \quad (2)
\]

\[
2RH \rightarrow R_2H_2 \quad \cdots \quad (3)
\]

where \( R \) represents the lactone, coumarin. Step (1) is proved by the pH independence of the rate-determining step, and step (3) is supported by the formula of the product and the fact that isomers are obtained. Step (2) is the necessary intermediate. It is uncertain whether \( R^- \) reacts with hydrogen ions or water molecules.

Patzak and Neugebauer (9) studied the polarographic reduction of coumarin in alcoholic tetraethylammonium bromide, which proceeded in two steps having half-wave potentials of -1.66 and -2.16 volts. The first of these was investigated more closely in lithium citrate, borate and phosphate buffers. It was found to correspond to an uptake of one electron.

(ii). Equipment and general technique.

The polarograph. - The polarograph used was an Evershed and Vignoles, Tinsley D.C. polarograph type 19/2, incorporating a derivative circuit. A simplified circuit, showing the important characteristics of a polarograph, has been given in figure 1, section II(i). The current from the dropping mercury electrode system is recorded by a galvanometer. In the rising part of a polarographic step the
average current during the life of a drop is changing rapidly with the potential of the electrode. To obtain the correct average current for a given potential it is necessary that the potential is held constant over a period at least as long as the life of one drop. With the usual galvanometer damping, a considerably longer period is required for the galvanometer to record the correct value of the average current. Thus, if the potential of the electrode is changed continuously, as is the normal procedure, a reasonable approximation to the true current-voltage curve can only be obtained if the rate of change is very slow. With the Tinsley instrument used with the necessary galvanometer damping to minimise oscillations due to the periodic current variations observed with a dropping mercury electrode, it was found that galvanometer lag was considerable. Consequently, in any investigation in which the shape of the current-voltage curve was important the polarograph was operated manually and the average current was measured at successive fixed potentials of the electrode.

The dropping electrode system. — The dropping mercury electrode system used was that described by Lingane and Laitinen (74), and is shown in figure 16. This system was chosen as being the simplest and most convenient for the adjustment and measurement of the head of mercury. It has been shown by various authors (e.g. 19, 54, 75) that the diffusion current is proportional to the square root of the pressure on the dropping mercury. In fact, this is a necessary consequence
The dropping electrode system.

Figure 16. Cell employing a permanent external anode and arrangement of the dropping electrode according to Lingane and Laitinen.
of the Ilkovic equation, since, from the Poiseuille relation, equation (108), (page 81), \( m \) is directly and \( t \) inversely proportional to the pressure on the dropping mercury. Thus, two marks were etched on the vertical stand-tube, and by raising or lowering the mercury reservoir the height of the mercury level could be adjusted to one or other of the marks. In this way, two polarograms could be obtained for each solution and by measuring \( m \) and \( t \) for each polarogram and assuming the validity of the Ilkovic equation duplicate results could be obtained and compared.

Polythene tubing was used for connecting the various glass tubes as shown, since there is less likelihood of contamination of the mercury with polythene than with rubber tubing.

Triple distilled mercury was used, and was the purest available.

The capillary tubing was 10.2 cm. long and had an internal diameter of 0.033 mm.

The cell used was of the H-type recommended by Lingane and Laitinen, and shown in figure 16. It consisted of two compartments separated by a sintered glass disc fused into the middle of the cross-arm. The solution to be analysed was placed in the dropping mercury compartment and the external anode in the other. To prevent streaming of solution from one compartment to the other a 3-4 per cent agar gel saturated with potassium chloride was also placed in the cross-arm on
the side of the reference anode. Since the mobilities of the chloride and potassium ions are very similar, the liquid junction potential observed when using this type of salt bridge is only a few millivolts and was thus neglected. The reference anode consisted of mercury, covered with a layer of calomel. With saturated potassium chloride solution in the anode compartment the potential of the d.m.e. can thus be directly related to that of the S.C.E. after correction for ohmic drop due to the resistance of the cell.

**Calibration of the polarograph galvanometer.** - The following simple method was used to calibrate the current-measuring galvanometer in the polarograph. A precision resistance box was connected to the polarograph in place of the dropping electrode system. This is shown by R in the diagram, which is a simplified circuit of the polarograph. The potential drop across the drum was accurately standardised by means of the Weston standard cell incorporated in the instrument. The setting of the resistance box R, and the setting of the Ayrton shunt F, were adjusted so that the applied e.m.f. and the deflection of the galvanometer were both sufficiently large for accurate measurements.
Let $E$ be the reading of the potentiometer drum (i.e., the total potential drop across the standard resistance, and $R_g$ the resistance of the parallel circuit comprised of the galvanometer and the Ayrton shunt. From Ohm's law the current through the circuit is

$$i = \frac{E}{R + R_g} \quad \ldots \ldots \ldots \ldots \ldots \quad (109)$$

$E$, $R$ and the setting of the Ayrton shunt were adjusted to produce a conveniently measurable deflection, and the values of $E$, $R$ and the deflection were noted. Then, without changing the setting of the shunt, the value of $R$ was increased by about two-fold, which caused the galvanometer deflection to decrease accordingly. The value of $E$ was then increased until the galvanometer deflection was restored exactly to its original value. Since both the current (deflection) and the value of $R$ are constant for the two sets of corresponding values of $R$ and $E$, then

$$\begin{align*}
E_1 &= i(R_1 + R_g) \\
E_2 &= i(R_2 + R_g)
\end{align*} \quad \ldots \ldots \ldots \ldots \ldots \quad (110)$$

or

$$i = \frac{E_2 - E_1}{R_2 - R_1} \quad \ldots \ldots \ldots \ldots \ldots \quad (111)$$

By this means the galvanometer reading was calibrated for various scale readings, and settings of the Ayrton shunt. It was found that the response of the galvanometer, as recorded on the chart of the instrument, was linear, and also that values of the current obtained on different scales were in
agreement with one another.

**Measurement of cell resistance.** - Using the arrangement shown in figure 16 the potential of the dropping electrode, relative to the saturated calomel electrode, is given by the external applied e.m.f. minus the potential drop due to the resistance in the circuit; that is

\[ E_{d.e.} = E_{appl} - iR \]

where \( R \) is the average resistance across the cell during the formation of a drop. According to Ilkovic, \( R = \frac{4}{3}R_{\min} \), where \( R_{\min} \) is the minimum value of the resistance at the moment when the drop falls. According to Zlotowski and Kolthoff (76) the measurement of the cell resistance by means of the classical Wheatstone bridge technique is inaccurate because the minimum value of the resistance during drop life is so poorly defined. The method they used to determine the average value of the resistance was to measure the slope of the straight line deposition branch of the current-voltage curve of the supporting electrolyte. The slope of this line \( (dE/di) \) is approximately numerically equal to the resistance, and they claim satisfactory agreement between this value and the value calculated on theoretical grounds (62).

Using the method just described the resistance across the H-cell was found to be approximately 600 ohms. Thus, for currents not exceeding 10 microamperes the ohmic drop across the cell was deemed small enough to be neglected.
Measurement of the capillary characteristics, \( m \) and \( t \). -

It has been shown in a previous section that, at a given temperature, the diffusion current, \( i_d \), is very nearly proportional to \( m^{2/3} t^{1/6} \), and so it is necessary to have a knowledge of the factors which govern \( m \) and \( t \).

The value of \( t \) at any potential of the dropping electrode was simply measured by timing the formation of a certain number of drops (usually ten drops) by means of a stop-watch.

The value of \( m \) under any condition of the dropping electrode is not so easily determined. In theory, this could be done by weighing the weight of mercury flowing from the capillary, in a given time, under the prevailing conditions. In practice, such a procedure would be extremely tedious.

The factors that govern the value of \( m \) can be predicted by the Poiseuille equation, equation (108), (page 81). In order to apply this equation to the dropping electrode it is necessary to employ the relationship \( m = \frac{Vd}{t} \), where \( d \) is the density of mercury. Thus

\[
m = \frac{Vd}{t} = \frac{\pi r^4 Pd}{8\gamma} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \quad (112)
\]

The value of \( P \) used in this equation is the effective pressure on the dropping mercury, expressed in c.g.s. units (dyne cm\(^{-2}\)). This effective pressure is given by the total applied hydrostatic pressure of the liquid column minus a back pressure exerted by the interfacial tension at the surface of the growing drops. According to Kucera (77) this back pressure is expressible by
where \( c_f \) is the interfacial tension in c.g.s. units (dyne cm\(^{-1}\)) and \( r_d \) is the radius of the spherical drop at any instant during its life. Kolthoff and Lingane (78) have shown that the mean back pressure during the drop life is given by

\[
P_{\text{back}} = \frac{2c_f}{r_d} \quad \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots (113)
\]

and

\[
P_{\text{back}} = \frac{8c_f}{3} \left( \frac{4\pi d}{3mt} \right)^{1/3} \quad \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots (114)
\]

where \( t \) is the drop time. Hence, equation (112) becomes

\[
m = \frac{8\pi d}{8c_f \gamma} \left[ hgd - \frac{8c_f}{3} \left( \frac{4\pi d}{3mt} \right)^{1/3} \right] \quad \cdots \cdots \cdots \cdots \cdots \cdots (115)
\]

In the case of mercury at 25\( ^\circ \)C, \( d = 13.53 \) gm cm\(^{-3}\) and \( \gamma = 0.0152 \) dyne sec cm\(^{-2}\) (poise). We also have \( g = 980.6 \) cm sec\(^{-2}\)

If \( m \) is expressed in mg sec\(^{-1}\) and if the radius of the capillary \( r \) and its length \( \ell \) are expressed in cm., then equation (115) simplifies to

\[
m = 4.64 \times 10^9 \frac{r^4}{\ell} \left\{ h - \frac{7.73 \times 10^{-3} \sigma}{m^{1/3} t^{1/3}} \right\} \quad \cdots (116)
\]

In solutions of electrolytes the interfacial tension \( \sigma' \) may be taken as 400 dyne cm\(^{-1}\) for a rough calculation of the back pressure. For normal capillaries \( m^{1/3} t^{1/3} \) has a value of about 1 mg\(^{1/3}\) and so the back pressure amounts to 3.1 cm. of mercury and so is by no means negligible.

Equation (116) predicts that \( m \) should vary slightly with the medium, because of the interfacial tension in the back pressure term. The percentage change in \( m \) in air and a solution is given by
\[ \Delta m\% = 0.77 \left( \frac{\sigma_s}{(m_s t_s)^{1/3}} - \frac{\sigma_a}{(m_a t_a)^{1/3}} \right) \]

where the subscripts \(s\) and \(a\) refer to the solution and air respectively. Since the back pressure is small compared to \(h\), equation (117) may be simplified to

\[ \Delta m\% = \frac{0.77}{h} \left( \frac{\sigma_s}{(m_s t_s)^{1/3}} - \frac{\sigma_a}{(m_a t_a)^{1/3}} \right) \]  \hspace{1cm} (118)

This equation was tested experimentally by Lingane and Loveridge (79). The agreement between observed and calculated values of \(\Delta m\%\) was fairly good. In air, due to adhesion of the mercury drops to the glass around the capillary orifice, the drops become much larger than if freely suspended. This causes uncertainties in the calculated value of \(\Delta m\%\). It was found that the value of \(m\) in air was 0.5 to 3.6 per cent greater than in an aqueous solution, the difference being inversely proportional to \(h\). Consequently, in precise work \(m\) should be measured in the solution in question rather than in air.

For a particular solution the value of \(m\) is not constant since \(\sigma\) and \(t\) are functions of the dropping electrode potential. It has been shown (80) that the drop time is very nearly directly proportional to the surface tension and so the variation of \(m\) with electrode potential can be determined in terms of the drop time, \(t\), in the following way: if \(m\) is measured, at a given applied pressure, at two different
voltages $E_1$ and $E_2$, then the ratio of the value of $m$ at the two voltages, from equation (116), is given by

$$\frac{m_2}{m_1} = \left( \frac{h - \frac{7.73 \times 10^{-3} \sigma_2}{m_2^{1/3} t_2^{1/3}}}{h - \frac{7.73 \times 10^{-3} \sigma_1}{m_1^{1/3} t_1^{1/3}}} \right)^{-1}$$

which, by a rearrangement of terms and a binomial expansion, neglecting terms of the second order and higher, becomes

$$m_2 = m_1 \left[ 1 - \frac{7.73 \times 10^{-3}}{h} \left( \frac{\sigma_2}{m_2^{1/3} t_2^{1/3}} - \frac{\sigma_1}{m_1^{1/3} t_1^{1/3}} \right) \right]$$

Since the correction term is small, $m_2$ is approximately equal to $m_1$, and since $\sigma$ is proportional to $t$ this equation can be simplified to

$$m_2 = m_1 \left[ 1 - \frac{7.73 \times 10^{-3} \sigma_1}{hm_1^{1/3} t_1^{1/3}} \left( \left( \frac{t_2}{t_1} \right)^{2/3} - 1 \right) \right] \ldots (121)$$

The magnitude of the correction term may now be estimated for a normal polarographic reduction. It may be assumed that the value of $\sigma$ at the electrocapillary maximum in the absence of capillary-active substances is about 425 dyne cm$^{-1}$. If $m_1 = 2$ mg. sec$^{-1}$ and $t_1 = 4$ seconds then $(7.73 \times 10^{-3} \sigma_1/hm_1^{1/3} t_1^{1/3})$ becomes approximately equal to 1.64/h. In the experimental sections it is shown that the value of $t_2/t_1$ may, in an extreme case, fall as low as 0.6 but, in general, is not as low as this. In this extreme case $(t_2/t_1)^{2/3}$ is approximately 0.7 and equation (121) becomes
The correction term is thus about 2 per cent. This correction is small, but is not negligible.

Thus, if m is determined under a given set of conditions then its value under the conditions operating in a particular experiment can be calculated by making use of equation (121). Experimentally, the value of m was determined by collecting the mercury drops flowing from the capillary in a certain time under the supporting electrolyte solution, from which air had been removed. The globule of mercury was washed with distilled water, then with acetone and weighed after drying for a few minutes at room temperature.

Choice of supporting electrolyte. - The polarography of nickel has been investigated in several types of supporting electrolyte solution, but many, such as cyanide, thiocyanate, pyridine and ammoniacal solutions are of no concern in the present investigation. The types of supporting electrolyte which require consideration can be confined to perchlorate, nitrate, chloride, sulphate and various types of buffered solutions. For the investigation of nickel ion alone any of these types of solution would be suitable provided that the pH was below that at which nickel hydroxide is precipitated (about pH 6.5 to 7.0 in the absence of complexing agents).

The polarography of coumarin has been investigated in buffered supporting electrolytes of various types, and has been described in a previous section. It was found that,
provided coumarin was entirely in the lactone form (below pH 7), the results were independent of pH, and so it should be possible to use unbuffered supporting electrolytes. However, it is not possible to go below about pH 3.5 to 4.0 as the coumarin wave would then be obscured by hydrogen discharge.

In commercial plating baths nickel is usually deposited from a Watts type of solution, the composition of which is given in section I. In addition to nickel sulphate and chloride this solution contains boric acid.

Thus, the choice of supporting electrolyte to be used had to be made with respect to the foregoing considerations.

From the theoretical standpoint the perchlorate supporting electrolyte would have been the best to use. However, alkali perchlorates are not available in Analar grades and so, to avoid purification of large quantities of material an alternative supporting electrolyte was sought, and found. In the major part of the investigations the use of nitrate supporting electrolyte was avoided since the supporting electrolyte discharge interferes, to a certain extent, with the coumarin wave.

The choice of supporting electrolyte was thus narrowed down to that between chloride, sulphate or one of the buffer types. For the first part of the work a supporting electrolyte of deci-molar potassium chloride was used. This was subsequently proved to be an excellent choice. However, the effects of other base electrolytes, and also of boric acid
were investigated.

Experimental measurement of current-voltage curves. - For the measurement of accurate current-voltage curves the conditions must be carefully controlled. In the following paragraphs the precautions necessary to ensure that this is so are discussed.

Since oxygen is reducible at the dropping mercury electrode, giving an extended double step which may seriously interfere with many determinations, it was necessary to remove it completely from the solution before recording polarograms. This was done usually by the passage of commercial hydrogen from a cylinder through the solution in the cell, by means of a side-arm provided, for about fifteen minutes. In the earlier determinations commercial nitrogen was used, and was satisfactory but was not found to remove the last traces of oxygen (as determined polarographically) so effectively as the hydrogen. Probably, the hydrogen contained less oxygen than the nitrogen, but, in any case the last traces of oxygen in a solution are very difficult to remove by purely physical means and so no purification of the gases was attempted. This procedure seems to be justified by the fact that no anomalous results which could be assigned to the interference of oxygen were obtained. Before passing the hydrogen through the cell it was saturated with water vapour by bubbling it through a wash bottle containing distilled water. This procedure minimises volume changes in the test solution due to evaporation.
The H-cell was immersed in a bath of water maintained at 25±0.5°C. Lingane and Kolthoff (81) have calculated that the temperature coefficient of the diffusion current is between about 1.3 and 1.6 per cent per degree for most common ions, a result which is in agreement with the experimental values of Nejedly (82) who measured the diffusion currents of various metal ions at various temperatures between 20°C and 95°C. Thus, with temperature control of ±0.5°C, variations in the diffusion current due to temperature variations are maintained at a maximum of about ±1 per cent.

The test solutions were prepared by taking appropriate aliquots, by volume, of various stock solutions, which had been prepared previously, and making up with distilled water to a known volume in a graduated flask. The preparation of the stock solutions is described at appropriate points in the experimental text.

The preparation and purification of the organic compounds used in this work are given in Appendix I. For supporting electrolyte solutions Analar materials were used as supplied.

The stock nickel solution was prepared from B.D.H. Analar nickel sulphate, NiSO₄·6H₂O, NiSO₄·7H₂O and was standardised gravimetrically by precipitation as the dimethylglyoxime.

* * * * * * *
(iii). Polarography of nickel-coumarin solutions in a supporting electrolyte of 0.1 molar potassium chloride.

For the preparation of the supporting electrolyte a 1.0 molar stock solution was prepared from Analar grade potassium chloride. 10 ml. of this stock solution were used for each 100 ml. of test solution. The residual current obtained from this electrolyte in the absence of reducible materials was very small, being about 0.2 µa per volt in the range 0 - 1.9 volts vs. the S.C.E. The potassium chloride was thus thought to be of suitable purity for polarographic work. The pH's of the test solutions were checked with a Cambridge pH meter and in no case was it found that there was a large deviation from neutrality in nickel-coumarin solutions; all the solutions had a pH within the range 6.8 to 7.2. Since the solutions were unbuffered there is no guarantee that the pH in the diffusion layer did not vary from these values. The polarographic behaviour of nickel solutions and of coumarin solutions were first examined independently.

Polarography of nickel. - The current-voltage curves obtained for various concentrations of nickel sulphate are shown in figure 18. It can be seen that at the lower concentrations the curves do not have maxima. Maxima appear at concentrations of 0.75 millimole/litre and above, and the relative heights of the maxima show the normal increase with concentration (see section II(iv)). There is no simple
Figure 18. Typical nickel polarograms

Figure 19. Determination of "I" for nickel

Capillary characteristic:
- $h = 38.5$ cm.
- $h = 31.5$ cm.
relationship between the relative heights of the maxima and the concentration of the nickel ion. For a given nickel concentration the relative height of the maximum, when present, decreases with increasing drop time. The maximum is effectively suppressed by the addition of gelatin to a concentration of 0.001 per cent for a nickel concentration of one millimole/litre.

It has been shown in section II(ii) that, as a first approximation, the modified Ilkovic equation can be reduced to

\[
\frac{I_d}{m^{2/3}t^{1/6}} = IC \quad \text{(45)}
\]

Thus \(\frac{I_d}{m^{2/3}t^{1/6}}\) should be proportional to the concentration \(C\), the proportionality constant being given by the "diffusion current constant", \(I\).

Values of the diffusion current at various nickel concentrations are given in Table 5, for two different heads of mercury, and are shown graphically in figure 19. The proportionality of \(I_d/m^{2/3}t^{1/6}\) with concentration is good, straight lines going through the origin being obtained. The values of \(I\) that were obtained were slightly different at the two dropping mercury pressures, being 3.38 at the shorter drop time and 3.23 at the longer drop time. This difference is about 5 per cent and should therefore be outside the experimental error, especially as these results correspond to the mean of observations at six different concentrations. Variations in \(I\) with different capillaries have been reported
Table 5

Diffusion currents at various concentrations of nickel ion in 0.1M potassium chloride at 25°C.

Air removed from the solutions with hydrogen.

<table>
<thead>
<tr>
<th>NiSO₄ mmoles/1.</th>
<th>m mg/sec</th>
<th>t sec</th>
<th>( \frac{m^{2/3}t^{1/6}}{t^{2/3}} )</th>
<th>( \frac{t_d}{\mu A} )</th>
<th>( \frac{t_d}{m^{2/3}t^{1/6}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>2.139</td>
<td>3.62</td>
<td>2.057</td>
<td>1.740</td>
<td>0.846</td>
</tr>
<tr>
<td>0.25</td>
<td>1.752</td>
<td>4.64</td>
<td>1.877</td>
<td>1.610</td>
<td>0.858</td>
</tr>
<tr>
<td>0.50</td>
<td>2.076</td>
<td>3.90</td>
<td>2.042</td>
<td>3.69</td>
<td>1.811</td>
</tr>
<tr>
<td>0.50</td>
<td>1.737</td>
<td>4.71</td>
<td>1.871</td>
<td>3.08</td>
<td>1.646</td>
</tr>
<tr>
<td>0.75</td>
<td>2.139</td>
<td>3.74</td>
<td>2.068</td>
<td>5.39</td>
<td>2.604</td>
</tr>
<tr>
<td>0.75</td>
<td>1.752</td>
<td>4.60</td>
<td>1.875</td>
<td>4.53</td>
<td>2.416</td>
</tr>
<tr>
<td>1.00</td>
<td>2.076</td>
<td>3.90</td>
<td>2.042</td>
<td>6.89</td>
<td>3.375</td>
</tr>
<tr>
<td>1.00</td>
<td>1.737</td>
<td>4.71</td>
<td>1.871</td>
<td>5.96</td>
<td>3.185</td>
</tr>
<tr>
<td>1.50</td>
<td>2.139</td>
<td>3.74</td>
<td>2.068</td>
<td>10.46</td>
<td>5.058</td>
</tr>
<tr>
<td>1.50</td>
<td>1.752</td>
<td>4.60</td>
<td>1.875</td>
<td>9.12</td>
<td>4.809</td>
</tr>
<tr>
<td>2.00</td>
<td>2.139</td>
<td>3.74</td>
<td>2.068</td>
<td>13.33</td>
<td>6.445</td>
</tr>
<tr>
<td>2.00</td>
<td>1.752</td>
<td>4.60</td>
<td>1.875</td>
<td>12.20</td>
<td>6.509</td>
</tr>
</tbody>
</table>
Table 6

Comparison of the experimental results with those of Kolthoff and Lingane and with calculated values at 25°C.
Nickel sulphate concentration 1.00 millimole/litre in a supporting electrolyte of 0.1M potassium chloride.

<table>
<thead>
<tr>
<th>Source</th>
<th>$m^{2/3}t^{1/6}$</th>
<th>$I_d$, $\mu A$</th>
<th>$I$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental</td>
<td>2.042</td>
<td>6.89</td>
<td>3.375</td>
</tr>
<tr>
<td></td>
<td>1.871</td>
<td>6.04</td>
<td>3.230</td>
</tr>
<tr>
<td>Kolthoff and Lingane</td>
<td>1.60</td>
<td>5.40</td>
<td>3.375</td>
</tr>
<tr>
<td>Original Ilkovic equation</td>
<td>-</td>
<td>-</td>
<td>3.19*</td>
</tr>
<tr>
<td>Modified Ilkovic equation</td>
<td>-</td>
<td>-</td>
<td>3.32*</td>
</tr>
</tbody>
</table>

*For the calculations of $I$ it was necessary to know the value of the diffusion coefficient of the nickel ion. The value of the diffusion coefficient at infinite dilution can be calculated from ionic conductance data to be $0.69 \times 10^{-5}$ cm$^2$ sec$^{-1}$, (83). For the modified Ilkovic equation $m^{-1/3}t^{1/6}$ was taken as $1.0$ mg$^{-1/3}$ sec$^{1/2}$ which was a close approximation to the actual values.
by other observers for other systems and have been attributed to stirring effects within the mercury drop (68). However, in Table 6 the experimental results are compared with those of Kolthoff and Lingane (83) and also with those calculated from the original and modified Ilkovic equations. It can be seen that the experimental results are in good agreement with those of Kolthoff and Lingane and also with those calculated by means of the modified Ilkovic equation even though no correction to the diffusion coefficient has been made to allow for the effect of ionic strength.

The current-voltage curves having no maxima, that is, those obtained below a concentration of 0.75 millimole/litre, were analysed according to the treatment given in section II(iii). In addition, a current-voltage curve was analysed for a nickel sulphate concentration of 1.00 millimole/litre for a gelatin concentration of 0.001 per cent. The results are given in Table 7 and represented graphically in figure 20.

In three cases out of the four it is seen that the gradient of the "log $I/(I_d-I)$ plot" increases steadily with increasing negative voltage as predicted theoretically for a totally irreversible wave. In the remaining case a fairly good straight line was obtained, the slope of which was approximately the same as that to be expected at the foot of the wave. Values of $\alpha n_a$ were calculated from the values of the slopes of the curves at the head and the foot of the wave. This method is probably not so accurate as the alternative
Analysis of nickel polarograms in 0.1M potassium chloride.
Air removed from the solutions with hydrogen.
Temperature 25°C.

(a). NiSO₄ 0.25 mmole/l., t = 4.64 sec., E₁/₂ = -1.026 volt.

<table>
<thead>
<tr>
<th>E_d.e., volts</th>
<th>I, μA</th>
<th>I/I_d</th>
<th>log I/I_d</th>
<th>log H</th>
<th>log k_f,h</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.80</td>
<td>0.0</td>
<td>0.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.86</td>
<td>0.024</td>
<td>0.015</td>
<td>2.180</td>
<td>2.01</td>
<td>5.01</td>
</tr>
<tr>
<td>0.90</td>
<td>0.033</td>
<td>0.020</td>
<td>2.321</td>
<td>2.21</td>
<td>5.30</td>
</tr>
<tr>
<td>0.94</td>
<td>0.063</td>
<td>0.039</td>
<td>2.610</td>
<td>2.52</td>
<td>5.61</td>
</tr>
<tr>
<td>0.98</td>
<td>0.270</td>
<td>0.168</td>
<td>1.304</td>
<td>1.19</td>
<td>4.28</td>
</tr>
<tr>
<td>1.00</td>
<td>0.442</td>
<td>0.275</td>
<td>1.578</td>
<td>1.45</td>
<td>4.54</td>
</tr>
<tr>
<td>1.02</td>
<td>0.714</td>
<td>0.444</td>
<td>1.902</td>
<td>1.73</td>
<td>4.82</td>
</tr>
<tr>
<td>1.04</td>
<td>1.020</td>
<td>0.634</td>
<td>0.238</td>
<td>0.01</td>
<td>3.10</td>
</tr>
<tr>
<td>1.06</td>
<td>1.295</td>
<td>0.804</td>
<td>0.614</td>
<td>0.28</td>
<td>3.37</td>
</tr>
<tr>
<td>1.08</td>
<td>1.410</td>
<td>0.876</td>
<td>0.848</td>
<td>0.43</td>
<td>3.52</td>
</tr>
<tr>
<td>1.10</td>
<td>1.485</td>
<td>0.923</td>
<td>1.075</td>
<td>0.59</td>
<td>3.68</td>
</tr>
<tr>
<td>1.12</td>
<td>1.560</td>
<td>0.970</td>
<td>1.494</td>
<td>0.86</td>
<td>3.95</td>
</tr>
<tr>
<td>1.16</td>
<td>1.590</td>
<td>0.988</td>
<td>1.900</td>
<td>1.10</td>
<td>2.19</td>
</tr>
<tr>
<td>1.20</td>
<td>1.610</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 7 (cont.)

(b). NiSO₄ 0.50 mmole/l., t = 3.90 sec., Eᵢ/₂ = -1.016 volt

<table>
<thead>
<tr>
<th>E̅_d,e' volts</th>
<th>I, μa</th>
<th>I/I_d</th>
<th>log ( \frac{I}{I_d} - 1 )</th>
<th>log H</th>
<th>log k_f,h</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.90</td>
<td>0.0</td>
<td>0.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.92</td>
<td>0.11</td>
<td>0.030</td>
<td>2.488</td>
<td>3.39</td>
<td>5.51</td>
</tr>
<tr>
<td>0.94</td>
<td>0.26</td>
<td>0.071</td>
<td>2.880</td>
<td>2.80</td>
<td>5.92</td>
</tr>
<tr>
<td>0.96</td>
<td>0.37</td>
<td>0.100</td>
<td>1.047</td>
<td>2.945</td>
<td>4.07</td>
</tr>
<tr>
<td>0.98</td>
<td>0.75</td>
<td>0.203</td>
<td>1.422</td>
<td>1.285</td>
<td>4.41</td>
</tr>
<tr>
<td>1.00</td>
<td>1.29</td>
<td>0.350</td>
<td>1.731</td>
<td>1.58</td>
<td>4.71</td>
</tr>
<tr>
<td>1.03</td>
<td>2.34</td>
<td>0.634</td>
<td>0.239</td>
<td>0.01</td>
<td>3.13</td>
</tr>
<tr>
<td>1.05</td>
<td>3.00</td>
<td>0.813</td>
<td>0.638</td>
<td>0.30</td>
<td>3.42</td>
</tr>
<tr>
<td>1.08</td>
<td>3.57</td>
<td>0.968</td>
<td>1.474</td>
<td>0.845</td>
<td>3.97</td>
</tr>
<tr>
<td>1.10</td>
<td>3.69</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 7 (cont.)

(c) NiSO₄ 0.50 mmole/l., t = 4.71 sec., E½ = 1.027 volt.

<table>
<thead>
<tr>
<th>E_d.e., volts</th>
<th>I, µa</th>
<th>I/I_d</th>
<th>log ( \frac{I}{I_d} )</th>
<th>log H</th>
<th>log k_f,h</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.86</td>
<td>0.0</td>
<td>0.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.90</td>
<td>0.030</td>
<td>0.010</td>
<td>9.992</td>
<td>2.47</td>
<td>5.55</td>
</tr>
<tr>
<td>0.94</td>
<td>0.110</td>
<td>0.036</td>
<td>9.568</td>
<td>4.12</td>
<td></td>
</tr>
<tr>
<td>0.98</td>
<td>0.380</td>
<td>0.123</td>
<td>1.147</td>
<td>1.04</td>
<td></td>
</tr>
<tr>
<td>1.00</td>
<td>0.720</td>
<td>0.234</td>
<td>1.484</td>
<td>1.36</td>
<td></td>
</tr>
<tr>
<td>1.02</td>
<td>1.360</td>
<td>0.441</td>
<td>1.897</td>
<td>1.73</td>
<td>4.81</td>
</tr>
<tr>
<td>1.04</td>
<td>1.970</td>
<td>0.639</td>
<td>0.247</td>
<td>0.015</td>
<td>3.10</td>
</tr>
<tr>
<td>1.06</td>
<td>2.510</td>
<td>0.814</td>
<td>0.640</td>
<td>0.305</td>
<td>3.39</td>
</tr>
<tr>
<td>1.08</td>
<td>2.900</td>
<td>0.940</td>
<td>1.195</td>
<td>0.68</td>
<td>3.76</td>
</tr>
<tr>
<td>1.10</td>
<td>3.020</td>
<td>0.979</td>
<td>1.667</td>
<td>0.97</td>
<td>2.05</td>
</tr>
<tr>
<td>1.12</td>
<td>3.085</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 7 (cont.)

(d). NiSO₄ 1.00 mmole/l., t = 4.60 sec., E₁/₂ = -0.987 volt
Gelatin added to concentration of 0.001 per cent.

<table>
<thead>
<tr>
<th>-E&lt;sub&gt;d,e&lt;/sub&gt;, volts.</th>
<th>I/I&lt;sub&gt;d&lt;/sub&gt;</th>
<th>log (I/I&lt;sub&gt;d&lt;/sub&gt;-I)</th>
<th>log H</th>
<th>log k&lt;sub&gt;f,h&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.80</td>
<td>0.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.84</td>
<td>0.021₅</td>
<td>3.342</td>
<td>2.22</td>
<td>5.31</td>
</tr>
<tr>
<td>0.88</td>
<td>0.055</td>
<td>3.761</td>
<td>2.68</td>
<td>5.77</td>
</tr>
<tr>
<td>0.90</td>
<td>0.074</td>
<td>3.905</td>
<td>2.82</td>
<td>5.91</td>
</tr>
<tr>
<td>0.94</td>
<td>0.174</td>
<td>1.322</td>
<td>1.20₅</td>
<td>4.29₅</td>
</tr>
<tr>
<td>0.98</td>
<td>0.436</td>
<td>1.889</td>
<td>1.72</td>
<td>4.81</td>
</tr>
<tr>
<td>1.00</td>
<td>0.600</td>
<td>0.176</td>
<td>1.9₅</td>
<td>3.04₅</td>
</tr>
<tr>
<td>1.02</td>
<td>0.747</td>
<td>0.470</td>
<td>0.18</td>
<td>3.27</td>
</tr>
<tr>
<td>1.04</td>
<td>0.851</td>
<td>0.758</td>
<td>0.37₅</td>
<td>3.46₅</td>
</tr>
<tr>
<td>1.06</td>
<td>0.914</td>
<td>1.02₆₅</td>
<td>0.56</td>
<td>3.65</td>
</tr>
<tr>
<td>1.10</td>
<td>0.96₉</td>
<td>1.48₉</td>
<td>0.86₅</td>
<td>3.95₅</td>
</tr>
<tr>
<td>1.14</td>
<td>0.99₇</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1.20</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure 20. Analysis of nickel polarograms.

(For conditions - see Table 7.)
method used, due to the difficulty in drawing tangents at the limits of a curve. The alternative method is to plot \( \log k_{\text{f,h}} \) vs. potential, which theory predicts should be a straight line for an irreversible wave. It is seen that, apart from a tailing off at the head of the wave in one case, good straight lines were obtained. Values of \( \alpha n_a \) were calculated and should be more reliable than those obtained from the "log \( I/(I_d-I) \) plot". In Table 8 the results are coordinated, and also compared with those given in the literature. No direct comparison can be made since different supporting electrolytes were used, but certain points are noteworthy. It is seen that the value of \( \alpha n_a \) in a supporting electrolyte of 0.1M potassium chloride at 25°C is larger than in 1M potassium nitrate at the same gelatin concentration at 35°C. If variations in concentration of supporting electrolyte and temperature only have a small effect on the value of \( \alpha n_a \), this observation is in agreement with that of Pavlik (70), who found that in the presence of a high concentration of chloride the wave had a more nearly normal slope. Table 8 also confirms experimentally that gelatin has a marked effect on the kinetics of the electrode process in 0.1M potassium chloride.

**Polarography of coumarin.** - The current-voltage curves obtained for various concentrations of coumarin in 0.1M potassium chloride are shown in figure 21. In general, maxima are absent, but appear at a concentration of 3 millimole/litre. Values of the diffusion current at various concentrations of
Characteristics of nickel polarograms.
Comparison of experimental results with those given in the literature.

<table>
<thead>
<tr>
<th>NiSO₄ m mole/л.</th>
<th>Supporting electrolyte</th>
<th>Temp. °C</th>
<th>m mg/sec</th>
<th>Gelatin concn. %</th>
<th>αnₐ*</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>0.1M KCl</td>
<td>25</td>
<td>1.752</td>
<td>-</td>
<td>0.82</td>
<td>-</td>
</tr>
<tr>
<td>0.50</td>
<td>&quot;</td>
<td>1.737</td>
<td>2.076</td>
<td>-</td>
<td>0.935</td>
<td>0.775</td>
</tr>
<tr>
<td>1.00</td>
<td>&quot;</td>
<td>1.752</td>
<td>0.001</td>
<td>0.65</td>
<td>0.43</td>
<td>0.58</td>
</tr>
<tr>
<td>0.50</td>
<td>0.2M KNO₃</td>
<td>1.935</td>
<td>0.005</td>
<td>-</td>
<td>0.32</td>
<td>0.37</td>
</tr>
<tr>
<td>1.00</td>
<td>1M KNO₃</td>
<td>2.04</td>
<td>0.001</td>
<td>0.56</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1.00</td>
<td>&quot;</td>
<td>0.005</td>
<td>0.45</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1.00</td>
<td>&quot;</td>
<td>0.01</td>
<td>0.32</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* Methods of evaluating αnₐ

(a) log kF,h vs. -E_d,e
(b) log I/(I_d-I) vs. -E_d,e, slope at head of wave
(c) log I/(I_d-I) vs. -E_d,e, slope at foot of wave
Figure 21. Typical coumarin polarograms.

Figure 22. Determination of "I" for coumarin.

Capillary characteristic:

- $h = 38.5$ cm.
- $h = 31.5$ cm.

Concentration, mmole/litre
Table 9

Diffusion currents at various concentrations of coumarin in 0.1M potassium chloride at 25°C.

Air removed from the solutions with hydrogen.

Capillary characteristics:

(a) $m = 2.132$ mg/sec  
$\quad h = 38.5$ cm.  
$t = 2.92$ sec (at -1.70 v.)

(b) $m = 1.737$ mg/sec  
$\quad h = 31.5$ cm.  
$t = 3.60$ sec (at -1.70 v.)

<table>
<thead>
<tr>
<th>Coumarin mmole/1.</th>
<th>(a) $I_d/\mu A$</th>
<th>$I_d/m^{2/3}t^{1/6}$</th>
<th>(b) $I_d/\mu A$</th>
<th>$I_d/m^{2/3}t^{1/6}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>3.69</td>
<td>1.865</td>
<td>3.30</td>
<td>1.848</td>
</tr>
<tr>
<td>2.00</td>
<td>7.50</td>
<td>3.789</td>
<td>6.69</td>
<td>3.744</td>
</tr>
<tr>
<td>3.00</td>
<td>11.18</td>
<td>5.647</td>
<td>9.84</td>
<td>5.507</td>
</tr>
</tbody>
</table>
coumarin, and at two different heads of mercury, are given in Table 9, and shown graphically in figure 22. It is seen that the dependence of the diffusion current on coumarin concentration is linear and values of the diffusion current constant, $I$, agree well for the two dropping mercury pressures. Values obtained for $I$ were 1.87 for position (a) and 1.85 for position (b). These results are somewhat higher than the value of 1.75 obtained from figures given by Harle and Lyons (8) in a different type of supporting electrolyte (buffered solutions of the phosphate or phthalate type, of varying pH). The number of electrons involved in the reduction can be calculated by means of the Ilkovic equation. In the absence of other information Harle and Lyons used a value for $D$ of $0.8 \times 10^{-5}$ cm$^2$ sec$^{-1}$. This is the value for quinaldic acid which structurally resembles coumarin.

From the modified Ilkovic equation, namely

$$\frac{I_d}{Cm^{2/3}t^{1/6}} = I = 607nD^{1/2}(1 + 17D_m^{1/3} - 1/3 - 1/6)$$

the value of $n$ is calculated to be 1.04, that is, 1, and thus the reduction is a one electron process. The value of the coumarin diffusion coefficient under these conditions can then be calculated to be $0.86 \times 10^{-5}$ cm$^2$ sec$^{-1}$.

To test the reversibility of the coumarin reduction two
Table 10

Characteristics of coumarin polarograms in 0.1M potassium chloride at 25° C.

Air removed from the solutions with hydrogen.

Capillary characteristics: - h = 31.5 cm., m = 1.737 mg/sec.

<table>
<thead>
<tr>
<th>$E_{d,e}$ volts</th>
<th>$1.00$ mmole/litre</th>
<th>$2.00$ mmole/litre</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$I, \mu A$</td>
<td>log $\frac{I}{I_d-I}$</td>
</tr>
<tr>
<td>$1.40$</td>
<td>0.0</td>
<td>-</td>
</tr>
<tr>
<td>$1.46$</td>
<td>0.014</td>
<td>3.629</td>
</tr>
<tr>
<td>$1.48$</td>
<td>0.076</td>
<td>2.363</td>
</tr>
<tr>
<td>$1.50$</td>
<td>0.226</td>
<td>2.866</td>
</tr>
<tr>
<td>$1.52$</td>
<td>0.664</td>
<td>1.400</td>
</tr>
<tr>
<td>$1.54$</td>
<td>1.410</td>
<td>1.872</td>
</tr>
<tr>
<td>$1.56$</td>
<td>2.204</td>
<td>0.302</td>
</tr>
<tr>
<td>$1.58$</td>
<td>2.778</td>
<td>0.723</td>
</tr>
<tr>
<td>$1.60$</td>
<td>3.020</td>
<td>1.027</td>
</tr>
<tr>
<td>$1.62$</td>
<td>3.234</td>
<td>1.665</td>
</tr>
<tr>
<td>$1.66$</td>
<td>3.304</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure 23. Characteristics of coumarin polarograms.

(a) 1.00 mmole/L.

(b) 2.00 mmole/L.
current-voltage curves have been analysed by the "log I/(I_d-I) vs. -E_{d.e}" plot. Experimental values are given in Table 10 and the "log plots" in figure 23.

The "log plots" give straight lines but the slopes, with values of 23.30 and 23.60 volt^{-1}, are larger than the theoretical value of 16.9 volt^{-1} to be expected for a reversible one electron reduction. In this facet of the work the experimental results are not in agreement with those of Harle and Lyons, who were working with buffered electrolytes. This may account for the difference, or alternatively, the "log plot" treatment, derived for soluble reduction products, may fail for an insoluble reduction product.

**Polarography of nickel in presence of coumarin.**

**Preliminary investigations.** - In the absence of any experience of the polarography of the nickel ion in the presence of coumarin it was decided in the first place to perform two series of experiments. In the first series the concentration of the nickel ion was kept constant while the coumarin concentration was varied, and in the second series the coumarin concentration was kept constant while the nickel concentration was varied. The concentration ranges chosen were those most suitable for polarographic determinations, namely, about millimolar.

**Run 1.** - A series of solutions was prepared in which the nickel sulphate concentration was constant at approximately one millimole/litre, the coumarin concentration
being varied. The current-voltage curves obtained for each solution are reproduced in figure 24. The curves shown are reproductions of curves automatically recorded by the polarograph after correction for the residual current, and the galvanometer oscillations have been omitted. Due to the finite time response of the galvanometer the curves are probably displaced from their true positions by about 0.02 volt to more negative potentials.

Run 2. - A series of solutions was prepared in which the coumarin concentration was kept constant, the nickel sulphate concentration being varied accordingly. The current-voltage curves are reproduced in figure 25.

Run 3. It was thought desirable to investigate the reproducibility and reliability of the results and also to check that the order of mixing the solutions had no effect on the results. To test this, six solutions containing identical concentrations of potassium chloride, nickel sulphate and coumarin, in each, were prepared in the six possible orders of mixing. The strengths of the nickel sulphate and coumarin chosen were 1.07 and 0.69 millimole/litre respectively. Six polarograms identical to curves of figures 24(c) and 25(e) were obtained, and this shows that the technique being used is both reproducible and reliable.

Analysis of the results. - It can be seen from figure 24 that at small coumarin concentrations the nickel maximum is effectively suppressed. With increasing coumarin concentration
Figure 24. Polarograms of nickel (1.00 mmole/l.) at various coumarin concentrations.
Figure 24 (cont.)

- Coumarin concentrations, mmole/l.

- $E_{de}$, volts

- $\mu A$

- $1.04$

- $1.18$

- $1.38$

- $1.73$

- $2.08$

- $2.77$
Figure 25. Polarograms of nickel (varying concentration) at a coumarin concentration of 0.69 mmole/l.

- E_d.e. volts

-5

0

0.11

0.32

0.53

0.80

1.07

1.60

2.67

nickel mmole/l.

(a)

(b)

(c)

(d)

(e)

(f)

(g)
the shape of the nickel wave is altered and its position is rapidly shifted to more negative potentials. This effect is illustrated by Table 11 which gives the "half-wave potential" of the nickel wave, and also gives the height of the coumarin wave, at various coumarin concentrations. In figure 26, the values of $E_{1/2}$ for nickel are plotted against coumarin concentration. There is a sharp transition in the graph at a coumarin concentration of about 0.95 millimole/litre. This is also the point at which the shape of the nickel wave becomes distorted. It seems probable that the wave is no longer a typical polarographic wave, the term "half-wave potential" losing its significance. However, it is convenient to retain the term for reference purposes.

The diffusion current of the nickel ion, in contrast to its "half-wave potential", is indifferent to the presence of coumarin. On the other hand, the half-wave potential of the coumarin remains constant, but its diffusion current is less than if the nickel had been absent. This is plainly shown in figure 27 in which the height of the coumarin wave has been plotted against coumarin concentration. Also shown in this diagram is the wave height to be expected if coumarin alone was present. It can be seen that the decrease in the wave height is appreciable.

In figure 25 the current-voltage curves obtained at a coumarin concentration of 0.69 millimole/litre have been reproduced at various nickel concentrations. It can be seen
Values of \( E_{1/2} \) for nickel and the height of the coumarin wave as a function of coumarin concentration.

Supporting electrolyte: 0.1M potassium chloride, at 25°C.

Air removed from the solutions with nitrogen.

Nickel sulphate concentration = 1.07 millimole/litre.

For nickel, \( I_d \) constant at 8.47 \( \mu \)A.

For coumarin, \( E_{1/2} \) constant at -1.54 volts.

Capillary characteristic: \( m = 2.621 \text{ mg/sec} \).

<table>
<thead>
<tr>
<th>Coumarin mmole/l.</th>
<th>( -E_{1/2} ) volts vs. S.C.E.</th>
<th>( I_d ) for coumarin ( \mu )A</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.03</td>
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</tr>
<tr>
<td>0.346</td>
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<td>0.969</td>
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<td>1.730</td>
<td>1.38</td>
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<tr>
<td>2.076</td>
<td>1.42</td>
<td>4.73</td>
</tr>
<tr>
<td>2.768</td>
<td>1.47</td>
<td>6.10</td>
</tr>
</tbody>
</table>
Figure 26. "Half-wave potential" of nickel as a function of coumarin concentration.

Figure 27. Effect of nickel on the height of the coumarin wave.
Table 12

Values of the heights of the nickel and coumarin waves as a function of the nickel concentration.

Conditions as in Table 11.

Coumarin concentration = 0.692 millimole/litre.

For nickel, $E_{1/2} = -1.08$ volts

For coumarin, $E_{1/2} = -1.54$ volts

<table>
<thead>
<tr>
<th>NiSO$_4$ mmole/l.</th>
<th>$I_d$ for nickel $\mu$A</th>
<th>$I_d$ for coumarin $\mu$A</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.0</td>
<td>3.15</td>
</tr>
<tr>
<td>0.107</td>
<td>0.97</td>
<td>2.95</td>
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<tr>
<td>0.321</td>
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<td>2.52</td>
</tr>
<tr>
<td>0.535</td>
<td>4.14</td>
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</tr>
<tr>
<td>0.803</td>
<td>6.10</td>
<td>1.87</td>
</tr>
<tr>
<td>1.070</td>
<td>8.47</td>
<td>1.77</td>
</tr>
<tr>
<td>1.605</td>
<td>11.62</td>
<td>1.57</td>
</tr>
<tr>
<td>2.675</td>
<td>18.42</td>
<td>1.48</td>
</tr>
</tbody>
</table>
Figure 28. Heights of nickel and coumarin waves as a function of nickel concentration.

Figure 29. Total current at -1.7 volts at a nickel concentration of 1.07 mmole/l.
that the position of the nickel wave is independent of its concentration but is different from its position in coumarin-free solutions. It is, in fact, in the same position as the nickel wave in "Run 1" for this coumarin concentration.

It can also be seen that the height of the coumarin wave decreases with increasing nickel concentration, but, as expected, its half-wave potential remains constant.

In Table 12 the heights of the coumarin wave and of the nickel wave are presented, and in figure 28 are plotted against nickel concentration. The height of the nickel wave is seen to be proportional to its concentration, and is in agreement with the value previously obtained. The height of the coumarin wave decreases with increasing nickel concentration, rapidly at first, then more slowly to a seemingly constant value.

**Interpretation and confirmation of the results.** - A complete interpretation of the results is required to explain:

1. the variation of the position of the nickel wave with coumarin concentration
2. the constancy of the nickel diffusion current at varying coumarin concentrations
3. the constancy of the coumarin half-wave potential
4. the decrease in the height of the coumarin wave with increasing nickel concentration.

An interpretation of these facts is offered which requires two basic assumptions:
(a) the coumarin reduction product, or an intermediate, reacts with nickel ions in the diffusion layer, to give a product which is either insoluble or not capable of being reduced below -1.7 volts.

(b) coumarin is adsorbed at the mercury-solution interface, thus hindering the nickel reduction, and the extent of the adsorption is a function of the cathode potential and the coumarin concentration in the bulk of the solution.

The evidence in favour of these assumptions is discussed separately in the following pages.

(a). Interpretation of the diffusion current phenomena at -1.7 volts. - It has been shown that in the presence of nickel the height of the coumarin wave is decreased, and the extent of the decrease is dependent on the nickel concentration. This result has been illustrated graphically in figures 27 and 28. To account for these phenomena it is suggested that the coumarin reduction product, or an intermediate product, reacts with incoming nickel ions in the diffusion layer in such a way that reduction of the nickel ion can no longer take place, possibly by formation of an insoluble compound or a stable, non-reducible complex compound.

Assuming that the above is correct, suppose that for each ion of nickel that reacts in this way the equivalent of $n^*$ molecules of coumarin is involved. From the modified Ilkovic equation the flux of coumarin molecules at the dropping electrode surface is directly proportional to the quantity
$K_{R \cdot R} D_{R}^{1/2}$ where C and D have their usual meanings, and R represents coumarin. K is the correction term in the Ilkovic equation and is equal to $(1 + 17D_{m}^{1/2}t^{-1/3}t^{1/6})^2$. The flux of the nickel ion is proportional to $K_{Ni \cdot Ni} D_{Ni}^{1/2}$. Each nickel ion reacts with the equivalent of $n^* \cdot$ coumarin molecules so that equivalent quantities of nickel ions and coumarin molecules exist at the electrode surface when the flux of coumarin molecules is $n^* \cdot$ times the flux of nickel ions, that is, when

$$n^* K_{Ni \cdot Ni} D_{Ni}^{1/2} = K_{R \cdot R} D_{R}^{1/2}.$$

Thus, the net flux of nickel ion at the electrode surface is proportional to $(K_{Ni \cdot Ni} D_{Ni}^{1/2} - \frac{1}{n^*} K_{R \cdot R} D_{R}^{1/2})$

The reduction of each nickel ion requires two electrons, so that the net contribution of nickel ion to the total current will be proportional to $2(K_{Ni \cdot Ni} D_{Ni}^{1/2} - \frac{1}{n^*} K_{R \cdot R} D_{R}^{1/2})$

The reduction of each coumarin molecule requires one electron so the contribution to the total current will be proportional to $K_{R \cdot R} D_{R}^{1/2}$. The proportionality constants are defined by the Ilkovic equation, and hence the total current at potentials of $-1.7$ volts is given by

$$I_T = 607m^{2/3}t^{1/6} \left\{ 2(K_{Ni \cdot Ni} D_{Ni}^{1/2} - \frac{1}{n^*} K_{R \cdot R} D_{R}^{1/2}) + K_{R \cdot R} D_{R}^{1/2} \right\}$$

provided that the term $(K_{Ni \cdot Ni} D_{Ni}^{1/2} - \frac{1}{n^*} K_{R \cdot R} D_{R}^{1/2})$ cannot have a negative value and hence is taken as zero when $\frac{1}{n^*} K_{R \cdot R} D_{R}^{1/2}$ is greater than $K_{Ni \cdot Ni} D_{Ni}^{1/2}$. In this latter case the total current is given by
\[ I_T = 607 \, m^{2/3} \, t^{1/6} K_{R} C_{R}^{1/2} \] \hspace{1cm} (124)

and thus is the same as in the absence of nickel.

When \( K_{Ni} C_{Ni}^{1/2} \) is greater than \( \frac{1}{n} K_{R} C_{R}^{1/2} \) the total current is given by

\[ I_T = 607 \, m^{2/3} \, t^{1/6} \left( 2 K_{Ni} C_{Ni}^{1/2} + K_{R} C_{R}^{1/2} \left( 1 - \frac{2}{n} \right) \right) \] \hspace{1cm} (125)

Thus, the apparent height of the coumarin wave is given by

\[ I_{app.} = 607 \, m^{2/3} \, t^{1/6} \left( K_{R} C_{R}^{1/2} \left( 1 - \frac{2}{n} \right) \right) \] \hspace{1cm} (126)

Expressions (124), (125) and (126) can be simplified by writing them in terms of "diffusion current constants", defined thus by the modified Ilkovix equation:

\[ \frac{I}{m^{2/3} \, t^{1/6}} = IC \quad \text{where} \quad I = 607 \, nD_{K}^{1/2} \]

Expression (125) for the total current at \(-1.7\) volts then becomes

\[ \frac{I_T}{m^{2/3} \, t^{1/6}} = I_{Ni} C_{Ni} + \left( 1 - \frac{2}{n} \right) I_{R} C_{R} \] \hspace{1cm} (127)

provided that \( I_{Ni} C_{Ni} \) is greater than \( \frac{2}{n} I_{R} C_{R} \), i.e. nickel is in excess.

In the presence of excess coumarin, i.e. when \( \frac{2}{n} I_{R} C_{R} \) is greater than \( I_{Ni} C_{Ni} \), this expression reduces to

\[ \frac{I_T}{m^{2/3} \, t^{1/6}} = I_{R} C_{R} \] \hspace{1cm} (128)

The contribution of the nickel ion to the total current at \(-1.7\) volts is given by
and the apparent height of the coumarin wave in the presence of excess nickel is given by

\[ \frac{I_{\text{Ni}}}{m^{2/3}t^{1/6}} = I_{\text{Ni}}C_{\text{Ni}} - \frac{2}{n^*} I_R C_R \]  

(129)

Thus, the diffusion current phenomena at -1.7 volts should be governed by expressions (127-130).

Applying the foregoing to the experimental results, it was found in "Run 2" that the apparent height of the coumarin wave in the presence of excess nickel was one-half of its value in nickel-free solutions. That is

\[ \frac{I_{\text{app}}}{I_{\text{real}}} = \frac{1 - 2/n^*}{1} = \frac{1}{2} \]  

from which \( n^* = 4 \)

From equation (127) the total current at -1.7 volts is thus

\[ I_T = m^{2/3}t^{1/6} \left( I_{\text{Ni}}C_{\text{Ni}} + \frac{1}{2} I_R C_R \right) \]  

(131)

when coumarin is not in excess.

In "Run 1", \( C_{\text{Ni}} \) was constant at 1.07 millimole/litre and at this concentration and these conditions it was found that

\[ m^{2/3}t^{1/6}I_{\text{Ni}}C_{\text{Ni}} = 8.47 \mu A \]

For a coumarin concentration of 1.00 millimole/litre it was found that

\[ m^{2/3}t^{1/6}I_RC_R = 4.6 \mu A \]

These results, on application of equations (131) and (128), were used to construct the lines in figure 29. The circles in
this diagram represent the experimental values obtained at individual concentrations and it can be seen that they lie very close to one of the constructed straight lines.

At \(-1.7\) volts the contribution of the nickel ion to the total current is given by equation (129) and should therefore be equal to zero when \(I_{Ni} = \frac{2}{n^*} I_{R \text{C}}\). For \(C_{Ni} = 1.07\) mmole/l, using the experimental results, this occurs when \(\frac{2}{n^*} \times 4.6 C_{R} = 8.47\). From figure 29, this is seen to be when \(C_{R}\) equals 3.7 mmole/litre, so that

\[
n^* = \frac{2 \times 4.60}{8.47} \times 3.7 = 4.02
\]

i.e. \(n^* = 4\) as before.

Experimental confirmation of the foregoing theory. - In figure 29 the experimental results from "Run 1" are compared with those expected from the foregoing. It can be seen that the agreement is good. Unfortunately, the concentration range chosen was not great enough to completely verify the theory. Consequently, further experiments were performed in the same way as before, but the concentration ranges were extended and chosen in the light of experience gained.

**Run 4.** Nickel sulphate 0.50 mmole/l., coumarin varied from 0.5 to 4.0 mmole/l.

**Run 5.** Nickel sulphate 1.00 mmole/l., coumarin varied from 0.25 to 4.5 mmole/l.

**Run 6.** Coumarin 1.50 mmole/l., nickel sulphate varied from 0.50 to 3.00 mmole/l.
Each run was performed with two different values of the mercury flow rate. The results are given in Tables 13-15.

In figure 30 the values of $I_m^{2/3}t^{1/6}$ at $-1.7$ volts are plotted against coumarin concentration for nickel concentrations of 0.50 and 1.00 mmole/litre. Also shown in this diagram are the values to be expected on the foregoing theory, assuming that four molecules of coumarin react in the diffusion layer with each nickel ion. It can be seen that the agreement is good, especially when it is recalled that the theoretical lines are ideal ones calculated assuming complete precipitation (or complete removal in a complex) of nickel ion in the diffusion layer according to a stoichiometrical relationship. If imperfect interaction occurs the experimental points would be expected to lie slightly above the theoretical lines. Thus, it can be seen that if any integer other than four is used to calculate theoretical values the experimental values are no longer in good agreement with the calculated, even allowing for the possibility of non-ideal behaviour just mentioned.

In figure 31 values of $I_{app}^{2/3}t^{1/6}$ obtained from the apparent height of the coumarin wave are plotted against nickel concentration. In the presence of a large excess of nickel the height of the wave is almost exactly half its value in nickel-free solutions.

In view of the very good agreement between the experimental results and the theoretical results for $n^* = 4$,
Table 13

Diffusion current phenomena at -1.7 volts.
Supporting electrolyte 0.1M potassium chloride at 25°C.
Air removed from the solutions with hydrogen.
Nickel sulphate concentration 0.50 mmole/litre.

(a). Capillary characteristics:–

\[
h = 38.5 \text{ cm}, \quad m = 2.132 \text{ mg/sec} (-1.7 \text{ v.})
\]
\[
t = 2.92 \text{ sec} (-1.7 \text{ v.})
\]
\[
m^{2/3} t^{1/6} = 1.981 \text{ mg}^{2/3} \text{ sec}^{-1/2}
\]

<table>
<thead>
<tr>
<th>Coumarin mmole/l.</th>
<th>Apparent height of coumarin wave, (\mu)a</th>
<th>Total current at -1.7 v.</th>
<th>Coumarin (\frac{I}{m^{2/3} t^{1/6}})</th>
<th>Total (\frac{I}{m^{2/3} t^{1/6}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
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<td>-</td>
<td>-</td>
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</tr>
<tr>
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<td>14.62</td>
<td>-</td>
<td>7.38</td>
</tr>
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</table>
Table 13 (cont.)

(b). Capillary characteristics:

- $h = 31.5$ cm.
- $m = 1.737 \text{ mg/sec. at } -1.7 \text{ v.}$
- $t = 3.60 \text{ sec. at } -1.7 \text{ v. vs. the S.C.E.}$
- $m^{2/3}t^{1/6} = 1.788 \text{ mg}^{2/3}\text{sec}^{1/2}$

<table>
<thead>
<tr>
<th>Coumarin mmole/l.</th>
<th>Apparent height of coumarin wave, $\mu\text{a}$</th>
<th>Total current at $-1.7\text{v.}$ $\mu\text{a}$</th>
<th>Coumarin $\frac{T}{m^{2/3}t^{1/6}}$</th>
<th>Total $\frac{T}{m^{2/3}t^{1/6}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
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<td>-</td>
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</table>
Table 14

Diffusion current phenomena at -1.7 v. vs. the S.C.E.
Supporting electrolyte 0.1M potassium chloride at 25°C
Nickel sulphate concentration 1.00 mmole/litre.

(a). Capillary characteristics: \( m = 2.602 \text{ mg/sec} \)
\( t = 2.75 \text{ sec} \)
\( m^{2/3} t^{1/6} = 2.234 \text{ mg}^{2/3} \text{sec}^{-1/2} \)

<table>
<thead>
<tr>
<th>Coumarin mmole/l.</th>
<th>Apparent height of coumarin wave, ( \mu \text{A} )</th>
<th>Total current at -1.7V, ( \mu \text{A} )</th>
<th>Coumarin ( \frac{I}{m^{2/3} t^{1/6}} )</th>
<th>Total ( \frac{I}{m^{2/3} t^{1/6}} )</th>
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</thead>
<tbody>
<tr>
<td>0.0</td>
<td>-</td>
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</table>

* \( m^{2/3} t^{1/6} = 1.981 \text{ mg}^{2/3} \text{sec}^{-1/2} \) (cf. Table 13(a)).
Table 14 (cont.)

(b). Capillary characteristics:— m = 1.977 mg/sec.
\[ t = 3.70 \text{ sec.} \]
\[ m^{2/3}t^{1/6} = 1.959 \text{ mg}^{2/3} \text{sec}^{-1/2} \]

<table>
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<tr>
<th>Coumarin mmole/l.</th>
<th>Apparent height of coumarin wave, ( \mu \text{A} )</th>
<th>Total current at (-1.7\text{v}^*), ( \mu\text{A} )</th>
<th>Coumarin ( I ) ( m^{2/3}t^{1/6} )</th>
<th>Total ( I ) ( m^{2/3}t^{1/6} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3.30</td>
</tr>
<tr>
<td>0.25</td>
<td>0.615</td>
<td>-</td>
<td>0.31</td>
<td>3.61</td>
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<td>1.325</td>
<td>-</td>
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<td>-</td>
<td>0.91</td>
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<td>-</td>
<td>1.14</td>
<td>4.44</td>
</tr>
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<td>2.165</td>
<td>-</td>
<td>1.105</td>
<td>4.41</td>
</tr>
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<td>1.20</td>
<td>2.465</td>
<td>-</td>
<td>1.26</td>
<td>4.56</td>
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<tr>
<td>1.50</td>
<td>2.845</td>
<td>-</td>
<td>1.45</td>
<td>4.75</td>
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<td>3.725</td>
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<td>5.20</td>
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<tr>
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<td>4.845</td>
<td>-</td>
<td>2.47</td>
<td>5.77</td>
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<td>3.00</td>
<td>-</td>
<td>11.50*</td>
<td>-</td>
<td>6.43*</td>
</tr>
<tr>
<td>3.75</td>
<td>-</td>
<td>13.28*</td>
<td>-</td>
<td>7.43*</td>
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<tr>
<td>4.50</td>
<td>-</td>
<td>15.58*</td>
<td>-</td>
<td>8.67*</td>
</tr>
</tbody>
</table>

* \( m^{2/3}t^{1/6} = 1.788 \text{ mg}^{2/3} \text{sec}^{-1/2} \) (cf. Table 13(b)).
Apparent height of the coumarin wave in the presence of nickel. Supporting electrolyte 0.1M potassium chloride at 25°C. Air removed from the solutions with hydrogen.

Coumarin concentration 1.50 millimole/litre.

Capillary characteristics:
(a). \( m^{2/3} \cdot t^{1/6} = 1.981 \text{ mg}^{2/3} \text{sec}^{-1/2} \) (cf. Table 13(a)).
(b). \( m^{2/3} \cdot t^{1/6} = 1.788 \text{ mg}^{2/3} \text{sec}^{-1/2} \) (cf. Table 13(b)).

<table>
<thead>
<tr>
<th>NiSO₄ mmole/l.</th>
<th>( I_{\text{app}}, \mu A )</th>
<th>( \frac{I_{\text{app}}}{m^{2/3} \cdot t^{1/6}} )</th>
<th>( I_{\text{app}}, \mu A )</th>
<th>( \frac{I_{\text{app}}}{m^{2/3} \cdot t^{1/6}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>-</td>
<td>2.79</td>
<td>-</td>
<td>2.79</td>
</tr>
<tr>
<td>0.50</td>
<td>3.90</td>
<td>1.97</td>
<td>3.71</td>
<td>2.07</td>
</tr>
<tr>
<td>1.00</td>
<td>3.20*</td>
<td>1.43</td>
<td>2.84**</td>
<td>1.45</td>
</tr>
<tr>
<td>1.50</td>
<td>2.79</td>
<td>1.41</td>
<td>2.46</td>
<td>1.38</td>
</tr>
<tr>
<td>2.00</td>
<td>2.73</td>
<td>1.38</td>
<td>2.44</td>
<td>1.36**</td>
</tr>
<tr>
<td>2.50</td>
<td>2.73</td>
<td>1.38</td>
<td>(2.03)</td>
<td>(1.14)</td>
</tr>
<tr>
<td>3.00</td>
<td>(2.37)</td>
<td>(1.20)</td>
<td>2.50</td>
<td>1.40</td>
</tr>
</tbody>
</table>

\( m^{2/3} \cdot t^{1/6} = 2.234 \text{ mg}^{2/3} \text{sec}^{-1/2} \) (cf. Table 14(a)).

\( m^{2/3} \cdot t^{1/6} = 1.959 \text{ mg}^{2/3} \text{sec}^{-1/2} \) (cf. Table 14(b)).
Figure 30. Total diffusion currents at -1.7 volts.

(for explanation - see text)

(a) Nickel sulphate

0.50 mmole/l.

Capillary:
- C = 38.5 cm.
- C = 31.5 cm.

(b) Nickel sulphate

1.00 mmole/l.

Capillary:
- C = 38.5 cm.
- C = 31.5 cm.

Values of \( \frac{e_i}{m^2 s t/l} \)

Coumarin conc. - mmole/litre

Values of \( \frac{e_i}{m^2 s t/l} \)

Coumarin conc. - mmole/litre
Figure 31. Apparent height of the coumarin wave as a function of the nickel concentration. (For explanation - see text).

Coumarin concentration 1.50 mmole/l.

Capillary characteristic:

- $h = 38.5$ cm.
- $h = 31.5$ cm.

Values of $\frac{1}{m^{2/3}l}$
and the fact that any other integer would give widely differing theoretical results, the foregoing results would seem to establish that the net electrode reaction at a potential of -1.7 volts may be formulated:

\[
\text{Ni(H}_2\text{O)}_6^{++} + 4 \text{C-ring} + (4\text{H}^+) + 4\text{e} = ?
\]

It is not yet possible to determine the course of the reaction and the products are not known. It is also unknown whether hydrogen ions or water molecules are involved, and how many are concerned. The reaction is discussed further at a later stage.

(b). Adsorption of coumarin at the dropping electrode. - At concentrations of 0.75 millimole/litre, or greater, the nickel wave has a pronounced maximum. This maximum is very effectively suppressed by the presence of coumarin in the solution. It has been seen in section II(iv) that, in general, maxima are suppressed by the addition of small quantities of surface-active compounds to the aqueous solution. The function of the maximum suppressor is to form an adsorbed layer on the aqueous side of the mercury-solution interface which prevents streaming of the diffusion layer. As a result of this adsorption at the surface of the mercury the interfacial tension is lowered and the shape of the electrocapillary curve is altered. The nature of the electrocapillary curve and the effect of capillary-active substances on it has been discussed.
in section II(iv).

Coumarin, in small concentrations, acts as a maximum suppressor in the case of nickel, which strongly suggests that coumarin is capillary-active at the mercury-solution interface. If this is so, then an explanation for the distortion of the nickel waves in polarograms obtained when coumarin is present in larger concentrations can be offered, as follows.

Assume that initially the applied e.m.f. is such that the potential of the dropping electrode is below the reduction potential of the nickel ion, and that the extent of adsorption of coumarin is a function of the cathode potential and the coumarin concentration in the bulk of the solution. If the dropping electrode potential is then made steadily more negative the normal reduction potential of nickel will eventually be reached. If, at this potential coumarin is still adsorbed, nickel ions may be prevented from reaching the mercury surface. On making the potential of the mercury drop still more negative the electric field surrounding the drop becomes stronger until eventually the positively charged nickel ions may penetrate the coumarin layer. With a further slight increase of negative potential the flux of nickel ions reaching the dropping electrode surface becomes great enough to dissipate the layer of coumarin, and thereafter the reduction of the nickel ions can proceed in the normal way, the diffusion current soon reaching the value it would have in the absence of coumarin.
It can reasonably be expected that the amount of adsorbed coumarin depends on its concentration in the bulk of the solution. At higher concentrations the adsorption would be more extensive. In the presence of a relatively high concentration of supporting electrolyte the electric field is confined to a region very close to the surface of the dropping electrode (and would be modified by the presence of adsorbed dipoles) and hence reduction of the nickel ion would be more difficult with the thicker adsorbed layers. This would explain the progressive shift of the nickel reduction potential to more negative potentials with increasing coumarin concentrations.

The curved portion of figure 26, and also the distortion of the nickel waves, can be explained in this manner. For the straight line portion of the graph (where the nickel wave has a fairly normal shape) it is suggested that at these lower coumarin concentrations the adsorbed layer is incomplete, or has not yet reached a certain critical thickness, and the reduction of the nickel ion is only slightly influenced. The transition point in the diagram would then correspond to the filling up of the layer or the reaching of a certain critical thickness.

Evidence in favour of the above mechanism can be obtained by the following simple method. It has been shown in section II(iv) that the time of formation of the mercury drops is very nearly proportional to the interfacial tension at the
mercury-solution interface. Thus, the electrocapillary curve of mercury, which is modified in the presence of adsorbed substances, can be plotted by noting the time of formation of the mercury drops at various potentials of the dropping electrode, and used to investigate the nature of any adsorption.

In Table 16 the mercury drop times at varying coumarin concentrations and potentials of the dropping electrode are given, and the curves obtained from these results are shown in figure 32.

It is seen that coumarin does markedly lower the drop time, and hence it also lowers the interfacial tension. The electrocapillary maximum is depressed rather than shifted to more positive or negative potentials. The negative branch of the curve would appear to have been changed more than the positive branch but this may be simply due to the fact that so little of the positive branch can be observed. (At potentials more positive than zero, chloride ion oxidises the dropping electrode to calomel). Since coumarin has a large dipole moment it cannot therefore be adsorbed with either the positive or negative end of its dipole to the mercury surface. It is possibly adsorbed edgewise but this would probably also give a resultant dipole moment perpendicular to the mercury surface. It would seem that the most probable orientation for the molecule is for it to be adsorbed flat with the line of action of its dipole parallel to the mercury surface. The orientation of the molecule is discussed more fully in a later
Table 16

Values of the mercury drop time as a function of coumarin concentration and dropping electrode potential in 0.1M potassium chloride at 25°C.
Air removed from the solutions with hydrogen.

<table>
<thead>
<tr>
<th>$E_{d,e}$ volts</th>
<th>Coumarin concentrations, millimole/litre</th>
<th>0.0</th>
<th>0.10</th>
<th>0.50</th>
<th>1.00</th>
<th>2.50</th>
<th>4.50</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Drop times, in seconds</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0</td>
<td>3.91</td>
<td>3.91</td>
<td>3.88</td>
<td>3.84</td>
<td>3.84</td>
<td>3.80</td>
<td></td>
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<tr>
<td>0.1</td>
<td>4.08</td>
<td>4.05</td>
<td>4.03</td>
<td>3.96</td>
<td>-</td>
<td>3.92</td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>4.21</td>
<td>4.17</td>
<td>4.12</td>
<td>4.04</td>
<td>4.00</td>
<td>3.98</td>
<td></td>
</tr>
<tr>
<td>0.3</td>
<td>4.33</td>
<td>4.22</td>
<td>4.16</td>
<td>4.10</td>
<td>-</td>
<td>4.01</td>
<td></td>
</tr>
<tr>
<td>0.4</td>
<td>4.36</td>
<td>4.26</td>
<td>4.19</td>
<td>4.12</td>
<td>4.12</td>
<td>4.02</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>4.35</td>
<td>4.26</td>
<td>4.19</td>
<td>4.12</td>
<td>4.09</td>
<td>4.02</td>
<td></td>
</tr>
<tr>
<td>0.6</td>
<td>4.35</td>
<td>4.25</td>
<td>4.16</td>
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<td>4.00</td>
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<tr>
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<td>-</td>
<td>3.98</td>
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</tr>
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<td>4.05</td>
<td>4.03</td>
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<tr>
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<td>4.08</td>
<td>4.07</td>
<td>4.00</td>
<td>-</td>
<td>3.79</td>
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</tr>
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<td>1.0</td>
<td>4.06</td>
<td>3.97</td>
<td>3.97</td>
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<td>3.82</td>
<td>3.70</td>
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<td>3.86</td>
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<td>3.82</td>
<td>-</td>
<td>3.60</td>
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<td>3.74</td>
<td>-</td>
<td>3.70</td>
<td>3.58</td>
<td>3.51</td>
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<td>3.67</td>
<td>3.59</td>
<td>-</td>
<td>3.58</td>
<td>-</td>
<td>3.42</td>
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</tr>
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<td>1.4</td>
<td>3.49</td>
<td>3.43</td>
<td>-</td>
<td>3.45</td>
<td>3.43</td>
<td>3.28</td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>3.30</td>
<td>3.25</td>
<td>-</td>
<td>3.24</td>
<td>-</td>
<td>3.17</td>
<td></td>
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<td>3.10</td>
<td>3.01</td>
<td>-</td>
<td>3.02</td>
<td>3.02</td>
<td>3.02</td>
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<tr>
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<td>2.85</td>
<td>2.80</td>
<td>-</td>
<td>2.79</td>
<td>-</td>
<td>2.79</td>
<td></td>
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<td>1.8</td>
<td>2.60</td>
<td>2.53</td>
<td>-</td>
<td>2.53</td>
<td>2.53</td>
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</tr>
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</table>
Figure 32. Effect of coumarin on the electrocapillary curve in 0.1 M KCl.

Drop time in seconds vs. $E_{d.e.}$, volts

Coumarin conc. mmole/litre
section, together with further experimental results (see section IV).

The potentials at which most of the coumarin is desorbed (complete desorption does not seem to occur within the observable potential range) are consistent with those at which the nickel ion is reduced in an equivalent coumarin concentration. This affords strong evidence in favour of the suggestion that the distortion of the current-voltage curves for nickel are due to the adsorption of coumarin at the dropping electrode.

Further confirmation can be obtained as follows. If the distortion of the nickel wave is due to adsorption of coumarin at the mercury-electrolyte interface, the distortion should not be peculiar to nickel alone. The waves of other metal ions which are reducible polarographically at potentials similar to nickel should be distorted in a similar way. In 0.1M potassium chloride, zinc has a half-wave potential of 0.995 volts and cobalt (II) a half-wave potential of -1.20 volts, both with respect to the S.C.E. The polarograms obtained for 1.00 millimolar solutions of these elements for a few concentrations of coumarin are shown in figure 33. On comparison with nickel polarograms obtained for similar coumarin concentrations (shown in figure 24) it is seen that the cobalt wave is distorted in a very similar manner to the nickel wave, and although the zinc wave is distorted in a different way to the cobalt and nickel waves the galvanometer
Figure 33. Effect of coumarin on zinc and cobalt (II) waves

- Zinc sulphate
  1.00 mmole/l.
- Cobalt chloride
  1.00 mmole/l.

Coumarin concentrations:
- (1) 0.10
- (2) 1.50
- (3) 2.00 mmole/litre
oscillations become "normal" at exactly the same potentials.

The foregoing results would seem to establish beyond reasonable doubt that the distortion of the polarographic nickel waves is due to adsorption of coumarin at the dropping electrode.

Effect of coumarin on the kinetics of the nickel reduction. - It was shown by Strassner and Delahay (49) that gelatin had a marked effect on the kinetics of the polarographic reduction of the nickel ion in 1M potassium nitrate. Their results have been summarised in section III(i). Since the presence of an adsorbed compound at the surface of the dropping electrode would cause a modification of the double layer structure, and possibly a change in the characteristics of the current-voltage curve, the effect of several concentrations of coumarin on the reduction of the nickel ion in 0.1M potassium chloride was investigated. The results are given in Table 17 and represented graphically in figure 34. The results are summarised in Table 18 and also compared with those previously obtained in the absence of coumarin.

It can be seen that at coumarin concentrations of 0.85 millimole/litre, and below, that the shape of the nickel wave is not greatly influenced by the presence of coumarin. The value of the half-wave potential is slightly shifted to more negative potentials, but the value of $\alpha n_a$, as determined from graphs of $\log k_{f,h}^\prime$ vs. $-E_{d,e}$ is sensibly constant. Above coumarin concentrations of 0.85 millimole/litre the shape of
Characteristics of nickel polarograms at various coumarin concentrations in 0.1M potassium chloride at 25°C.

Air removed from the solutions with hydrogen.

Nickel sulphate concentration 1.00 millimole/litre in all cases.

(a). Coumarin concentration 0.10 millimole/litre

$t = 4.79$ seconds at $E_{d.e} = -1.05$ volts.

<table>
<thead>
<tr>
<th>$E_{d.e}$ volts</th>
<th>$I/I_d$ φ(H)</th>
<th>log $I/I_d$</th>
<th>log H</th>
<th>log $k_f, h$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.80</td>
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<td>-</td>
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<tr>
<td>0.90</td>
<td>0.014</td>
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<td>4.73</td>
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</tr>
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<td>1.20</td>
<td>1.0</td>
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<td>-</td>
<td>-</td>
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</tbody>
</table>
Table 17 (cont.)

(b). Coumarin concentration 0.20 millimole/litre.

\[ t = 4.79 \text{ seconds at } E_{d.e} = -1.05 \text{ volts.} \]

<table>
<thead>
<tr>
<th>(E_{d.e}) volts</th>
<th>(I/I_d) (\varphi(H))</th>
<th>(\log \frac{I}{I_d-I})</th>
<th>(\log H)</th>
<th>(\log k_f,h)</th>
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<tbody>
<tr>
<td>0.80</td>
<td>0.0</td>
<td>-</td>
<td>-</td>
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<tr>
<td>0.90</td>
<td>0.11</td>
<td>2.055</td>
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<tr>
<td>0.94</td>
<td>0.056</td>
<td>2.775</td>
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<td>0.934</td>
<td>1.142</td>
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<td>3.73</td>
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<td>1.14</td>
<td>0.975</td>
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<td>1.18</td>
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</tbody>
</table>
Table 17 (cont.)

(c). Coumarin concentration 0.35 millimole/litre.

\[ t = 4.79 \text{ seconds at } E_{\text{d.e}} = -1.05 \text{ volts.} \]

<table>
<thead>
<tr>
<th>(-E_{\text{d.e}}) volts</th>
<th>(\frac{I}{I_d})</th>
<th>(\log \frac{I}{I_{d-h}})</th>
<th>(\log H)</th>
<th>(\log k_{f,h})</th>
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<td>0.80</td>
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<td>-</td>
<td>-</td>
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<td>3.187</td>
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<td>0.040</td>
<td>2.619</td>
<td>2.53</td>
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</tr>
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<td>0.177</td>
<td>1.332</td>
<td>1.22</td>
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<td>4.63</td>
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<td>0.079</td>
<td>1.88</td>
<td>4.96</td>
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<td>0.708</td>
<td>0.385</td>
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<td>0.697</td>
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<td>0.902</td>
<td>0.962</td>
<td>0.51</td>
<td>3.59</td>
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<td>1.10</td>
<td>0.950</td>
<td>1.272</td>
<td>0.73</td>
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<tr>
<td>1.14</td>
<td>0.988</td>
<td>1.905</td>
<td>1.10</td>
<td>2.18</td>
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<tr>
<td>1.18</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 17 (cont.)

(d). Coumarin concentration 0.50 millimole/litre.

\[ t = 4.79 \text{ seconds at } -1.05 \text{ volts}. \]

<table>
<thead>
<tr>
<th>(-E_{d,e}) volts</th>
<th>(\frac{I}{I_d}) (\phi(H))</th>
<th>(\log \frac{I}{I_d-1})</th>
<th>(\log H)</th>
<th>(\log k_f,h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.80</td>
<td>0.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.90</td>
<td>0.0094</td>
<td>3.977</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.94</td>
<td>0.028</td>
<td>2.463</td>
<td>2.35</td>
<td>5.43</td>
</tr>
<tr>
<td>0.98</td>
<td>0.119</td>
<td>1.131</td>
<td>1.03</td>
<td>4.11</td>
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<tr>
<td>1.00</td>
<td>0.243</td>
<td>1.506</td>
<td>1.38</td>
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<td>0.418</td>
<td>1.857</td>
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<td>1.04</td>
<td>0.594</td>
<td>0.165</td>
<td>1.95</td>
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<td>1.06</td>
<td>0.777</td>
<td>0.543</td>
<td>0.23</td>
<td>3.31</td>
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<td>1.08</td>
<td>0.862</td>
<td>0.796</td>
<td>0.40</td>
<td>3.48</td>
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<td>1.10</td>
<td>0.939</td>
<td>1.186</td>
<td>0.67</td>
<td>3.75</td>
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<td>1.14</td>
<td>0.989</td>
<td>1.961</td>
<td>1.15</td>
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<tr>
<td>1.18</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 17 (cont.)

(e). Coumarin concentration 0.75 millimole/litre.

\[ t = 4.77 \text{ seconds} \]

<table>
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<tr>
<th>(-\frac{E_{d.e}}{\text{volts}})</th>
<th>(\frac{I/I_d}{\phi(\text{H})})</th>
<th>(\log \frac{I}{I_d-1})</th>
<th>(\log H)</th>
<th>(\log k_{f,h})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.90</td>
<td>0.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.94</td>
<td>0.016</td>
<td>2.217</td>
<td>2.06</td>
<td>5.14</td>
</tr>
<tr>
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<td>0.083</td>
<td>2.955</td>
<td>2.97</td>
<td>4.05</td>
</tr>
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<td>0.165</td>
<td>1.297</td>
<td>1.18</td>
<td>4.26</td>
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<td>0.310</td>
<td>1.652</td>
<td>1.51</td>
<td>4.59</td>
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<td>1.04</td>
<td>0.498</td>
<td>1.996</td>
<td>1.81</td>
<td>4.89</td>
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<td>1.06</td>
<td>0.675</td>
<td>0.316</td>
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<td>0.882</td>
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<td>1.12</td>
<td>0.937</td>
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<td>0.66</td>
<td>3.74</td>
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<td>1.14</td>
<td>0.968</td>
<td>1.475</td>
<td>0.85</td>
<td>3.93</td>
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<td>1.18</td>
<td>0.998</td>
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<td>-</td>
<td>-</td>
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<tr>
<td>1.22</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
(f). Coumarin concentration 0.85 millimole/litre.

t = 4.76 seconds.

<table>
<thead>
<tr>
<th>$E_d$ volts</th>
<th>$I/I_d$ $\varphi(H)$</th>
<th>$\log \frac{I}{I_d - I}$</th>
<th>$\log H$</th>
<th>$\log k_{f,h}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.90</td>
<td>0.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.94</td>
<td>0.015</td>
<td>2.169</td>
<td>2.05</td>
<td>5.13</td>
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<td>0.98</td>
<td>0.072</td>
<td>2.887</td>
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<td>5.89</td>
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<td>0.115</td>
<td>1.112</td>
<td>1.01</td>
<td>4.09</td>
</tr>
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<td>1.02</td>
<td>0.252</td>
<td>1.529</td>
<td>1.40</td>
<td>4.48</td>
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<td>0.426</td>
<td>1.871</td>
<td>1.71</td>
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<td>1.06</td>
<td>0.620</td>
<td>0.212</td>
<td>1.97</td>
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<td>0.745</td>
<td>0.468</td>
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<td>3.28</td>
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<td>0.864</td>
<td>0.803</td>
<td>0.41</td>
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<td>0.934</td>
<td>1.154</td>
<td>0.64</td>
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<td>1.18</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 17 (cont.)

(g). Coumarin concentration 1.00 millimole/litre.

\[ t = 4.74 \text{ seconds.} \]

<table>
<thead>
<tr>
<th>$-\mathbb{E}_{d.e}$ volts</th>
<th>( \frac{I}{I_d} )</th>
<th>( \log \frac{I}{I_d} )</th>
<th>( \log H )</th>
<th>( \log k_{f,h} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.90</td>
<td>0.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.94</td>
<td>0.008</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.98</td>
<td>0.035</td>
<td>2.560</td>
<td>2.47</td>
<td>5.55</td>
</tr>
<tr>
<td>1.00</td>
<td>0.035</td>
<td>2.560</td>
<td>2.47</td>
<td>5.55</td>
</tr>
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<td>0.062</td>
<td>2.820</td>
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<td>0.088</td>
<td>2.985</td>
<td>2.89</td>
<td>5.97</td>
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<td>0.129</td>
<td>1.171</td>
<td>1.06</td>
<td>4.14</td>
</tr>
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<td>0.175</td>
<td>1.326</td>
<td>1.21</td>
<td>4.29</td>
</tr>
<tr>
<td>1.12</td>
<td>0.245</td>
<td>1.511</td>
<td>1.38</td>
<td>4.46</td>
</tr>
<tr>
<td>1.14</td>
<td>0.355</td>
<td>1.741</td>
<td>1.59</td>
<td>4.67</td>
</tr>
<tr>
<td>1.16</td>
<td>0.530</td>
<td>0.052</td>
<td>1.86</td>
<td>4.94</td>
</tr>
<tr>
<td>1.18</td>
<td>0.811</td>
<td>0.633</td>
<td>0.30</td>
<td>3.38</td>
</tr>
<tr>
<td>1.20</td>
<td>0.970</td>
<td>1.510</td>
<td>0.86</td>
<td>3.94</td>
</tr>
<tr>
<td>1.22</td>
<td>1.018</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1.24</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
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</table>
(h). Coumarin concentration 1.25 millimole/litre.  
\( t = 4.61 \) seconds.

<table>
<thead>
<tr>
<th>( E_{d.e} ) volts</th>
<th>( \frac{I/I_d}{\phi(H)} )</th>
<th>( \log \frac{I}{I_d} )</th>
<th>( \log H )</th>
<th>( \log k_{f,h} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.04</td>
<td>0.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
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<td>2.02</td>
<td>5.11</td>
</tr>
<tr>
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<td>0.045</td>
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<td>2.59</td>
<td>5.67</td>
</tr>
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<td>0.089</td>
<td>2.990</td>
<td>2.90</td>
<td>5.98</td>
</tr>
<tr>
<td>1.20</td>
<td>0.160</td>
<td>1.280</td>
<td>1.17</td>
<td>4.25</td>
</tr>
<tr>
<td>1.24</td>
<td>0.370</td>
<td>1.769</td>
<td>1.61</td>
<td>4.69</td>
</tr>
<tr>
<td>1.26</td>
<td>0.609</td>
<td>0.192</td>
<td>1.97</td>
<td>3.05</td>
</tr>
<tr>
<td>1.28</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure 34. Effect of coumarin on the characteristics of the nickel wave.
(Nickel sulphate concentration - 1.00 mmole/l. in all cases).

Values of \( \frac{t}{t_d} \)

Values of \( \log \frac{k_{f,h}}{k_{f,h}} \)

Values of \( \log \frac{t}{t_d - t} \)

- \( t \) / (t_d - t)

- \( t \) / (t_d + t)

- \( t \) / (t_d - t)

- \( t \) / (t_d + t)

- \( t \) / (t_d - t)

- \( t \) / (t_d + t)

\(-E_{d,e}, \) volts

0.8 0.9 1.0 1.1 1.2
Figure 34 (cont.)

Values of \( \frac{\bar{I}}{\bar{I}_d} \)

Values of \( \frac{1}{\bar{I}_d} \), \( 0.75 \text{ mmole/l. coumarin} \)

\( 0.85 \text{ mmole/l. coumarin} \)

\( 1.00 \text{ mmole/l. coumarin} \)

\( 1.25 \text{ mmole/l. coumarin} \)

\( \Delta \) \( \log \frac{\bar{I}}{\bar{I}_d - \bar{I}} \)

\( \square \) \( \log k_{f,h} \)

\( -E_{d.e.} \text{ volts} \)
Table 18

Summary of the characteristics of nickel polarograms at various coumarin concentrations in 0.1M potassium chloride at 25°C.

<table>
<thead>
<tr>
<th>NiSO₄ mmole/litre</th>
<th>Coumarin mmole/litre</th>
<th>-E₁/₂ volts</th>
<th>log kₕ,h slope at foot</th>
<th>αn₁ₐ</th>
<th>log kₕ,h slope</th>
<th>αn₁ₐ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00*</td>
<td>0.10</td>
<td>1.012</td>
<td>16.45</td>
<td>0.97₄</td>
<td>15.7</td>
<td>0.92₈</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.20</td>
<td>1.020</td>
<td>16.1</td>
<td>0.95₂</td>
<td>15.5</td>
<td>0.91₇</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.35</td>
<td>1.017</td>
<td>17.5</td>
<td>1.03₅</td>
<td>16.6</td>
<td>0.98₂</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.50</td>
<td>1.028</td>
<td>17.2</td>
<td>1.01₇</td>
<td>15.4</td>
<td>0.91₂</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.75</td>
<td>1.040</td>
<td>17.95</td>
<td>1.06₂</td>
<td>15.8</td>
<td>0.93₅</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.85</td>
<td>1.050</td>
<td>18.04</td>
<td>1.06₇</td>
<td>15.7</td>
<td>0.92₈</td>
</tr>
<tr>
<td>&quot;</td>
<td>1.00</td>
<td>1.155</td>
<td>9.4</td>
<td>(0.55₆)</td>
<td>6.9</td>
<td>(0.40₈)</td>
</tr>
<tr>
<td>&quot;</td>
<td>1.25</td>
<td>1.25</td>
<td>8.1</td>
<td>(0.47₉)</td>
<td>7.1</td>
<td>(0.4₂₀)</td>
</tr>
<tr>
<td>0.25**</td>
<td>0.00</td>
<td>1.026</td>
<td>15.45</td>
<td>0.91₄</td>
<td>13.8</td>
<td>0.81₆</td>
</tr>
<tr>
<td>0.50+</td>
<td>0.00</td>
<td>1.016</td>
<td>14.9</td>
<td>0.88₂</td>
<td>15.2</td>
<td>0.89₉</td>
</tr>
<tr>
<td>0.50*</td>
<td>0.00</td>
<td>1.027</td>
<td>14.5</td>
<td>0.85₈</td>
<td>15.8</td>
<td>0.93₅</td>
</tr>
</tbody>
</table>

Capillary characteristics:

* m = 1.737 mg/sec.
** m = 1.752 mg/sec.
+ m = 2.076 mg/sec.
the nickel wave is very different and the reduction potential is rapidly shifted to more negative potentials. Values of $\alpha_n a$ have been calculated for coumarin concentrations of 1.00 and 1.25 millimole/litre and are given for comparison purposes only since the values have no theoretical significance.

Thus, both coumarin and gelatin act as maximum suppressors for nickel polarograms, but, whereas gelatin has a marked effect on the kinetics of the electrode process, coumarin has only a slight effect below 0.85 millimole/litre, above which concentration, distortion of the nickel current-voltage curve occurs.

(iv). Polarography of nickel-coumarin solutions in a buffered supporting electrolyte of the phosphate type, pH 6.45

In the previous section the polarography of nickel-coumarin solutions in a supporting electrolyte of 0.1M potassium chloride was described. Several polarographic reductions, especially of organic compounds, are sensitive to pH and so it was decided to investigate the influence of pH on the results obtained in the previous section. The work of Harle and Lyons (8), described previously, shows the effect of pH on the coumarin reduction. Below pH 7 coumarin exists solely in the lactone form and gives a polarographic wave, the half-wave potential being independent of pH, which corresponds
to the addition of a single electron. Above pH 7 the lactone ring undergoes partial, or complete hydrolysis, depending on the pH, to non-reducible cis-coumarinic acid. The height of the coumarin wave thus depends on the pH of the solution, and for further investigation into the polarography of nickel-coumarin solutions it is necessary to select a pH below 7. According to Harle and Lyons the current at the top of the coumarin wave at pH 6.45 is diffusion controlled, and at this pH nickel hydroxide is not precipitated. This then, was the pH selected. The buffer solution was prepared so that the concentration of the alkali ion was 0.1 gram ion/litre.

The buffer solution was prepared as follows. A preliminary pH titration of 0.1 molar sodium hydroxide against 0.1 molar potassium dihydrogen phosphate was first performed. From the information gained a solution was prepared containing 103.4 grams of potassium dihydrogen phosphate, \( \text{KH}_2\text{PO}_4 \), and 9.61 grams of sodium hydroxide per litre. 10 mls. of this solution were used for each 100 mls. of test solution. The pH of a 100 ml. sample was checked with a meter and found to have a pH of 6.45.

Polarography of nickel. - The current-voltage curves obtained for various concentrations of nickel sulphate are shown in figure 35. The curves differ from those obtained in 0.1M potassium chloride in that they do not display the typical "spike" maxima, even at the highest concentration. At 2.0 mmole/litre there is a slight maximum of the rounded type.
Figure 35. Typical nickel polarograms in a phosphate supporting electrolyte

Figure 36. Determination of "I" for nickel in phosphate electrolyte.

Capillary:
- h = 38.5 cm.
- h = 31.5 cm.

Concentration, mmole/litre
The half-wave potential occurs at a slightly more negative value than in 0.1M potassium chloride. The dependence of the diffusion current on the nickel sulphate concentration and the capillary characteristics is given in Table 19, and shown graphically in figure 36.

It is seen that the proportionality of \( I_d/m^{2/3} t^{1/6} \) with concentration is good, the proportionality constants being slightly different at the two sets of conditions. Values of the diffusion current constant, \( I \), as determined from figure 36 were found to be 2.99 at the shorter drop time and 2.87 at the longer drop time. These values are a little smaller than the values of 3.38 and 3.23 obtained under similar conditions in 0.1M potassium chloride. Since the reduction still undoubtedly involves two electrons this change must result from a change in the diffusion coefficient of the nickel ion in the two media. By means of the relationship

\[
I = 607nD^{1/2}(1 + 17 D^{1/2} m^{-1/3} t^{1/6})
\]

the values of the diffusion coefficient were calculated to be 0.563 and 0.514 x \( 10^{-5} \) cm\(^2\) sec\(^{-1}\) for the shorter and longer drop times, respectively. The mobility of the nickel ion is thus smaller in a phosphate than in a chloride supporting electrolyte.

The characteristics of four current-voltage curves are given in Table 20 and shown graphically in figure 37. The results are summarised in Table 21. It can be seen in the graphs of \( \log I/(I_d-I) \) vs. \(-E_d\) that there is no evidence of
Table 19

Diffusion currents at various concentrations of nickel sulphate in pH 6.45 phosphate buffer at 25°C.
Air removed from the solutions with hydrogen.

<table>
<thead>
<tr>
<th>NiSO₄ mmole/litre</th>
<th>E_d.e. volts.</th>
<th>m²/₃t¹/₆</th>
<th>T_d µa</th>
<th>T_d/m²/₃t¹/₆</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.40</td>
<td>1.30</td>
<td>2.054</td>
<td>2.435</td>
<td>1.195</td>
</tr>
<tr>
<td>0.40</td>
<td>&quot;</td>
<td>1.858</td>
<td>2.145</td>
<td>1.154</td>
</tr>
<tr>
<td>0.80</td>
<td>&quot;</td>
<td>2.054</td>
<td>5.09</td>
<td>2.498</td>
</tr>
<tr>
<td>0.80</td>
<td>&quot;</td>
<td>1.858</td>
<td>4.33</td>
<td>2.330</td>
</tr>
<tr>
<td>1.00</td>
<td>&quot;</td>
<td>2.054</td>
<td>6.10</td>
<td>2.990</td>
</tr>
<tr>
<td>1.00</td>
<td>&quot;</td>
<td>1.858</td>
<td>5.33</td>
<td>2.868</td>
</tr>
<tr>
<td>1.50</td>
<td>1.60</td>
<td>1.998</td>
<td>8.95</td>
<td>4.479</td>
</tr>
<tr>
<td>1.50</td>
<td>1.30</td>
<td>1.858</td>
<td>8.01</td>
<td>4.310</td>
</tr>
<tr>
<td>2.00</td>
<td>1.70</td>
<td>1.972</td>
<td>11.77</td>
<td>5.969</td>
</tr>
<tr>
<td>2.00</td>
<td>1.30</td>
<td>1.858</td>
<td>10.53</td>
<td>5.664</td>
</tr>
</tbody>
</table>
Table 20

Characteristics of nickel polarograms in pH 6.45 phosphate buffer at 25°0.
Air removed from the solutions with hydrogen.

(a) Nickel sulphate 0.40 mmole/litre.

E\frac{1}{2} = -1.083 volt vs. the S.C.E., t = 4.51 seconds.

<table>
<thead>
<tr>
<th>-E_d.e. volts</th>
<th>I, (\mu A)</th>
<th>I/I_d (\phi(H))</th>
<th>log (\frac{I}{I_d - I})</th>
<th>log H</th>
<th>log (k_f,h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.90</td>
<td>0.0</td>
<td>0.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.94</td>
<td>0.032</td>
<td>0.015</td>
<td>2.180</td>
<td>2.04</td>
<td>5.13</td>
</tr>
<tr>
<td>0.98</td>
<td>0.060</td>
<td>0.028</td>
<td>2.459</td>
<td>2.35</td>
<td>5.44</td>
</tr>
<tr>
<td>1.00</td>
<td>0.129</td>
<td>0.060</td>
<td>2.806</td>
<td>2.72</td>
<td>5.81</td>
</tr>
<tr>
<td>1.02</td>
<td>0.244</td>
<td>0.114</td>
<td>1.188</td>
<td>1.00</td>
<td>4.09</td>
</tr>
<tr>
<td>1.04</td>
<td>0.407</td>
<td>0.190</td>
<td>1.370</td>
<td>1.25</td>
<td>4.34</td>
</tr>
<tr>
<td>1.06</td>
<td>0.689</td>
<td>0.321</td>
<td>1.675</td>
<td>1.53</td>
<td>4.62</td>
</tr>
<tr>
<td>1.08</td>
<td>0.971</td>
<td>0.453</td>
<td>1.917</td>
<td>1.75</td>
<td>4.84</td>
</tr>
<tr>
<td>1.10</td>
<td>1.350</td>
<td>0.629</td>
<td>0.230</td>
<td>0.00</td>
<td>3.09</td>
</tr>
<tr>
<td>1.12</td>
<td>1.678</td>
<td>0.782</td>
<td>0.555</td>
<td>0.24</td>
<td>3.33</td>
</tr>
<tr>
<td>1.14</td>
<td>1.775</td>
<td>0.828</td>
<td>0.681</td>
<td>0.33</td>
<td>3.42</td>
</tr>
<tr>
<td>1.16</td>
<td>1.896</td>
<td>0.884</td>
<td>0.882</td>
<td>0.46</td>
<td>3.55</td>
</tr>
<tr>
<td>1.18</td>
<td>1.974</td>
<td>0.920</td>
<td>1.062</td>
<td>0.58</td>
<td>3.67</td>
</tr>
<tr>
<td>1.20</td>
<td>2.043</td>
<td>0.953</td>
<td>1.302</td>
<td>0.75</td>
<td>3.84</td>
</tr>
<tr>
<td>1.24</td>
<td>2.072</td>
<td>0.966</td>
<td>1.453</td>
<td>0.83</td>
<td>3.92</td>
</tr>
<tr>
<td>1.30</td>
<td>2.145</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
(b). Nickel sulphate 0.80 mmole/litre

$E'_\nu = -1.063$ volts, $t = 4.51$ seconds.

<table>
<thead>
<tr>
<th>$E_{d.e.}$ volts</th>
<th>I, $\mu$A</th>
<th>$I/I_d\phi(H)$</th>
<th>log $I/I_d\phi^{-1}$</th>
<th>log H</th>
<th>log $k_f h$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.80</td>
<td>0.0</td>
<td>0.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.90</td>
<td>0.057</td>
<td>0.013</td>
<td>2.125</td>
<td>2.00</td>
<td>3.09</td>
</tr>
<tr>
<td>0.98</td>
<td>0.249</td>
<td>0.058</td>
<td>2.786</td>
<td>2.70</td>
<td>3.79</td>
</tr>
<tr>
<td>1.02</td>
<td>0.795</td>
<td>0.184</td>
<td>1.352</td>
<td>1.24</td>
<td>4.33</td>
</tr>
<tr>
<td>1.04</td>
<td>1.332</td>
<td>0.308</td>
<td>1.648</td>
<td>1.51</td>
<td>4.62</td>
</tr>
<tr>
<td>1.06</td>
<td>2.078</td>
<td>0.480</td>
<td>1.965</td>
<td>1.79</td>
<td>4.88</td>
</tr>
<tr>
<td>1.08</td>
<td>2.720</td>
<td>0.628</td>
<td>0.228</td>
<td>0.00</td>
<td>3.09</td>
</tr>
<tr>
<td>1.10</td>
<td>3.362</td>
<td>0.777</td>
<td>0.541</td>
<td>0.23</td>
<td>3.32</td>
</tr>
<tr>
<td>1.12</td>
<td>3.755</td>
<td>0.867</td>
<td>0.815</td>
<td>0.41</td>
<td>3.50</td>
</tr>
<tr>
<td>1.16</td>
<td>4.157</td>
<td>0.960</td>
<td>1.381</td>
<td>0.79</td>
<td>3.88</td>
</tr>
<tr>
<td>1.20</td>
<td>4.263</td>
<td>0.985</td>
<td>1.804</td>
<td>1.04</td>
<td>2.13</td>
</tr>
<tr>
<td>1.24</td>
<td>4.330</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 20 (cont.)

(c). Nickel sulphate 0.80 mmole/litre,

\[ E_{1/2} = -1.067 \text{ volts, } t = 3.64 \text{ seconds} \]

<table>
<thead>
<tr>
<th>(-E_{d.e.}) volts</th>
<th>(I_e) (\mu A)</th>
<th>(I/I_d) (\phi(H))</th>
<th>(\log \frac{I}{I_d-I})</th>
<th>(\log H)</th>
<th>(\log k_r h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.80</td>
<td>0.0</td>
<td>0.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.90</td>
<td>0.048</td>
<td>0.009</td>
<td>(3.979)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.98</td>
<td>0.296</td>
<td>0.058</td>
<td>(2.791)</td>
<td>(2.70)</td>
<td>(5.84)</td>
</tr>
<tr>
<td>1.02</td>
<td>0.850</td>
<td>0.167</td>
<td>(1.302)</td>
<td>(1.21)</td>
<td>(4.35)</td>
</tr>
<tr>
<td>1.04</td>
<td>1.458</td>
<td>0.286</td>
<td>(1.603)</td>
<td>(1.47)</td>
<td>(4.61)</td>
</tr>
<tr>
<td>1.06</td>
<td>2.077</td>
<td>0.408</td>
<td>(1.838)</td>
<td>(1.68)</td>
<td>(4.82)</td>
</tr>
<tr>
<td>1.08</td>
<td>3.120</td>
<td>0.613</td>
<td>(0.200)</td>
<td>(1.98)</td>
<td>(3.12)</td>
</tr>
<tr>
<td>1.10</td>
<td>3.738</td>
<td>0.735</td>
<td>(0.442)</td>
<td>0.16</td>
<td>(3.30)</td>
</tr>
<tr>
<td>1.12</td>
<td>4.300</td>
<td>0.845</td>
<td>(0.736)</td>
<td>0.36</td>
<td>(3.50)</td>
</tr>
<tr>
<td>1.16</td>
<td>4.803</td>
<td>0.944</td>
<td>(1.224)</td>
<td>0.70</td>
<td>(3.84)</td>
</tr>
<tr>
<td>1.20</td>
<td>4.983</td>
<td>0.980</td>
<td>(1.668)</td>
<td>0.97</td>
<td>(2.11)</td>
</tr>
<tr>
<td>1.30</td>
<td>5.090</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 20 (cont.)

(d). Nickel sulphate 1.00 mmole/litre

$E_{1/2} = -1.087$ volts, $t = 4.51$ seconds.

<table>
<thead>
<tr>
<th>$E_{d.e.}$</th>
<th>$I$, $\mu$A</th>
<th>$I/I_d$</th>
<th>$\phi(H)$</th>
<th>log $\frac{I}{I_d-I}$</th>
<th>log H</th>
<th>log $k_{f_i}$ $h$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.90</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
<td>$-$</td>
<td>$-$</td>
<td>$-$</td>
</tr>
<tr>
<td>0.94</td>
<td>0.039</td>
<td>0.007</td>
<td>3.868</td>
<td>$-$</td>
<td>$-$</td>
<td>$-$</td>
</tr>
<tr>
<td>0.98</td>
<td>0.147</td>
<td>0.028</td>
<td>2.453</td>
<td>2.36</td>
<td>5.45</td>
<td>$-$</td>
</tr>
<tr>
<td>1.00</td>
<td>0.271</td>
<td>0.051</td>
<td>2.726</td>
<td>2.65</td>
<td>5.74</td>
<td>$-$</td>
</tr>
<tr>
<td>1.02</td>
<td>0.475</td>
<td>0.089</td>
<td>2.991</td>
<td>2.90</td>
<td>5.99</td>
<td>$-$</td>
</tr>
<tr>
<td>1.04</td>
<td>0.911</td>
<td>0.171</td>
<td>1.314</td>
<td>1.20</td>
<td>4.29</td>
<td>$-$</td>
</tr>
<tr>
<td>1.06</td>
<td>1.540</td>
<td>0.288</td>
<td>1.609</td>
<td>1.47</td>
<td>4.56</td>
<td>$-$</td>
</tr>
<tr>
<td>1.08</td>
<td>2.296</td>
<td>0.431</td>
<td>1.879</td>
<td>1.71</td>
<td>4.80</td>
<td>$-$</td>
</tr>
<tr>
<td>1.10</td>
<td>3.354</td>
<td>0.629</td>
<td>0.230</td>
<td>0.00</td>
<td>3.09</td>
<td>$-$</td>
</tr>
<tr>
<td>1.12</td>
<td>4.187</td>
<td>0.785</td>
<td>0.564</td>
<td>0.24</td>
<td>3.33</td>
<td>$-$</td>
</tr>
<tr>
<td>1.14</td>
<td>4.672</td>
<td>0.877</td>
<td>0.851</td>
<td>0.44</td>
<td>3.53</td>
<td>$-$</td>
</tr>
<tr>
<td>1.16</td>
<td>5.009</td>
<td>0.940</td>
<td>1.193</td>
<td>0.68</td>
<td>3.77</td>
<td>$-$</td>
</tr>
<tr>
<td>1.18</td>
<td>5.155</td>
<td>0.967</td>
<td>1.469</td>
<td>0.84</td>
<td>3.93</td>
<td>$-$</td>
</tr>
<tr>
<td>1.20</td>
<td>5.203</td>
<td>0.976</td>
<td>1.618</td>
<td>0.92</td>
<td>2.01</td>
<td>$-$</td>
</tr>
<tr>
<td>1.24</td>
<td>5.330</td>
<td>1.00</td>
<td>$-$</td>
<td>$-$</td>
<td>$-$</td>
<td>$-$</td>
</tr>
</tbody>
</table>
Figure 37. Analysis of nickel polarograms in phosphate electrolyte.

(For conditions - see Table 20).

Values of $\frac{\tau}{\tau_d}$

Values of $\log \frac{t}{(t_d - t)}$

Values of $\log k_{f_{th}}$

Values of $\log k_{f_{h}}$

$E_{d,e,v.}$
Table 21

Summary of characteristics of nickel polarograms in pH 6.45 phosphate buffer at 25°C.

<table>
<thead>
<tr>
<th>NiSO₄ mmole/litre</th>
<th>m mg/sec</th>
<th>-E½ volts</th>
<th>log I/(I_d-I) slope at foot</th>
<th>αn_a</th>
<th>log k_f,h slope</th>
<th>αn_a</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.40</td>
<td>1.737</td>
<td>1.083</td>
<td>14.40</td>
<td>0.852</td>
<td>12.6</td>
<td>0.745</td>
</tr>
<tr>
<td>0.80</td>
<td>1.737</td>
<td>1.063</td>
<td>14.25</td>
<td>0.843</td>
<td>12.3</td>
<td>0.728</td>
</tr>
<tr>
<td>0.80</td>
<td>2.132</td>
<td>1.067</td>
<td>13.90</td>
<td>0.822</td>
<td>12.7</td>
<td>0.751</td>
</tr>
<tr>
<td>1.00</td>
<td>1.737</td>
<td>1.087</td>
<td>14.40</td>
<td>0.852</td>
<td>13.4</td>
<td>0.793</td>
</tr>
</tbody>
</table>
a doubling of slope at the head of the wave, and the graph approximates to a straight line. The slope of this line is a little greater than that of the log \( k_f \) vs. \(-E_d\) plot. The slopes of both sets of graphs have been equated to 16.9\( n_a \). The values of \( n_a \) obtained for the nickel reduction are a little smaller in the phosphate supporting electrolyte than in the chloride supporting electrolyte. The half-wave potential also occurs at a more negative potential than in the chloride electrolyte, and so the reduction is more "irreversible" in the phosphate electrolyte. Since there is no evidence of complex formation in a solution containing orthophosphate ions (84,85) it is presumably the hexaquo-nickel ion which is being reduced. It has been seen (70) that this ion is reduced more "irreversibly" than the chloro-complex ion.

**Polarography of coumarin.** - The current-voltage curves obtained for various concentrations of coumarin are shown in figure 38. Values of the diffusion current at various concentrations, and at two different heads of mercury, are given in Table 22, and shown graphically in figure 39.

The value of the diffusion current constant, \( I \), as calculated from figure 39 has a value of 1.90, which is about 2 per cent higher than in potassium chloride. The accurate measurement of the diffusion current is difficult because the presence of coumarin in the solution increases the residual current of the phosphate electrolyte. In spite of this, the agreement is fairly good. The value of the diffusion
Figure 38. Typical coumarin polarograms in phosphate electrolyte.

Figure 39. Determination of "I" for coumarin in phosphate electrolyte.

Values of \( \frac{\sqrt{t}}{m^{3/4}} \) vs. Concentration, mmole/litre

Capillary characteristic:
- \( h = 38.5 \text{ cm} \)
- \( h = 37.5 \text{ cm} \)
Diffusion currents at various concentrations of coumarin in pH 6.45 phosphate buffer at 25°C.

Capillary characteristics:

(a) \( h = 38.5 \) cm, \( m = 2.132 \) mg/sec, \( t = 2.92 \) sec at -1.7 v. \( m^{2/3} t^{1/6} = 1.981 \) mg\(^{2/3}\) sec\(^{-1/2}\)

(b) \( h = 31.5 \) cm, \( m = 1.737 \) mg/sec, \( t = 3.60 \) sec at -1.7 v. \( m^{2/3} t^{1/6} = 1.788 \) mg\(^{2/3}\) sec\(^{-1/2}\)

<table>
<thead>
<tr>
<th>Coumarin mmole/l.</th>
<th>( I_d, \mu A )</th>
<th>( \frac{I_d}{m^{2/3} t^{1/6}} )</th>
<th>( I_d, \mu A )</th>
<th>( \frac{I_d}{m^{2/3} t^{1/6}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>3.78</td>
<td>1.909</td>
<td>3.52</td>
<td>1.969</td>
</tr>
<tr>
<td>2.00</td>
<td>7.46</td>
<td>3.768</td>
<td>6.81</td>
<td>3.808</td>
</tr>
<tr>
<td>3.00</td>
<td>11.32</td>
<td>5.713</td>
<td>10.26</td>
<td>5.738</td>
</tr>
</tbody>
</table>
Characteristics of a coumarin polarogram in a pH 6.45 phosphate buffer at 25°C.
Capillary characteristics: h = 31.5 cm., m = 1.737 mg/sec.,
t = 3.60 seconds at -1.70 v.

<table>
<thead>
<tr>
<th>$-E_{d.e.}$ volts.</th>
<th>$I_r$ $\mu A$</th>
<th>$\log \frac{I}{I_d-I}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.40</td>
<td>0.0</td>
<td>-</td>
</tr>
<tr>
<td>1.44</td>
<td>0.019</td>
<td>-</td>
</tr>
<tr>
<td>1.48</td>
<td>0.347</td>
<td>1.039</td>
</tr>
<tr>
<td>1.50</td>
<td>0.859</td>
<td>1.509</td>
</tr>
<tr>
<td>1.52</td>
<td>1.642</td>
<td>1.942</td>
</tr>
<tr>
<td>1.54</td>
<td>2.395</td>
<td>0.328</td>
</tr>
<tr>
<td>1.56</td>
<td>3.003</td>
<td>0.764</td>
</tr>
<tr>
<td>1.58</td>
<td>3.323</td>
<td>1.227</td>
</tr>
<tr>
<td>1.60</td>
<td>3.436</td>
<td>1.612</td>
</tr>
<tr>
<td>1.62</td>
<td>3.512</td>
<td>-</td>
</tr>
<tr>
<td>1.66</td>
<td>3.520</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure 40. Characteristics of a coumarin polarogram in phosphate supporting electrolyte.
coefficient calculated by means of the modified Ilkovic equation, equation (47), is $0.89 \times 10^{-5} \text{ cm}^2\text{sec}^{-1}$.

The characteristics of a coumarin current-voltage curve are given in Table 23 and plotted in figure 40. The slope of the $\log I/(I_d-I)$ vs. $-E_{d,e}$ plot was found to be $21.9 \text{ volt}^{-1}$, which is in fairly good agreement with the values of 23.3 and 23.6 volt$^{-1}$ found in the chloride supporting electrolyte, but larger than the theoretical value of 16.9 volt$^{-1}$ to be expected for a reversible one electron reduction.

Thus, in this case, the experimental results are not in complete agreement with those of Harle and Lyons (8).

Polarography of nickel in presence of coumarin. - A series of solutions was prepared in which the nickel sulphate concentration was kept constant at 0.50 mmole/litre, the coumarin concentration being varied. The current-voltage curves obtained for each solution are reproduced in figure 41.

It can be seen that the nickel wave is influenced in much the same way as in the chloride supporting electrolyte, being slightly shifted to more negative potentials at the lower coumarin concentrations, and being distorted at the higher concentrations. It thus seems likely that coumarin affects the double layer structure around the mercury drop in a similar way in both types of supporting electrolyte. This assumption was tested by investigating the mercury electrocapillary curve at various coumarin concentrations. The results are given in Table 24 and the electrocapillary curves shown in figure 42.
Figure 41. Polarograms of nickel (0.50 mmole/l.) at various coumarin concentrations, in a phosphate supporting electrolyte.

Coumarin concentrations in mmole/l.:
(a) 0.50
(b) 1.00
(c) 1.50
(d) 2.00
(e) 2.50
Values of the mercury drop time as a function of coumarin concentration and dropping electrode potential in a pH 6.45 phosphate buffer at 25°C.

Air removed from the solutions with hydrogen.

h = 38.5 cm.

<table>
<thead>
<tr>
<th>E_d.e volts</th>
<th>Coumarin concentration, mmole/l.</th>
<th>Drop times, in seconds</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>1.00</td>
</tr>
<tr>
<td>0</td>
<td>3.94</td>
<td>3.94</td>
</tr>
<tr>
<td>0.1</td>
<td>4.16</td>
<td>4.02</td>
</tr>
<tr>
<td>0.2</td>
<td>4.26</td>
<td>4.08</td>
</tr>
<tr>
<td>0.3</td>
<td>4.32</td>
<td>4.14</td>
</tr>
<tr>
<td>0.4</td>
<td>4.35</td>
<td>4.17</td>
</tr>
<tr>
<td>0.5</td>
<td>4.35</td>
<td>4.17</td>
</tr>
<tr>
<td>0.6</td>
<td>4.34</td>
<td>4.14</td>
</tr>
<tr>
<td>0.7</td>
<td>4.30</td>
<td>4.12</td>
</tr>
<tr>
<td>0.8</td>
<td>4.23</td>
<td>4.10</td>
</tr>
<tr>
<td>0.9</td>
<td>4.14</td>
<td>4.04</td>
</tr>
<tr>
<td>1.0</td>
<td>4.05</td>
<td>3.96</td>
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<td>1.1</td>
<td>3.94</td>
<td>3.88</td>
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<td>1.2</td>
<td>3.82</td>
<td>3.77</td>
</tr>
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<td>1.3</td>
<td>3.64</td>
<td>3.64</td>
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<td>1.4</td>
<td>3.46</td>
<td>3.48</td>
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<td>1.5</td>
<td>3.28</td>
<td>3.28</td>
</tr>
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<td>1.6</td>
<td>3.08</td>
<td>3.08</td>
</tr>
<tr>
<td>1.7</td>
<td>2.84</td>
<td>2.87</td>
</tr>
<tr>
<td>1.8</td>
<td>2.58</td>
<td>2.63</td>
</tr>
</tbody>
</table>
Figure 42. Effect of coumarin on the electrocapillary curve in phosphate supporting electrolyte.

Concentrations in mmole/litre:
- 0
- 1.0
- 2.0
- 3.0

Drop time in seconds

-$E_{d.e.}$ volts
Table 25

Apparent height of the coumarin wave in presence of nickel, in a pH 6.45 phosphate supporting electrolyte at 25°C.

Nickel sulphate concentration 0.50 mmole/litre.

Capillary characteristics:

(a) \( h = 38.5 \) cm. 
\( m = 2.132 \) mg/sec. 
\( t = 2.92 \) sec. at \(-1.7\) v.

(b) \( h = 31.5 \) cm. 
\( m = 1.737 \) mg/sec. 
\( t = 3.60 \) sec. at \(-1.7\) v.

<table>
<thead>
<tr>
<th>Coumarin mmole/l.</th>
<th>Position</th>
<th>Apparent height ( \mu A )</th>
<th>Total current ( \mu A )</th>
<th>Total ( \frac{I}{m^{2/3}t^{1/6}} )</th>
<th>Coumarin Apparent ( \frac{I}{m^{2/3}t^{1/6}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>(a)</td>
<td>-</td>
<td>-</td>
<td>1.50</td>
<td>0.0</td>
</tr>
<tr>
<td>0.0</td>
<td>(b)</td>
<td>-</td>
<td>-</td>
<td>1.44</td>
<td>0.0</td>
</tr>
<tr>
<td>0.50</td>
<td>(a)</td>
<td>2.02</td>
<td>-</td>
<td>-</td>
<td>1.02</td>
</tr>
<tr>
<td>0.50</td>
<td>(b)</td>
<td>1.90</td>
<td>-</td>
<td>-</td>
<td>1.06</td>
</tr>
<tr>
<td>1.00</td>
<td>(a)</td>
<td>4.08</td>
<td>-</td>
<td>-</td>
<td>2.06</td>
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<td>(b)</td>
<td>3.51</td>
<td>-</td>
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<td>1.96</td>
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<tr>
<td>1.50</td>
<td>(a)</td>
<td>5.95</td>
<td>-</td>
<td>-</td>
<td>3.00</td>
</tr>
<tr>
<td>1.50</td>
<td>(b)</td>
<td>5.57</td>
<td>-</td>
<td>-</td>
<td>3.11</td>
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<tr>
<td>2.00</td>
<td>(a)</td>
<td>10.98</td>
<td>5.54</td>
<td>4.04</td>
<td></td>
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<td>2.00</td>
<td>(b)</td>
<td>9.78</td>
<td>5.47</td>
<td>4.03</td>
<td></td>
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<tr>
<td>2.50</td>
<td>(a)</td>
<td>12.47</td>
<td>6.30</td>
<td>4.80</td>
<td></td>
</tr>
<tr>
<td>2.50</td>
<td>(b)</td>
<td>11.57</td>
<td>6.45</td>
<td>5.01</td>
<td></td>
</tr>
</tbody>
</table>
Figure 43. Height of coumarin wave, in presence and absence of nickel, in phosphate electrolyte.

Capillary characteristic:
- $h = 38.5$ cm.
- $h = 37.5$ cm.

Nickel absent

Circles - nickel present
($0.50$ mmole/l.)

Values of $I/\text{mV}, \mu$ Values

Concentration, mole/litre
The curves in figure 42 closely resemble those in figure 32 which are electrocapillary curves obtained at various coumarin concentrations in 0.1M potassium chloride. The specific activity of the coumarin appears to be the same in both cases, not only with regard to the concentration of the coumarin, but also with respect to the potential of the dropping electrode. This fact supplies additional evidence in favour of the assumption that coumarin is adsorbed at the mercury-electrolyte interface.

It can be seen from figure 41, that for a given nickel concentration the height of the nickel wave is independent of the coumarin concentration, as also found for the chloride supporting electrolyte. The apparent heights of the coumarin wave at each concentration are given in Table 23. In figure 43 these results are compared with those given in Table 22 for the height of the coumarin wave alone and it can be seen that, within the experimental error, the presence of nickel in the solution makes no difference to the height of the coumarin wave. This result differs from that obtained in the 0.1 molar potassium chloride supporting electrolyte. In the following section this result is investigated further.

* * * * * *
(v). **Polarography of nickel-coumarin solutions in selected supporting electrolytes.**

It has been shown that in a supporting electrolyte of 0.1M potassium chloride the apparent height of the coumarin wave in the presence of excess nickel was one half its value in nickel-free solutions. In a buffered supporting electrolyte of a pH 6.45 phosphate solution the height of the wave was normal. To explain the unusual diffusion currents at -1.7 volts in the chloride electrolyte it was assumed that nickel ions reacted with a product of the coumarin reduction, or an intermediate, in the diffusion layer, to form an insoluble or non-reducible compound. To satisfy the experimental results it was necessary that each nickel ion should react with the equivalent of four coumarin molecules. In the phosphate supporting electrolyte no interaction between the nickel ions and coumarin reduction product occurs. This suggests that either a chloride electrolyte is necessary for interaction to occur, or that a phosphate electrolyte prevents the interaction. Alternatively, both suggestions may be correct. The suggestions can easily be tested experimentally, but first a consideration of the nature of the nickel ion in each supporting electrolyte is necessary.

In a solution containing chloride ions both hexaquo-nickel ions, $\left[\text{Ni(H}_2\text{O)}_6\right]^{++}$ and chloro-nickel ions $\left[\text{Ni(H}_2\text{O)}_5\text{Cl}\right]^+$ would be expected to be present (84,86). It has been reported (84,85) that there is no evidence of complex formation between nickel ions and orthophosphate ions in a phosphate solution,
and so the nickel ion in a phosphate supporting electrolyte exists as the hexaquo-ion.

To explain the experimental results a number of possibilities exist:

(a). Only the chloro-nickel ion will interact with the coumarin reduction product. Sufficient chloro-nickel ions can be supplied to the diffusion layer by the rapid conversion of hexaquo-nickel ions to chloro-nickel ions as chloro ions are used up. For this mechanism to occur a supporting electrolyte containing a relatively high proportion of chloride ions is necessary.

(b). Only the chloro-nickel ion will interact with the product of the coumarin reduction, but this interaction is prevented in a phosphate supporting electrolyte.

(c). Only the hexaquo-nickel ion will react with the product of the coumarin reduction. Since hexaquo-nickel ions are present in both chloride and phosphate supporting electrolytes, the phosphate actually prevents the suggested interaction.

(d). Both the hexaquo- and the chloro-nickel ion can interact with the product of the coumarin reduction. This case is experimentally indistinguishable from case (c).

Since phosphate is a non-complex forming supporting electrolyte for nickel solutions it may well prevent the interaction of nickel ions with the product of the coumarin reduction by virtue of its buffer capacity.
In Table 26 the apparent height of the coumarin wave in presence of excess nickel is given for a number of supporting electrolytes. In each case the nickel concentration was 1.00 mmole/litre and the coumarin concentration 1.50 mmole/l. In the case of the supporting electrolyte of 0.1M potassium chloride a nickel concentration of 1.00 mmole/litre was sufficient to bring the apparent height of the coumarin wave down to half its actual value. If the nickel concentration is very much higher than this the apparent height of the coumarin wave becomes increasingly difficult to measure accurately. Thus, the coumarin concentration was made as high as possible without causing the nickel discharge to merge with its own wave, which therefore appears as a separate wave.

In a supporting electrolyte of 0.1M potassium nitrate the apparent height of the coumarin wave in the presence of excess nickel is one half its value in nickel-free solutions. The actual results given in Table 26 are very close to 0.50 in spite of the difficulty of measuring the height of the coumarin wave with an accuracy much better than 0.1-0.2 μA. Nitrate is an electrolyte which does not form a complex with nickel and so the nickel ion exists solely in the hexaquo form. Since the nitrate supporting electrolyte behaves in the same way as the chloride supporting electrolyte, in that the apparent height of the coumarin wave in presence of excess nickel is one half its real value, then it is established that the hexaquo-nickel ion can react in the diffusion layer with
Figure 44. Nickel-coumarin polarograms in various supporting electrolytes.

- 1 M KCl
- 0.1 M KNO₃
- 0.1 M K₂SO₄
- 0.05 M KCl + 0.05 M pH 6.45 phosphate buffer
- pH 5.07 phthalate buffer

Nickel concentration: 1.00 mmole/l.
Coumarin concentration: 1.50 mmole/l.

- E_d.e. volts
Table 26

Apparent height of the coumarin wave in presence of excess nickel in selected supporting electrolytes at 25°C.
Coumarin concentration 1.50 mmole/litre in all cases.

Capillary characteristics:

(a) $h = 38.5$ cm.
$m = 2.132$ mg/sec.
$t = 2.92$ seconds

(b) $h = 31.5$ cm.
$m = 1.737$ mg/sec.
$t = 3.60$ seconds

<table>
<thead>
<tr>
<th>Supporting electrolyte</th>
<th>Nickel concentration</th>
<th>Position</th>
<th>$I_{app.}$ $\mu$A</th>
<th>$\frac{I_{app.}}{m^{2/3}t^{1/6}}$</th>
<th>$I_{app.}/I_{real}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1M KCl</td>
<td>0</td>
<td>(a)</td>
<td>-</td>
<td>2.79</td>
<td>1.00</td>
</tr>
<tr>
<td>&quot;</td>
<td>0</td>
<td>(b)</td>
<td>-</td>
<td>2.79</td>
<td>1.00</td>
</tr>
<tr>
<td>&quot;</td>
<td>1.00mM NiSO$_4$</td>
<td>(a)</td>
<td>-</td>
<td>1.43</td>
<td>0.51</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>(b)</td>
<td>-</td>
<td>1.45</td>
<td>0.52</td>
</tr>
<tr>
<td>0.1M KNO$_3$</td>
<td>1.00mM Ni(NO$_3$)$_2$</td>
<td>(a)</td>
<td>$\approx2.9$</td>
<td>$\approx1.46$</td>
<td>$\approx0.52$</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>(b)</td>
<td>2.7-2.8</td>
<td>1.51</td>
<td>0.54-0.56</td>
</tr>
<tr>
<td>0.1M K$_2$SO$_4$</td>
<td>1.00mM NiSO$_4$</td>
<td>(a)</td>
<td>$\approx4.95$</td>
<td>$\approx2.50$</td>
<td>$\approx0.90$</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>(b)</td>
<td>$\approx4.56$</td>
<td>$\approx2.55$</td>
<td>$\approx0.91$</td>
</tr>
<tr>
<td>0.05M KCl + 0.05M pH 6.45 phosphate</td>
<td>&quot;</td>
<td>(a)</td>
<td>5.60</td>
<td>2.83</td>
<td>1.01</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>(b)</td>
<td>5.08</td>
<td>2.84</td>
<td>1.02</td>
</tr>
<tr>
<td>0.1M phthalate buffer pH 5.07</td>
<td>1.00mM Ni(NO$_3$)$_2$</td>
<td>(a)</td>
<td>Coumarin wave obscured by hydrogen discharge</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


the product of the coumarin reduction, or intermediate. Thus, the possibilities (a) and (b), just given, can be rejected although it is still possible that chloro-nickel ions may interact in the manner suggested.

Since the hexaquo-nickel ion can interact with the coumarin reduction product then in the phosphate supporting electrolyte the phosphate must actively prevent the suggested interaction. Thus, it would be expected that in any base electrolyte containing phosphate the interaction would be prevented. This observation is confirmed in Table 26 since in a supporting electrolyte consisting of 0.05M potassium chloride and pH 6.45 phosphate buffer (0.05M with respect to alkali ion) no decrease in the height of the coumarin wave occurs.

In the 0.1M potassium sulphate supporting electrolyte the apparent height of the coumarin wave in presence of excess nickel falls only to 0.9 of its value in nickel-free solutions. This result can be explained if it is assumed that the nickel sulphate molecule does not interact with the product of the coumarin reduction. The stability constant of nickel sulphate has been given by various authors listed in reference (84). A typical value (87) may be used to calculate the concentration of hexaquo-nickel ion in the sulphate supporting electrolyte. We have

\[ K_1 = \frac{[\text{NiSO}_4]}{[\text{Ni}^{++}][\text{SO}_4^{2-}]} = 10^{2.40} = 251.2 \]

For a 0.1M potassium sulphate solution and a stoichiometric
nickel sulphate concentration of 1.00 mmole/litre it can be calculated that the concentration of the hexaquo-nickel ion is 0.038 mmole/litre. That is, 3.8 per cent of the nickel exists in the hexaquo form. If it is assumed that only hexaquo-nickel ion will react with the product of the coumarin reduction then only a small fraction of the nickel can interact. As hexaquo-nickel ions are used up in the diffusion layer more can be supplied by dissociation of nickel sulphate molecules in the diffusion layer, but to explain the experimental results it is necessary to assume that this process is not complete. This explanation is given without proof.

Harle and Lyons (8) claim to have used a pH 4.9 buffer of the phthalate type in their study of the polarography of coumarin. However, it can be seen from figure 44 that in a pH 5.07 phthalate supporting electrolyte the coumarin wave is obscured by the discharge of the base electrolyte.

It is significant to note that in figure 44 discharge of nickel occurs at identical potentials in the various types of supporting electrolyte, none of which is capillary-active. This observation, namely, that coumarin has an identical influence on the nickel reduction in different media, strongly suggests a surface phenomenon, that is, adsorption of coumarin at the dropping electrode. In fact, this is further evidence in favour of the previously suggested adsorption theory.

* * * * *
(vi). Polarography of nickel-coumarin solutions containing boric acid.

As pointed out in section I a Watts nickel solution contains boric acid, which the text books claim, acts as a buffer in maintaining the pH of a plating bath at the desired value. Some doubt was cast upon this claim since boric acid, on its own, behaves as a weak, monobasic acid with a dissociation constant of $6 \times 10^{-10}$, and cannot therefore act as a buffer at pH 4.5 - 6.0. (The possibility of a buffer system in boric acid-nickel solutions has not yet been considered). Therefore, since the function of boric acid in a plating bath has not been definitely established, it was decided to investigate the polarography of nickel-coumarin solutions in various concentrations of boric acid. For these investigations a supporting electrolyte of 0.1M potassium chloride was used. The residual current curves for various boric acid concentrations in this electrolyte are shown in figure 45 and it can be seen that at higher boric acid concentrations the residual current would interfere with the coumarin polarograms.

Boric acid is not capillary-active at the mercury-electrolyte interface since in solutions containing 0.2 and 1.0 mmole/litre of boric acid the electrocapillary curve was found to be identical with that obtained in 0.1M potassium chloride alone. Furthermore, boric acid at 1.0 and 3.5 mmole/litre had no influence on the results of coumarin (at a
Figure 45. Residual current at various boric acid concentrations.

Figure 46. Effect of boric acid on the apparent height of the coumarin wave in nickel solutions.
Table 27

Apparent height of the coumarin wave in presence of excess nickel in 0.1M potassium chloride, at 25°C, at various boric acid concentrations.

Coumarin concentration 1.50 mmole/litre in all cases.

Capillary characteristics:

(a) \( h = 38.5 \text{ cm.}, m^{2/3} t^{1/6} = 1.981 \text{ mg}^{2/3} \text{ sec}^{-1/2} \)

(b) \( h = 31.5 \text{ cm.}, m^{2/3} t^{1/6} = 1.788 \text{ mg}^{2/3} \text{ sec}^{-1/2} \)

<table>
<thead>
<tr>
<th>NiSO₄ mmole/l</th>
<th>Boric acid mmole/l</th>
<th>pH</th>
<th>Position</th>
<th>( \mu A )</th>
<th>( \mu A )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>( m^{2/3} t^{1/6} )</td>
<td>( m^{2/3} t^{1/6} )</td>
</tr>
<tr>
<td>1.00</td>
<td>0.10</td>
<td>5.70</td>
<td>(a)</td>
<td>3.16</td>
<td>1.59</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>(b)</td>
<td>3.94</td>
<td>1.64</td>
</tr>
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<td>0.20</td>
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<td>5.66</td>
<td>(a)</td>
<td>3.37</td>
<td>1.70</td>
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<td></td>
<td></td>
<td>(b)</td>
<td>3.01</td>
<td>1.68</td>
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<td>(a)</td>
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<td>(a)</td>
<td>4.55</td>
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<td>(b)</td>
<td>4.20</td>
<td>2.35</td>
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<td>(a)</td>
<td>4.97</td>
<td>2.51</td>
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<td>(b)</td>
<td>4.49</td>
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<td>50.0</td>
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<td>5.70</td>
<td>(a)</td>
<td>4.99</td>
<td>2.52</td>
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<td></td>
<td></td>
<td>(b)</td>
<td>4.52</td>
<td>2.53</td>
</tr>
<tr>
<td>10⁻¹M - residual current interferes with coumarin wave.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0</td>
<td>10.00</td>
<td>-</td>
<td>(a)</td>
<td>5.46</td>
<td>2.76</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>(b)</td>
<td>4.91</td>
<td>2.75</td>
</tr>
<tr>
<td></td>
<td>50.0</td>
<td>-</td>
<td>(a)</td>
<td>5.43</td>
<td>2.74</td>
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<td></td>
<td></td>
<td></td>
<td>(b)</td>
<td>4.96</td>
<td>2.78</td>
</tr>
</tbody>
</table>
concentration of 1.00 mmole/litre) on the electrocapillary curve. It also had no influence on the shape or position of the nickel discharge in nickel-coumarin solutions.

The apparent heights of the coumarin wave in presence of excess nickel, at various boric acid concentrations, are given in Table 27, and represented graphically in figure 46. Also given in Table 27 are the coumarin diffusion currents at two of the higher boric acid concentrations, but in absence of nickel, to confirm that boric acid does not alter the coumarin diffusion current. The pH's of the solutions were also determined and lie between 5.65 and 5.70 in each case. The pH was found not to vary with boric acid concentration.

It is seen from figure 46 that the apparent height of the coumarin wave increases with boric acid concentration to a value a little below its value in nickel-free solutions. An interpretation of this observation is given in sub-section (ix).

* * * * *

(viii). Controlled potential reductions on nickel-coumarin solutions.

The polarographic work just described has indicated that in certain supporting electrolytes the normal polarographic additivity of diffusion currents does not occur in solutions containing both nickel and coumarin. At -1.7 volts vs. the S.C.E. the apparent height of the coumarin wave in presence of excess nickel falls to one half its value in nickel-free
solutions. The polarographic method was able to show that this phenomenon could be accounted for by the interaction, in the diffusion layer, of one nickel ion with the product of the reduction of the equivalent of four coumarin molecules. Although the polarographic method is extremely useful in determining stoichiometric coefficients for the reactants in interactions of this sort it does not give any information about the nature or composition of the products. To gain information concerning the products it is necessary to perform the electrochemical reduction on a large enough scale to produce a sufficient quantity of product for identification. The operating conditions for the successful large scale electrolysis can be deduced from the polarographic results.

Lingane (88) has described an apparatus suitable for preparing appreciable quantities of material in electrochemical reductions. The reduction cell is shown in figure 47, and the circuit used, in figure 48. The potential of the cathode, with respect to the layer of solution in the immediate vicinity is measured by means of an agar salt bridge (4 per cent agar in saturated potassium chloride) the tip of which is placed about one millimetre from the surface of the cathode. In this way ohmic potential drop in the solution is reduced to a minimum. By means of the arrangement shown, the potential of the cathode is measured with respect to the saturated calomel electrode. By varying the rheostat, which acts as a potential divider, the potential of the cathode is maintained at the desired value.
Figure 47. Cell for electrolysis at controlled potential.

Figure 48. Circuit for electrolysis at controlled potential.
In the present case, for the study of the reduction products in nickel-coumarin solutions, it is seen from the polarographic data that the cathode potential should be maintained at -1.7 volts (vs. the S.C.E.) with respect to the solution in its immediate vicinity. In all, three reductions were performed, the products were separated and their properties were compared. The reductions performed were

(a) reduction of coumarin alone, in 0.1M potassium chloride

(b) reduction of coumarin in presence of nickel, in 0.1M potassium chloride

(c) reduction of coumarin in presence of nickel, in pH 6.45 phosphate buffer

all at room temperature, at -1.7 volts vs. the S.C.E.

(a). Electrochemical reduction of coumarin in 0.1M potassium chloride. - 0.6 grams of coumarin was dissolved in 400 mls. of 0.1M potassium chloride solution and placed in the cathode compartment of the reduction cell shown in figure 47. 0.1M potassium chloride was poured into the anode compartment until the liquid level was the same in both compartments. The electrolysis was then started. Efficient stirring of the solution in the cathode compartment is necessary otherwise the potential registered by the cathode may be in error. In general, potential control of ±0.1 volts was maintained. Variations of this magnitude are of no consequence in the present experiment. As the electrolysis proceeded a flocculent
white product was precipitated. After the electrolysis had been in progress for some hours it was then stopped, the cathode material was separated from the mercury and then filtered. The precipitate was washed and dried. Approximately 0.22 gram of white product was obtained.

(b). Electrochemical reduction of coumarin in presence of nickel, in 0.1M potassium chloride. - 0.6 gram of coumarin and 0.25 gram of nickel chloride, NiCl₂·6H₂O were dissolved in 400 ml. of 0.1M potassium chloride solution and placed in the cathode compartment of the reduction cell. 0.1M potassium chloride solution was poured to the same level in the other compartment. The concentration of nickel chloride was chosen so that there was approximately one nickel ion for each four coumarin molecules. (The solution is saturated with respect to coumarin). The electrolysis was started. Initially the current was about 55 milliamperes but fell to 20 milliamperes after 2½ hours, at which time the electrolysis was terminated. It was estimated that about 260 coulombs had been used. The product was obtained as a light-green precipitate. The cathode material was separated from the mercury and then filtered. The precipitate was washed, and dried at room temperature. Approximately 0.32 gram of the light green product was obtained. The filtered cathode solution was tested for nickel by the dimethylglyoxime test but no nickel was found. Thus, all the nickel had undergone reaction.
(c). Electrolysis of coumarin in presence of nickel, in a pH 6.45 phosphate buffer. - 0.6 gram of coumarin and 0.25 gram of nickel chloride, \( \text{NiCl}_2 \cdot 6\text{H}_2\text{O} \), were dissolved in 400 ml. of a pH 6.45 phosphate solution, prepared as described in section III(iv), and placed in the cathode compartment of the reduction cell. The phosphate buffer solution was poured to the same level in the other compartment. A little potassium chloride solution was also added to the anode compartment otherwise depolarization of the anode does not occur.

As before, the initial current had a value of about 55 milliamperes. As the electrolysis proceeded the product was obtained as a white precipitate. When sufficient had been obtained the electrolysis was terminated and the product isolated as before.

Comparison of the properties of the reduction products.
- The melting points of the three products were compared. The white product obtained from preparation (a) darkened above 220° and melted at 240-242°. The white product from preparation (c) darkened above 220° and melted at 238-240°. In the case of the light-green product from preparation (b) no melting point could be detected below 260° but, on removal of the melting-point tube, subsequent examination showed that a portion of the substance had indeed melted. The solid residue was olive-green in colour. A probable explanation is that the light-green product is a mixture of two compounds, one only of which melts below 260°.
The white products from (a) and (c) should be identical, and should be mixtures of meso- and racemic tetrahydroidi-4,4'-coumarinyls. The melting points given by Harle and Lyons (section I(ii)) for these compounds were 247° and 280°, with darkening above 220°. Since the white products obtained experimentally have not been resolved it is to be expected that the melting points would be below 247°, as is in fact the case.

The infra-red spectra of the three products are shown in figure 49. It can be seen that the three spectra are identical except for a slightly higher base line in case (b). No new peaks are present in case (b), nor are any peaks absent, and the shapes and heights are very similar. Thus, the same compound, namely tetrahydroidi-4,4'-coumarinyl, is present in each case, and it seems very unlikely that any new coordination compound is present.

Thus, the evidence indicates that no organo-metallic compound has been formed. The light-green product is probably a mixture of tetrahydricoumarin with an insoluble nickel compound. The only insoluble, light-green nickel compound which seems plausible is the hydroxide, especially as it will shortly be shown that the presence of hydroxide ions in the diffusion layer can readily be entertained. That the light-green compound actually contains nickel hydroxide is difficult to verify absolutely. Nickel hydroxide is a gelatinous precipitate containing variable amounts of water and here it is mixed with
Figure 49. Comparison of the infra-red spectra (nujol mull) of the reduction products.

Product of reduction (a)

Product of reduction (b)

Product of reduction (c)
an organic compound. Consequently, an analysis would be meaningless. Treatment of the light-green product with dilute hydrochloric acid gave a white residue, and a green solution in which nickel was present (dimethylglyoxime test). This result is in agreement with the light-green compound being a mixture of nickel hydroxide and the dimeric coumarin reduction product but it may be possible that decomposition has occurred. A better confirmation was obtained as follows. The white product is very sparingly soluble in the usual organic solvents, but was found to be quite soluble in dioxane. It was possible to extract a white compound from the light-green compound by means of this solvent. This white extract had a melting point of 240-242°, in agreement with that previously obtained.

(viii). Discussion of results.

In a buffered supporting electrolyte the net reaction for the polarographic reduction of coumarin, according to Harle and Lyons, is given by

\[ \text{2R} + 2e + (2H^+) = \text{R}_2\text{H}_2 \]

where \( R \) represents coumarin, \( \text{C}_{9}\text{H}_6\text{O}_2 \).

In an unbuffered supporting electrolyte, such as 0.1M potassium chloride, the hydrogen ions are supplied by water molecules and the net reaction can be written

\[ \text{2R} + 2e + 2\text{H}_2\text{O} = \text{R}_2\text{H}_2 + 2 \text{OH}^- \]

and so hydroxide ions should be present in the diffusion layer. It is seen that the flux of hydroxide ions produced in the
diffusion layer is the same as the flux of coumarin molecules diffusing into the diffusion layer. The hydroxide ions would be expected to react with nickel ions to produce insoluble nickel hydroxide, as in fact is believed to be the case in the large scale reduction performed at the mercury pool cathode. Thus, the following reaction might be expected to occur:

$$2R + 2e + 2H_2O + Ni^{++} = R_2H_2 + Ni(OH)_2$$

However, such an interpretation is not in agreement with the experimental results since this requires that two coumarin molecules should be equivalent to each nickel ion, and experiment requires four molecules per nickel ion. A mechanism must therefore be sought by means of which only half the hydroxide ions are allowed to cause precipitation of the nickel ion. It is suggested that one (or more) of the coumarin reduction products are able to coordinate to a nickel ion to produce a compound which can be reduced to nickel at the mercury cathode. Since half the nickel ions must be accounted for in this way the coumarin reduction product is capable of reacting with the same flux of nickel ion as the hydroxide ion.

Since each coumarin molecule, on reduction, gives rise to one hydroxide ion, and since two hydroxide ions react with each nickel ion, then the equivalent of two coumarin molecules will be required in the assumed complex. It is not known which of the reduction products will react with nickel ions. If nickel ion reacts with $R^-$ the complex is $[NiR_2]^+$; if nickel ion reacts with $RH^-$ the complex is $[Ni(RH_2)]^{++}$; and, if it reacts with
R₂H₂ the complex is [Ni(R₂H₂)]⁺⁺.

On reduction, the complex should give Ni(Hg) and the original coumarin reduction product. The net reaction can then be formulated

\[ 4R + 4e + 4H₂O + Ni^{++} \rightarrow 2R₂H₂ + Ni(OH)₂ + 2 OH^- \]

Whether, or not, the foregoing reactions occur, the action of the phosphate buffer is readily explained as removing hydroxide ions from the diffusion layer.

Boric acid does not act as a true buffer in the pH's used in the experiments (unbuffered 0.1M potassium chloride, which, in presence of the boric acid had a measured pH of 5.65 - 5.70) but production of hydroxide ions at the electrode surface would greatly increase the pH in the diffusion layer. Boric acid can thus probably remove a certain number of hydroxide ions from the diffusion layer, possibly according to

\[ H₂BO₃ + OH^- = H₂O + H₂BO⁻ \]

but it has been shown (89) that the nature of boric acid solutions is very complicated, and the reaction is probably more complex than the one given. From figure 46 it can be seen that the effectiveness of the boric acid in removing hydroxide ions from the diffusion layer increases greatly with concentration, but it is not completely effective even at the highest concentration that it was possible to use.

* * * * * * *
Section IV

Relationship between dipole moments and electrocapillary properties of coumarin derivatives.
(i). Dipole moments of some coumarin derivatives.

(a). General theory.

Molecular Polarization. It was first pointed out by Faraday (90) that, whilst under the influence of an electric field, the particles of a dielectric behave like a series of small insulated conductors, each consisting of a single molecule, which can be polarized as a whole. When such a polarization occurs, one side of the molecule acquires a positive charge and the other side a negative charge of the same magnitude, so that the molecule as a whole remains neutral. The pair of induced charges, being only a small distance apart, can be regarded as forming a small doublet or induced dipole. The magnitude of the dipole can be expressed by its moment which is given by the magnitude of the charges multiplied by the distance between them.

Mosotti (91) and Clausius (92) extended Faraday's idea and showed that the molecular polarization $P$ was related to its dielectric constant $\varepsilon$ and density $d$ by the relationship

$$\quad P = \frac{\varepsilon - \frac{1}{2}M}{\varepsilon + 2d} \quad \cdots \cdots \cdots \cdots \quad (132)$$

where $M$ is the molecular weight of the dielectric.

The type of polarization giving rise to an induced dipole is known as distortion polarization. The molecular distortion polarization of the dielectric is written as $P_D$. For some molecules this is the only polarization which can occur. These molecules have no permanent dipole moment.
was shown by Debye (93,94) that for molecules having a permanent dipole moment an additional form of polarization is possible. When an electric field is applied to such a molecule there is a tendency for it to turn so as to orientate itself in the field in a position of minimum potential energy, i.e. in a sense opposed to that of the field, and at low field strengths this tendency is proportional to the field strength. It is on this principle that the methods used for the determination of the actual values of the permanent moments are based. This type of polarization, which is peculiar to molecules having a permanent dipole moment is known as orientation polarization. The molecular orientation polarization of the dielectric is written as $\mu^P$.

It was shown by Debye (93,94), that for polar substances the total molecular polarization of a substance could be expressed by

$$T^P = \frac{\varepsilon - \frac{1}{2}M}{\varepsilon + 2d} = \frac{4}{3} \pi N \left( \chi + \frac{\mu^2}{3kT} \right) \ldots \ldots (133)$$

where

$T^P$ is the total molecular polarization, expressed in ccs.

$N$ is the Avogadro number

$\chi$ is the polarizability of the molecule, i.e. the moment induced by a field of unit intensity.

$\mu$ is the permanent dipole moment, expressed in Debye units, D, where the Debye unit is $10^{-18}$ e.s.u.
k is the Boltzmann constant
and T is the absolute temperature.

This equation comprises two distinct terms. The first, \( \frac{4}{3} \pi N \gamma \) is the distortion polarization, \( \beta P \). The other term, \( \frac{4}{3} \pi N \cdot \frac{\mu^2}{3kT} \) is the orientation polarization, \( \mu P \).

The distortion polarization term itself comprises two components. When an electric field is applied to a non-polar molecule, and an induced dipole is created, the major effect is a displacement of electrons, since their mass is so much smaller than that of the nuclei. The displacement of the electrons with respect to the nuclei is established extremely rapidly. The contribution of this effect to the molecular polarization is known as electron polarization, \( \beta P \). The nuclei are also displaced with respect to each other in an electric field. This charge displacement produces an induced dipole and its contribution to the molecular polarization is called the atom polarization, \( \alpha P \). The atom polarization is much smaller than the electron polarization.

Thus, the total molecular polarization is given by
\[
T^P = \beta P + \alpha P + \mu P \quad \cdots \cdots \cdots \quad (134)
\]

These three parts of the molecular polarization are associated with the three forms of internal energy of the molecule. The orientation polarization is closely connected with the rotational energy of the molecule, atom polarization is closely connected with molecular vibrations, and electron polarization with electronic transitions. Thus, the
polarization of a molecule depends upon the frequency of the electric field used in its determination. At frequencies less than about $10^9$ sec$^{-1}$ all three forms of polarization are possible. At frequencies very much higher than this, rotation of the molecule is too slow to make any contribution to the total polarization, and provided that the frequency is below infra-red frequencies only atom and electron polarization can occur. Similarly, between infra-red and ultra-violet frequencies only electron polarization occurs.

The dielectric constant cannot be measured at frequencies so high as infra-red and ultra-violet frequencies. At frequencies at which it can be measured the polarization corresponds to the sum of all three forms of polarization. For the calculation of dipole moments it is the orientation polarization which is required and so a method of evaluating it is necessary.

It was shown by Maxwell (95) that for non-polar, non-ferromagnetic substances the dielectric constant of a medium is related to its refractive index, measured for the same frequency of radiation, by

$$n^2 = \varepsilon \quad \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdOTS
is a constant independent of temperature, and is known as the specific refraction. The molecular refraction, \( R \), is given by

\[
R = \frac{n^2 - 1}{n^2 + 2} \times \frac{M}{d} \quad \ldots \ldots \ldots \ldots (137)
\]

and for optical wavelengths can be identified with the electron polarization. If refractive index measurements are made in the infra-red region of the spectrum, as well as in the visible region, the molecular refraction can be identified with the total distortion polarization \( \mathbf{P}^\mathbf{D} + \mathbf{A}^\mathbf{P} \). Such determinations in the infra-red region are not easy and for the evaluation of the atom polarization the suggestion of Smith (98) was used. This suggestion was that no great error would be introduced by assuming the atom polarization to be about five per cent of the electron polarization. Thus, we have

\[
\mu^\mathbf{P} = \mathbf{T}^\mathbf{P} - \mathbf{P}^\mathbf{D} = \mathbf{T}^\mathbf{P} - 1.05 \mathbf{R}_D \quad \ldots \ldots (138)
\]

where \( \mathbf{R}_D \) is the molecular refraction for the sodium D line.

Once the value of \( \mu^\mathbf{P} \) at any particular temperature has been evaluated, the value of the permanent dipole moment can be evaluated from

\[
\mu = \left\{ \frac{9k}{4\pi N} \right\}^{1/2} \left\{ \mu^\mathbf{T} \right\}^{1/2} = 0.012812 \left( \mu^\mathbf{T} \right)^{1/2} \cdot (139)
\]

(b). Determination of dipole moments from measurements on dilute solutions.

The Debye equation, equation (133), applies only when the polar molecules are so far apart that they cannot exert any influence on the orientation of one another in an
electric field. This would seem to limit its application to gases and vapours at low pressures. However, a modification of the treatment enables the method to be applied to dilute solutions of a polar compound in a non-polar solvent.

For a system containing \( i \) components it follows directly from the Clausius-Mosotti treatment that the "molecular polarization of the mixture" is given by

\[
P = \sum P_i f_i
\]

where \( f_i \) is the molar fraction of the \( i^{th} \) component in the mixture. This is known as the mixture law for polarization.

For a system comprising two components only, e.g. a dilute solution containing a single solute, the mixture law becomes

\[
P = P_1 f_1 + P_2 f_2
\]

If component 1 is a non-polar solvent, and it is assumed that its polarization is not influenced by the presence of solute molecules, then values of \( P_2 \) can be evaluated by determination of \( P \) at various known concentrations. The limiting value obtained as the solute concentration approaches zero can then be regarded as the molecular polarization of the solute under conditions such that the Debye equation holds. This treatment ignores any possible "solvent effect".

A similar relation applies for molecular refractions, viz

\[
R = R_1 f_1 + R_2 f_2
\]

which can therefore be treated in a similar way.
Thus, from equations (133) and (141) the Debye equation expressing the polarization of a solution becomes

$$P = P_1 f_1 + P_2 f_2 = \frac{\varepsilon - \frac{1}{\varepsilon} \cdot \frac{M_1 f_1 + M_2 f_2}{d}}{\varepsilon + 2} \quad \cdots (143)$$

The calculations involved in the use of this equation are quite lengthy, since from the weights of the two components taken, it is necessary to calculate the molar fractions for each concentration. A simpler method is to use the mixture law in the form

$$p = p_1 w_1 + p_2 w_2 = \frac{\varepsilon - \frac{1}{\varepsilon} \cdot v}{\varepsilon + 2} \quad \cdots \cdots (144)$$

where the p's are now specific polarizations, w_1 and w_2 are weight fractions and v (=l/d) is the specific volume. The p_2 values can then be multiplied by the molecular weight M_2 of the solute to give P_2 for each concentration. P_2 can then be plotted against w_2 and extrapolated to zero concentration, as before.

A general failing of both these methods is that the variations of P_2 and p_2 with concentration do not follow any simple relationship, and hence there is no way of using statistical methods in performing the extrapolation. Another failing is that the possible error in the values of P_2 deduced from the experimental data are inversely proportional to the concentrations of the solutions. Consequently, the values for low concentrations, which are the most important in the extrapolation to zero concentration, are the most inaccurate. Methods which avoid the necessity for calculating the
polarization at each concentration have been developed, and which also give more satisfactory extrapolation to zero concentration. For the calculation of experimental results the simplest method is probably that due to Halverstadt and Kumler (99). In this method it is assumed that the dielectric constant and specific volume of the solutions are linear functions of the weight fraction of the solute. Thus

\[ \begin{align*}
\varepsilon &= \varepsilon_1 (1 + \alpha w_2) \\
v &= v_1 (1 + \beta w_2)
\end{align*} \]  \hspace{1cm} (145)

From equation (144)

\[ p = p_1 (1 - w_2) + p_2 w_2 \]  \hspace{1cm} (146)

and so

\[ p_2 = p_1 + (p - p_1)/w_2 \]  \hspace{1cm} (147)

Thus, at zero concentration

\[ p_2^0 = p_1 + \lim_{w_2 \to 0} \left( \frac{\partial p}{\partial w_2} \right) \]  \hspace{1cm} (148)

From equation (144)

\[ \frac{\partial p}{\partial w_2} = \frac{3v}{(\varepsilon + 2)^2} \frac{\partial \varepsilon}{\partial w_2} + \frac{\varepsilon - 1}{\varepsilon + 2} \frac{\partial v}{\partial w_2} \]  \hspace{1cm} (149)

Now, as \( w_2 \to 0 \), \( v \to v_1 \) and \( \varepsilon \to \varepsilon_1 \)

and since

\[ \frac{\partial \varepsilon}{\partial w_2} = \alpha \quad \text{and} \quad \frac{\partial v}{\partial w_2} = \beta \]
we have
\[ p_2^0 = p_1 + \frac{3 \alpha v_1}{(\varepsilon_1 + 2)^2} + \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2} \beta \ldots \ldots (150) \]

Since,
\[ p_1 = \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2} v_1 \]

then
\[ p_2^0 = \frac{3 \alpha v_1}{(\varepsilon_1 + 2)^2} + \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2} (v_1 + \beta) \ldots \ldots (151) \]

Even if the assumption that \( \varepsilon \) and \( v \) are linear with \( w_2 \) over the concentration range chosen is not justified the method can still be used if the limiting values of \( \varepsilon \partial \varepsilon / \partial w_2 \) and \( v \partial v / \partial w_2 \) as zero concentration is reached are used.

Similarly the specific refraction is given by
\[ n_2^0 = \frac{3 \varepsilon v_1}{(n_1^2 + 2)^2} + \frac{n_1^2 - 1}{n_1^2 + 2} (v_1 + \beta) \ldots \ldots (152) \]

(c). Experimental Procedure.

Measurement of dielectric constants of dilute solutions. - Any method of determination of dielectric constants depends ultimately on the measurement of the capacity of a condenser. A number of general methods of doing this, applicable to the present conditions, have been described by Smith (100). In the present instance a resonance method was used. The method is based on the result that if an inductance \( L \), a capacity \( C \), and a resistance \( R \) are arranged in series in a circuit, the impedance of the circuit is given by
\[ \sqrt{R^2 + \left( \frac{2\pi fL - \frac{1}{2\pi fC}}{4\pi fL} \right)^2} \]

where \( f \) is the frequency of the current passing in the circuit. The impedance is a minimum, and the current a maximum when \( 4\pi^2 f^2 LC = 1 \). If this condition holds, the circuit is said to be tuned, or in a state of resonance, since if \( R \) is small the current will rise to very high values.

If both the frequency and the inductance of the circuit are kept constant, resonance occurs when the capacity \( C \) has a definite value. Hence, if a variable condenser is arranged in parallel with a condenser which contains the test solution between its plates, resonance occurs when the variable condenser is set to such a value that the sum of the capacities has the desired value. Since the capacity of the "dielectric cell" varies with the medium with which it is filled, different settings of the variable condenser are required to reach a state of resonance, and, from the settings of the variable condenser, the dielectric constant of the test solution can be calculated, as will be shown later.

The apparatus used for the determinations was first described by Flew, Smith and Witten (101). The parallel circuit comprising the dielectric cell and a precision variable condenser is included in the circuit of a variable oscillator, the frequency of which is matched to that of an oscillator whose frequency is controlled by a quartz crystal having a natural frequency of 1000 kc/s. The tuned circuit of the variable oscillator is shown in figure 50. The variable
Figure 50. Tuned circuit for capacity measurements.

Figure 51. Glass dielectric cell.
frequency is mixed with that from the fixed oscillator in a special mixer valve. The output of this valve is fed to a valve voltmeter having self-bias and anode bend detection, with a 0-500 microammeter as the anode load.

When the variable oscillator is tuned through 1000 kc/s, the anode current rises and falls in the manner characteristic of a resonance curve; however, when the frequency passes through that of the crystal, the anode current falls very suddenly to give a very sharp, distinct dip. From the width of this dip and the actual reproducibility of the capacitor setting, the sensitivity of the instrument was estimated to be about 0.005 pF.

The method of evaluating the dielectric constant of a known material is as follows. It is first necessary to calibrate the dielectric cell. This can be done by making measurements when the cell is filled with two materials of known dielectric constant. Let $C_0$ be the capacity of the cell when evacuated, and let $C_a, C_b, C_c$ be the readings of the precision condenser when the cell is filled with materials having dielectric constants of $\varepsilon_a$, $\varepsilon_b$, and $\varepsilon_c$ respectively. There are also additional capacities incorporated with the circuit due to capacities of the wire connections and other stray capacities. Let the sum of all these capacities be denoted by $C_s$. Thus, at resonance, for the three measurements we have

$$C_a + C_0\varepsilon_a + C_s = C_b + C_0\varepsilon_b + C_s = C_c + C_0\varepsilon_c + C_s$$
from which it follows that

\[
\frac{\varepsilon_c - \varepsilon_a}{\varepsilon_b - \varepsilon_a} = \frac{c_a - c_c}{c_a - c_b} \quad \cdots \cdots \cdots \quad (153)
\]

and \(\varepsilon_c\) can be evaluated if \(\varepsilon_a\) and \(\varepsilon_b\) are known.

**The precision condenser.** - The standard precision variable air condenser used in the tuning circuit was manufactured by H.W. Sullivan, Ltd. (London). It had a nominal capacitance range of 60 to 380 pF, the scale accuracy being about \(\pm 0.01\) pF. From the calibration chart supplied with the instrument it was seen that for the major part of the capacitance range, linearity between the scale setting and corresponding capacitance was obeyed.

**The dielectric cell.** - The dielectric cell was of the Sayce-Briscoe type (102) as modified by Le Fevre (103) and Few, Smith and Witten (101). The cell, which was of all glass construction, is shown in figure 51. It comprises two concentric glass tubes, the inner tube being closed at its lower end. Access to the annular space between the tubes is provided by narrow tubes of stout capillary tubing with about 2 mm. bore. These side-arms are fitted with ground glass caps to minimise evaporation of solvent and prevent entry of atmospheric moisture. The outer tube is sealed to the inner tube in such a way that the inner tube extends beyond the outer, in the manner shown. This permits the whole of the portion of cell which contains solution to be immersed in a thermostat. The inner surface of the outer tube, and the outer
surface of the inner tube are silvered over the lower three-quarters of their length, thereby giving two condenser plates. Contact to these is given by platinum wires sealed through the bottom of the inner tube and through the wall of the outer tube, respectively. Good electrical contact between the leads from the measuring circuit and the platinum contact wires is obtained by filling both this side-arm, and also the small cup sealed to the top of the inner tube, with mercury.

The cell was silvered in the manner recommended by Sugden (104), by reduction of ammoniacal silver solution with glucose. Better results were obtained by making the silver solution three times as strong as Sugden's solution. The cell was first cleaned by treating with a mixture of alcohol and nitric acid, washed with distilled water and dried. It was then silvered, the silvering being complete in about half-an-hour. The cell was thoroughly washed with distilled water and when not in use was filled with dry benzene to protect the silvered surfaces.

When immersed in an oil thermostat this type of cell is very nearly an "ideal" condenser; that is, one for which the capacity is very nearly proportional to the dielectric constant of the material with which it is filled.

The cell was filled with the test solution via the long side-arm by means of a flask provided with a delivery tube which fitted onto the side-arm in a ground glass joint. The transfer of solution was accomplished by the pressure of dry
nitrogen and can readily be performed without introduction of air bubbles into the cell.

The cell was calibrated by making measurements when containing dry nitrogen ($\varepsilon = 1.0005$) and purified benzene ($\varepsilon = 2.2725$) respectively. It was found to have a capacity of about $80 \text{ pF}$ per dielectric constant unit, and since it is possible to measure the capacity to within about $\pm 0.01 \text{ pF}$ then the dielectric constant of a solution can be determined with an accuracy of $\pm 0.00013$ of a dielectric constant unit.

The ideality of the cell was checked by measuring the dielectric constant of purified carbon disulphide ($\varepsilon = 2.6342$). The experimental value determined in this way was very close to the accepted value, certainly within the rather small experimental error.

The cell was placed in a holder in an oil thermostat, maintained at $25 \pm 0.001^\circ \text{C}$, so that the leads to the oscillator, and especially the screened cable, were as short as possible (to minimise stray capacities). All earths were made to the same point.

Measurements of refractive indices and densities. - The refractive indices of the solvent and solutions were measured with a Pulfrich refractometer maintained at $25 \pm 0.005^\circ \text{C}$ by the circulation of water from a thermostat. To minimise errors due to evaporation of solvent or absorption of atmospheric moisture while thermal equilibrium was attained the solutions were previously equilibrated by placing the flasks containing
them in the thermostat.

Densities were measured by means of a calibrated Sprengel-Ostwald pyknometer having a volume of about 25 cc., and having parallel side-arms of capillary tubing which could be closed with ground glass caps. With temperature control of \( \pm 0.01^\circ C \) densities can be measured to within 0.00002 gram/cc. It was calibrated with distilled water.

Measurements on solutions. - Not all the coumarin derivatives which were investigated had an appreciable solubility in benzene or the other conventional solvents. The most suitable solvent in this respect was found to be dioxane, but it was realised that dioxane is not considered to be a typical "dipole solvent" as the presence of the two oxygen atoms in the ring structure may cause interaction between solvent and solute.

The purification of the dioxane is given in Appendix I, as also are the preparations of the coumarin derivatives.

For the determinations, six or seven solutions of graded concentrations were prepared. The dielectric constants of the solvent and solutions were made as soon as possible after making up the solutions, as these are the most susceptible to change. A measurement on the pure solvent was made at the beginning and end of the series to check that no change had occurred which would nullify the results. The refractive index and density measurements were then made as soon as conveniently possible.
(d). **Analysis of the results.**

From equations (151) and (152) we have

\[
p_2^0 = \frac{3\alpha v_1}{(\varepsilon_1 + 2)^2} + \frac{\varepsilon_1 - 1}{\varepsilon_2 + 2} (v_1 + \beta)
\]

and

\[
r_2^0 = \frac{3\gamma v_1}{(n_1^2 + 2)^2} + \frac{n_1^2 - 1}{n_1^2 + 2} (v_1 + \beta)
\]

For dioxane, \(\varepsilon_1 = 2.2052\), \(n_1 = 1.42006\) and \(v_1 = 0.97276\) cc/gm and so

\[
p_2^0 = 0.16503 \alpha + 0.28660 (v_1 + \beta) \quad (154)
\]

\[
r_2^0 = 0.18089 \gamma + 0.25310 (v_1 + \beta) \quad (155)
\]

The results obtained for coumarin, 6-aminocoumarin, 6-acetamidocoumarin and 6-sulphamylcoumarin are given in Tables 28-31, and are summarised in Table 32. In Table 33 experimental values of \(R_D\) are compared with values calculated from bond refraction data. For coumarin, the calculated value of the molecular refraction is significantly lower than the experimental value. The calculated value was obtained by assuming that the heterocyclic ring was completely non-aromatic. Hence, the observed "exaltation of refraction" indicates that it does, in fact, as would be expected, have a considerable amount of aromatic character. If then, the molecular refractions are calculated for the coumarin derivatives assuming the experimental value for coumarin, as
Table 28

Coumarin, C_{9}H_{6}O_{2} = 146.05

Polarizations and dipole moment in dioxane.

<table>
<thead>
<tr>
<th>w_{2}</th>
<th>\varepsilon</th>
<th>\nu</th>
<th>n</th>
<th>n^{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>2.2052</td>
<td>0.97276</td>
<td>1.42006</td>
<td>2.01657</td>
</tr>
<tr>
<td>0.006583</td>
<td>2.3274</td>
<td>0.97147</td>
<td>1.42147</td>
<td>2.02058</td>
</tr>
<tr>
<td>0.011604</td>
<td>2.4216</td>
<td>0.97087</td>
<td>1.42242</td>
<td>2.02328</td>
</tr>
<tr>
<td>0.015017</td>
<td>2.4922</td>
<td>0.97023</td>
<td>1.42306</td>
<td>2.02510</td>
</tr>
<tr>
<td>0.023535</td>
<td>2.6524</td>
<td>0.96891</td>
<td>1.42490</td>
<td>2.03034</td>
</tr>
<tr>
<td>0.030208</td>
<td>2.8057</td>
<td>0.96773</td>
<td>1.42583</td>
<td>2.03299</td>
</tr>
<tr>
<td>0.035939</td>
<td>2.8909</td>
<td>-</td>
<td>1.42698</td>
<td>2.03627</td>
</tr>
<tr>
<td>0.057359</td>
<td>3.3261</td>
<td>0.96292</td>
<td>1.43077</td>
<td>2.04710</td>
</tr>
</tbody>
</table>

\alpha_{0} = 18.62 \quad \beta_{0} = -0.168 \quad \gamma_{0} = 0.60

p_{2}^{0} = 3.3036 \quad r_{2}^{0} = 0.3142

Thus

\tau P = 482.49 \text{ ccs.} \quad R_{D} = 45.89 \text{ ccs.}

Hence

\mu = 434.31 \text{ ccs.}

\mu = 4.61 \times 10^{-18} \text{ e.s.u.
Table 29

6-aminocoumarin, \( \text{NH}_2\text{C}_9\text{H}_5\text{O}_2 = 161.06 \)

Polarizations and dipole moment in dioxane.

<table>
<thead>
<tr>
<th>( w_2 )</th>
<th>( \varepsilon )</th>
<th>( v )</th>
<th>( n )</th>
<th>( n^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>2.2052</td>
<td>0.97276</td>
<td>1.42006</td>
<td>2.01657</td>
</tr>
<tr>
<td>0.000244</td>
<td>2.2120</td>
<td>0.97269</td>
<td>1.42012</td>
<td>2.01674</td>
</tr>
<tr>
<td>0.000658</td>
<td>2.2249</td>
<td>0.97261</td>
<td>1.42022</td>
<td>2.01702</td>
</tr>
<tr>
<td>0.001348</td>
<td>2.2471</td>
<td>0.97242</td>
<td>1.42037</td>
<td>2.01745</td>
</tr>
<tr>
<td>0.002601</td>
<td>2.2855</td>
<td>0.97210</td>
<td>1.42064</td>
<td>2.01822</td>
</tr>
<tr>
<td>0.005337</td>
<td>2.3700</td>
<td>0.97141</td>
<td>1.42127</td>
<td>2.02001</td>
</tr>
</tbody>
</table>

\( \alpha_0 = 30.90 \) \hspace{1cm} \( \beta_0 = -0.25 \) \hspace{1cm} \( \gamma_0 = 0.64 \)

\( p_2^0 = 5.3066 \) \hspace{1cm} \( r_2^0 = 0.2988 \)

Thus

\( T_P = 854.68 \text{ ccs.} \) \hspace{1cm} \( R_D = 48.12 \text{ ccs.} \)

Hence

\( p^P = 804.15 \text{ ccs.} \)

\( \mu = 6.27 \times 10^{-18} \text{ e.s.u.} \)
Table 30

6-acetamido coumarin, \( \text{CH}_3\text{CO.NH.C}_9\text{H}_5\text{O}_2 \) = 203.18

Polarizations and dipole moment in dioxane.

<table>
<thead>
<tr>
<th>( w_2 )</th>
<th>( \varepsilon )</th>
<th>( \nu )</th>
<th>( n )</th>
<th>( n^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>2.2052</td>
<td>0.97276</td>
<td>1.42006</td>
<td>2.01657</td>
</tr>
<tr>
<td>0.000092</td>
<td>2.2089</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.000237</td>
<td>2.2133</td>
<td>0.97271</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.000615</td>
<td>2.2266</td>
<td>0.97256</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.000899</td>
<td>2.2348</td>
<td>0.97248</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.001517</td>
<td>2.2497</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.001705</td>
<td>2.2576</td>
<td>0.97223</td>
<td>1.42044</td>
<td>2.01764</td>
</tr>
<tr>
<td>0.002067</td>
<td>2.2686</td>
<td>0.97211</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

\( \alpha_0 = 35.0 \) \( \beta_0 = -0.314 \) \( \gamma_0 = 0.628 \)

\( \rho_2^0 = 5.9650 \) \( \rho_2^0 = 0.2802 \)

Thus

\( \mu^P = 1211.97 \text{ ccs.} \) \( \mu^D = 56.93 \text{ ccs.} \)

Hence

\( \mu = 1152.2 \text{ ccs.} \)

\( \mu = 7.51 \times 10^{-18} \text{ e.s.u.} \)
Table 31

6-sulphamylcoumarin, \( \text{NH}_2\text{SO}_2\cdot\text{C}_9\text{H}_7\text{O}_2 \) = 225.1

Polarizations and dipole moment in dioxane.

<table>
<thead>
<tr>
<th>( w_2 )</th>
<th>( \varepsilon )</th>
<th>( \nu )</th>
<th>( n )</th>
<th>( n^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>2.2052</td>
<td>0.97276</td>
<td>1.42006</td>
<td>2.01657</td>
</tr>
<tr>
<td>0.000291</td>
<td>2.2073</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.000681</td>
<td>2.2134</td>
<td>0.97258</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.001081</td>
<td>-</td>
<td>-</td>
<td>1.42028</td>
<td>2.01718</td>
</tr>
<tr>
<td>0.001146</td>
<td>2.2185</td>
<td>0.97244</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.001758</td>
<td>-</td>
<td>-</td>
<td>1.42045</td>
<td>2.01767</td>
</tr>
<tr>
<td>0.001820</td>
<td>2.2294</td>
<td>0.97213</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.002554</td>
<td>-</td>
<td>-</td>
<td>1.42052</td>
<td>2.01783</td>
</tr>
<tr>
<td>0.002983</td>
<td>2.2425</td>
<td>0.97172</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.003945</td>
<td>-</td>
<td>-</td>
<td>1.42079</td>
<td>2.01865</td>
</tr>
<tr>
<td>0.004764</td>
<td>2.2598</td>
<td>0.97117</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.005276</td>
<td>2.2670</td>
<td>-</td>
<td>1.42104</td>
<td>2.01933</td>
</tr>
</tbody>
</table>

\[ \alpha_0 = 11.86 \quad \beta_0 = -0.334 \quad \gamma_0 = 0.522 \]

\[ p_2^0 = 2.1404 \quad r_2^0 = 0.2561 \]

Thus

\[ t_P = 481.80 \text{ ccs.} \quad R_D = 57.65 \text{ ccs.} \]

Hence

\[ \mu_P = 421.27 \text{ ccs.} \]

\[ \mu = 4.54 \times 10^{-18} \text{ e.s.u.} \]
Table 32

Summary of the experimental results and, for coumarin, a comparison with literature values.

<table>
<thead>
<tr>
<th>Coumarin derivative</th>
<th>TP</th>
<th>R_D</th>
<th>DP</th>
<th>μ_p</th>
<th>μ, Debye units</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coumarin</td>
<td>482.5</td>
<td>45.9</td>
<td>48.2</td>
<td>434.3</td>
<td>4.61</td>
<td>D&lt;sup&gt;25&lt;/sup&gt;</td>
</tr>
<tr>
<td>Coumarin (105)</td>
<td>457</td>
<td>-</td>
<td>42</td>
<td>415</td>
<td>4.48</td>
<td>B&lt;sup&gt;25&lt;/sup&gt;</td>
</tr>
<tr>
<td>Coumarin (106)</td>
<td>477.5</td>
<td>-</td>
<td>48.5</td>
<td>429</td>
<td>4.51</td>
<td>B&lt;sup&gt;20&lt;/sup&gt;</td>
</tr>
<tr>
<td>6-amino-</td>
<td>854.7</td>
<td>48.1</td>
<td>50.5</td>
<td>804.2</td>
<td>6.27</td>
<td>D&lt;sup&gt;25&lt;/sup&gt;</td>
</tr>
<tr>
<td>6-acetamido-</td>
<td>1212.0</td>
<td>56.9</td>
<td>59.8</td>
<td>1152.2</td>
<td>7.51</td>
<td>D&lt;sup&gt;25&lt;/sup&gt;</td>
</tr>
<tr>
<td>6-sulphamyl-</td>
<td>481.8</td>
<td>57.6₅</td>
<td>60.5</td>
<td>421.3</td>
<td>4.54</td>
<td>D&lt;sup&gt;25&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

D<sup>25</sup> - dioxane as solvent, at 25°C
B<sup>25</sup> - benzene as solvent, at 25°C
B<sup>20</sup> - benzene as solvent, at 20°C
Table 33

Comparison of experimental molecular refractions with calculated values.*

<table>
<thead>
<tr>
<th>Coumarin derivative</th>
<th>R_D (exp.)</th>
<th>R_D (calc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coumarin</td>
<td>45.9</td>
<td>39.35</td>
</tr>
<tr>
<td>6-amino-</td>
<td>48.1</td>
<td>49.30</td>
</tr>
<tr>
<td>6-acetamido-</td>
<td>56.9</td>
<td>58.76</td>
</tr>
<tr>
<td>6-sulphamyl-</td>
<td>57.65</td>
<td>56.91</td>
</tr>
</tbody>
</table>

Values of R_D were calculated from bond refraction data given in the literature (107,100). The values used in the calculations are given in the following table, which gives bond refractions for the sodium D line:

<table>
<thead>
<tr>
<th></th>
<th>cc.</th>
<th>cc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-H</td>
<td>1.676</td>
<td>C-S</td>
</tr>
<tr>
<td>C-C</td>
<td>1.296</td>
<td>C-N</td>
</tr>
<tr>
<td>C=C</td>
<td>4.17</td>
<td>S-O</td>
</tr>
<tr>
<td>C-ar-C_ar</td>
<td>2.688</td>
<td>N-H</td>
</tr>
<tr>
<td>C-0 (ethers)</td>
<td>1.54</td>
<td>S-N (estimated)</td>
</tr>
<tr>
<td>C=0</td>
<td>3.32</td>
<td></td>
</tr>
</tbody>
</table>

*For the derivatives of coumarin, values of R_D were calculated by adding the refractions of the respective bonds to the experimental values for coumarin.*
in the table, it can be seen that the calculated values are in good agreement with the experimental values.

It can be seen from Table 32 that, for coumarin, the experimental results obtained in the dioxane solvent are a little higher than the literature results, for which benzene was used as the solvent. Such a result is not unexpected when it is recalled that the results obtained in the dioxane solvent are likely to contain a higher contribution from the "solvent effect". An observation such as this is quite normal. However, since the same solvent was used for all the coumarin derivatives a direct comparison of the results is possible.

**Coumarin.** - The main contribution to the dipole moment arises from the relatively large dipoles of the C-O-C and C=O bonds in the pyrone ring. Le Fevre and Le Fevre (105) calculated that the line of action of the resulting dipole was inclined at an angle of 15° to the axis of the C=O bond, in a sense towards the oxygen atom, thus

![Coumarin structure](image)

**6-aminocoumarin.** - The effect of the amino group has been to increase the dipole moment by 1.66 D. Aniline has dipole moments of 1.53 and 1.77 D in benzene and dioxane, respectively (108). The abnormally high value in dioxane is due to hydrogen bonding of the amino hydrogen atoms to the
oxygen atoms of the dioxane molecules (108). This hydrogen bonding is also possible in 6-aminocoumarin and so the amino group should have a dipole moment of approximately 1.77 D. The approximate resultant dipole moment of 6-aminocoumarin can be obtained by vector addition from a study of the geometry of the molecule:

![Diagram of 6-aminocoumarin]

The result is 6.34 D, which is only slightly higher than the experimentally determined value of 6.27 D.

6-acetamidocoumarin. - Both aliphatic and aromatic amides have rather large dipole moments (about 3.4 - 3.6 D). Bates and Hobbs (109), on the assumption that the amide exists purely in the keto form, calculated that the dipole moment of acetamide should be about 3.1 D, directed along an axis inclined at 68° to the axis of the C-C bond. In 6-acetamidocoumarin the relative directions of the two large dipoles are difficult to assess. The difference between the moments of coumarin and 6-acetamidocoumarin is experimentally determined as 2.9 D, which indicates that although the dipoles act in approximately the same sense they are probably at an appreciable angle to one another (32° by vector method assuming a value of 3.5 D for the amide moment).
6-sulphamylcoumarin. - Little can be said about this compound as not much is known about the resultant effect of a sulphamyl group attached to a benzene ring. The dipole moment is almost the same as that of coumarin but the direction of action is not known.

(ii). Investigation of the electrocapillary properties of the coumarin derivatives.

The properties of the electrocapillary curve of mercury have been described in section II(iv). It was also shown in that section that a curve similar to the electrocapillary curve could be obtained by plotting the time of formation of mercury droplets issuing from a fine bore capillary tube at various potentials of the dropping mercury. The polarograph was used in this way to investigate the electrocapillary properties of coumarin in 0.1M potassium chloride and a pH 6.45 phosphate buffer. The use of potassium chloride as the supporting electrolyte prevented the use of this technique at potentials more positive than 0.0 volt (vs. the S.C.E.) since chloride ion then depolarises the dropping mercury. It was hoped to extend the potential range over which the electrocapillary properties of the coumarin derivatives were to be investigated by using 0.1M potassium nitrate as the supporting electrolyte. (Nitrate ion is not capillary-active). The time of formation of the mercury droplets in 0.1M potassium nitrate is given as a function of electrode potential in Table 34, and
in Tables 35-38 the effects of graded concentrations of the coumarin derivatives are shown. The results obtained at potentials more positive than 0.0 volt are still extremely erratic and thus these values have been omitted from figures 52-55, which show graphically the effect of the derivatives.

It can be seen that, except for coumarin, which causes an apparently abnormal depression of the curve at -1.0 to -1.4 volts, the curves are symmetrical (as far as it is possible to tell) about the electrocapillary maximum. For each compound, including coumarin, the electrocapillary maximum has not been shifted from its normal potential. This suggests that when the derivatives are adsorbed at the mercury-solution interface there is little or no resultant dipole moment perpendicular to the mercury surface. The derivatives all have large dipole moments and hence these are aligned parallel to the mercury surface. The lines of action of the dipoles are, on symmetry grounds, parallel to the ring planes of the derivatives. Although it is possible that all the derivatives are adsorbed edgewise, with dipoles parallel to the mercury surface, it seems more likely that they are adsorbed flat, in which case the dipoles must, of necessity, be parallel to the mercury surface.

Thus, it appears that the coumarin derivatives, except for coumarin itself, have a similar effect on the shape of the electrocapillary curve. However, the concentration of derivative required to cause a given amount of change varies
Table 34

Values of the mercury drop time as a function of the dropping electrode potential in 0.1M potassium nitrate.

$h = 38.5$ cm.

<table>
<thead>
<tr>
<th>Ed.e volts</th>
<th>Drop time, seconds</th>
<th>Ed.e volts</th>
<th>Drop time, seconds</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4</td>
<td>3.31</td>
<td>-0.8</td>
<td>4.27</td>
</tr>
<tr>
<td>0.3</td>
<td>3.48</td>
<td>0.9</td>
<td>4.22</td>
</tr>
<tr>
<td>0.2</td>
<td>3.63</td>
<td>1.0</td>
<td>4.06</td>
</tr>
<tr>
<td>0.1</td>
<td>3.88</td>
<td>1.1</td>
<td>3.97</td>
</tr>
<tr>
<td>0.0</td>
<td>4.03</td>
<td>1.2</td>
<td>3.83</td>
</tr>
<tr>
<td>-0.1</td>
<td>4.15</td>
<td>1.3</td>
<td>3.70</td>
</tr>
<tr>
<td>0.2</td>
<td>4.27</td>
<td>1.4</td>
<td>3.52</td>
</tr>
<tr>
<td>0.3</td>
<td>4.33</td>
<td>1.5</td>
<td>3.30</td>
</tr>
<tr>
<td>0.4</td>
<td>4.37</td>
<td>1.6</td>
<td>3.11</td>
</tr>
<tr>
<td>0.5</td>
<td>4.38</td>
<td>1.7</td>
<td>2.87</td>
</tr>
<tr>
<td>0.6</td>
<td>4.36</td>
<td>1.8</td>
<td>2.62</td>
</tr>
<tr>
<td>0.7</td>
<td>4.34</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 35

Values of the mercury drop time as a function of coumarin concentration and dropping electrode potential in 0.1M potassium nitrate at 25°C. h = 38.5 cm.

<table>
<thead>
<tr>
<th>Ed.e. volts</th>
<th>Coumarin concentration, millimole/litre</th>
<th>Drop times in seconds</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.10</td>
<td>0.25</td>
</tr>
<tr>
<td>+0.4</td>
<td>3.54</td>
<td>-</td>
</tr>
<tr>
<td>0.3</td>
<td>3.60</td>
<td>-</td>
</tr>
<tr>
<td>0.2</td>
<td>3.77</td>
<td>-</td>
</tr>
<tr>
<td>0.1</td>
<td>3.98</td>
<td>3.90</td>
</tr>
<tr>
<td>0.0</td>
<td>4.09</td>
<td>3.99</td>
</tr>
<tr>
<td>-0.1</td>
<td>4.20</td>
<td>4.09</td>
</tr>
<tr>
<td>0.2</td>
<td>4.27</td>
<td>4.18</td>
</tr>
<tr>
<td>0.3</td>
<td>4.33</td>
<td>4.23</td>
</tr>
<tr>
<td>0.4</td>
<td>4.36</td>
<td>4.25</td>
</tr>
<tr>
<td>0.5</td>
<td>4.37</td>
<td>4.26</td>
</tr>
<tr>
<td>0.6</td>
<td>4.35</td>
<td>4.24</td>
</tr>
<tr>
<td>0.7</td>
<td>4.30</td>
<td>4.22</td>
</tr>
<tr>
<td>0.8</td>
<td>4.25</td>
<td>4.16</td>
</tr>
<tr>
<td>0.9</td>
<td>4.17</td>
<td>-</td>
</tr>
<tr>
<td>1.0</td>
<td>4.08</td>
<td>4.03</td>
</tr>
<tr>
<td>1.1</td>
<td>3.96</td>
<td>-</td>
</tr>
<tr>
<td>1.2</td>
<td>3.83</td>
<td>3.78</td>
</tr>
<tr>
<td>1.3</td>
<td>3.67</td>
<td>-</td>
</tr>
<tr>
<td>1.4</td>
<td>3.48</td>
<td>3.48</td>
</tr>
<tr>
<td>1.5</td>
<td>3.27</td>
<td>-</td>
</tr>
<tr>
<td>1.6</td>
<td>3.10</td>
<td>3.11</td>
</tr>
<tr>
<td>1.7</td>
<td>2.85</td>
<td>-</td>
</tr>
<tr>
<td>1.8</td>
<td>2.63</td>
<td>2.62</td>
</tr>
</tbody>
</table>
Values of the mercury drop time as a function of 6-aminocoumarin concentration and dropping electrode potential in 0.1M potassium nitrate. $h = 38.5$ cm.

<table>
<thead>
<tr>
<th>E.d.e. volts</th>
<th>6-aminocoumarin concentration, mmole/litre</th>
<th>Drop times in seconds</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.025</td>
<td>0.05</td>
</tr>
<tr>
<td>+0.4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.1</td>
<td>3.83</td>
<td>3.83</td>
</tr>
<tr>
<td>0.0</td>
<td>3.96</td>
<td>3.95</td>
</tr>
<tr>
<td>-0.1</td>
<td>4.09</td>
<td>-</td>
</tr>
<tr>
<td>0.2</td>
<td>4.19</td>
<td>4.17</td>
</tr>
<tr>
<td>0.3</td>
<td>4.26</td>
<td>-</td>
</tr>
<tr>
<td>0.4</td>
<td>4.31</td>
<td>4.28</td>
</tr>
<tr>
<td>0.5</td>
<td>4.32</td>
<td>-</td>
</tr>
<tr>
<td>0.6</td>
<td>4.31</td>
<td>4.28</td>
</tr>
<tr>
<td>0.7</td>
<td>4.28</td>
<td>-</td>
</tr>
<tr>
<td>0.8</td>
<td>4.22</td>
<td>4.21</td>
</tr>
<tr>
<td>0.9</td>
<td>4.13</td>
<td>-</td>
</tr>
<tr>
<td>1.0</td>
<td>4.04</td>
<td>4.04</td>
</tr>
<tr>
<td>1.1</td>
<td>3.91</td>
<td>-</td>
</tr>
<tr>
<td>1.2</td>
<td>3.77</td>
<td>3.78</td>
</tr>
<tr>
<td>1.3</td>
<td>3.63</td>
<td>-</td>
</tr>
<tr>
<td>1.4</td>
<td>3.49</td>
<td>3.47</td>
</tr>
<tr>
<td>1.5</td>
<td>3.28</td>
<td>-</td>
</tr>
<tr>
<td>1.6</td>
<td>3.09</td>
<td>-</td>
</tr>
<tr>
<td>1.7</td>
<td>2.84</td>
<td>-</td>
</tr>
<tr>
<td>1.8</td>
<td>2.60</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 37

Values of the mercury drop time as a function of 6-acetamido-
coumarin concentration and dropping electrode potential in
0.1M potassium nitrate. \( h = 38.5 \) cm.

<table>
<thead>
<tr>
<th><strong>E&lt;sub&gt;d.e.&lt;/sub&gt;</strong></th>
<th><strong>6-acetamidocoumarin concentration, mmole/litre</strong></th>
<th><strong>Drop times in seconds</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>volts</td>
<td>0.02</td>
<td>0.05</td>
</tr>
<tr>
<td>0.4</td>
<td>3.24</td>
<td>3.24</td>
</tr>
<tr>
<td>0.3</td>
<td>3.50</td>
<td>3.53</td>
</tr>
<tr>
<td>0.2</td>
<td>3.59</td>
<td>3.63</td>
</tr>
<tr>
<td>0.1</td>
<td>3.84</td>
<td>3.86</td>
</tr>
<tr>
<td>0.0</td>
<td>3.99</td>
<td>3.99</td>
</tr>
<tr>
<td>-0.1</td>
<td>4.10</td>
<td>4.08</td>
</tr>
<tr>
<td>0.2</td>
<td>4.21</td>
<td>4.14</td>
</tr>
<tr>
<td>0.3</td>
<td>4.29</td>
<td>4.19</td>
</tr>
<tr>
<td>0.4</td>
<td>4.34</td>
<td>4.22</td>
</tr>
<tr>
<td>0.5</td>
<td>4.34</td>
<td>4.22</td>
</tr>
<tr>
<td>0.6</td>
<td>4.33</td>
<td>4.20</td>
</tr>
<tr>
<td>0.7</td>
<td>4.33</td>
<td>4.17</td>
</tr>
<tr>
<td>0.8</td>
<td>4.33</td>
<td>4.14</td>
</tr>
<tr>
<td>0.9</td>
<td>4.33</td>
<td>4.07</td>
</tr>
<tr>
<td>1.0</td>
<td>4.04</td>
<td>3.97</td>
</tr>
<tr>
<td>1.1</td>
<td>3.91</td>
<td>3.98</td>
</tr>
<tr>
<td>1.2</td>
<td>3.78</td>
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<tr>
<td>1.3</td>
<td>3.75</td>
<td>3.60</td>
</tr>
<tr>
<td>1.4</td>
<td>3.46</td>
<td>3.46</td>
</tr>
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<td>1.5</td>
<td>3.47</td>
<td>3.25</td>
</tr>
<tr>
<td>1.6</td>
<td>3.08</td>
<td>3.07</td>
</tr>
<tr>
<td>1.7</td>
<td>2.86</td>
<td>2.87</td>
</tr>
<tr>
<td>1.8</td>
<td>2.66</td>
<td>2.63</td>
</tr>
</tbody>
</table>
Values of the mercury drop time as a function of 6-sulphamyl-coumarin concentration and dropping electrode potential in 0.1M potassium nitrate at 25°C. h = 38.5 cm.

<table>
<thead>
<tr>
<th>E d.e. (volts)</th>
<th>6-sulphamylcoumarin concentration, mmole/litre</th>
<th>Drop times in seconds</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.05</td>
<td>0.10</td>
</tr>
<tr>
<td>+0.4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.1</td>
<td>3.85</td>
<td>3.83</td>
</tr>
<tr>
<td>0.0</td>
<td>4.01</td>
<td>3.98</td>
</tr>
<tr>
<td>-0.1</td>
<td>4.14</td>
<td>4.12</td>
</tr>
<tr>
<td>0.2</td>
<td>4.23</td>
<td>4.20</td>
</tr>
<tr>
<td>0.3</td>
<td>4.31</td>
<td>4.26</td>
</tr>
<tr>
<td>0.4</td>
<td>4.33</td>
<td>4.30</td>
</tr>
<tr>
<td>0.5</td>
<td>4.34</td>
<td>4.33</td>
</tr>
<tr>
<td>0.6</td>
<td>4.33</td>
<td>4.29</td>
</tr>
<tr>
<td>0.7</td>
<td>-</td>
<td>4.26</td>
</tr>
<tr>
<td>0.8</td>
<td>4.24</td>
<td>4.22</td>
</tr>
<tr>
<td>0.9</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1.0</td>
<td>4.04</td>
<td>4.05</td>
</tr>
<tr>
<td>1.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1.2</td>
<td>-</td>
<td>3.80</td>
</tr>
<tr>
<td>1.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1.4</td>
<td>-</td>
<td>3.46</td>
</tr>
<tr>
<td>1.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1.6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1.7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1.8</td>
<td>-</td>
<td>2.65</td>
</tr>
</tbody>
</table>
Figure 52. Effect of coumarin on the electrocapillary curve.

Concentrations, mmole/litre

Figure 53. Effect of 6-aminocoumarin on the electrocapillary curve.

Concentrations, mmole/litre
Figure 54. Effect of 6-acetamidocoumarin on the electrocapillary curve.

Figure 55. Effect of 6-sulphamylcoumarin on the electrocapillary curve.
Figure 5b. Effect of coumarin derivatives on the mercury drop time at the electrocapillary maximum.

Drop time at electrocapillary maximum in 0.1M potassium nitrate.

- Coumarin
- 6-sulphamylcoumarin
- 6-aminocoumarin
- 6-acetamidocoumarin

Log concentration vs. Drop times in seconds.
widely. In this respect 6-acetamidocoumarin is the most, and coumarin the least, effective. This can be clearly seen in figure 56 in which the mercury drop times at the electrocapillary maximum are plotted against the logarithm of the concentration of the derivative in question. Straight lines have been drawn through the experimental points as this procedure seems to be as satisfactory as any other type of curve which could be drawn, especially as the reproducibility of the results is estimated to be only about 0.02 second.

The reason for the differences in the electrocapillary specific activities is not clear. The technique used only gives equilibrium conditions existing at the surface of the mercury drop, and new techniques would be required to gain additional information, such as rates of adsorption and desorption (109).

* * * * * * *
Section V

Investigation of the nature of plating solutions.
Absorption spectrophotometry. - The principles of absorption spectrophotometry are governed by two fundamental laws. The first of these, originally enunciated by Bouguer in 1729, and then a few years later by Lambert, states that the proportion of radiation absorbed by a substance is independent of the intensity of the incident radiation. The law can thus also be expressed in the form that each successive layer of thickness $dl$ absorbs the same fraction $dI/I$ of the radiation of intensity $I$ incident upon it; that is, $dI/I = -\mu dl$, where $\mu$ is a constant. On integration, we have

$$I = I_0 e^{-\mu l} \quad \ldots \ldots \ldots \ldots \ldots \ldots \cdot (156)$$

where $I_0$ is the intensity of the radiation incident on a layer of thickness $l$ and $I$ is the emergent intensity.

Alternatively, we may also write

$$I = I_0 x 10^{-kl} \quad \ldots \ldots \ldots \ldots \ldots \ldots \cdot (157)$$

where $K = 0.434 \mu$).

If the fraction of light transmitted, $I/I_0$, is denoted by $T$, then

$$\log \frac{1}{T} = Kl \quad \ldots \ldots \ldots \ldots \ldots \ldots \cdot (158)$$

$\log \frac{1}{T}$ is a quantity known as the optical density, represented by $D$.

The second law of absorption is that due to Beer (1852). This states that the amount of absorption depends only on the number of absorbing substances through which the radiation
passes. If the absorbing substance is dissolved in a non-absorbing medium the optical density will be proportional to the concentration of the solution. By combining Beer's law with Lambert's law we have

\[ I = I_0 \times 10^{-E \cdot c \cdot l} \]  \hspace{1cm} (159)

where \( E \) is a constant and \( c \) represents the concentration of the solution. Thus

\[ D = E \cdot c \quad \ldots \ldots \ldots \ldots \quad (160) \]

The numerical value of \( E \) depends on the units of concentration and length. When the concentration is expressed in gram molecules/litre and the length in centimetres, a special symbol \( \varepsilon \) is used instead of \( E \), and the quantity \( \varepsilon \) is called the molar or molecular extinction coefficient.

Equation (160) predicts that the optical density of a solution is directly proportional to the concentration of absorbing substance and to the path length through which the radiation passes. This equation can be used to evaluate \( \varepsilon \) if the other quantities are known. By evaluating \( \varepsilon \) for a range of wavelengths of the incident radiation an "absorption spectrum" is obtained.

For the determination of absorption spectra a Unicam S.P.500 absorption spectrophotometer was used, the optical density and wavelength scales being calibrated by means of potassium chromate in 0.05M potassium hydroxide using data given in the literature (110). Optical densities of all solutions were directly referred to the corresponding solvent,
both liquids being placed in matched silica cells of 1.000 cm.
path length. In use, the cells were placed in the same
positions in the cell holder, and presented the same face to
the incident light on each occasion.

**Ion exchange.** - For the ion exchange experiments two
types of exchange resin were used. The first of these was
Zeo-karb 225 resin, a strongly acidic, cation-exchanger with
sulphonic functional groups. The other was De-acidite FF resin,
a strongly basic, anion-exchanger with quaternary methyl-
ammonium groups.

The resins were washed several times with distilled
water to remove impurities, then packed into two ion exchange
columns. The columns were "backwashed" to ensure that they were
evenly packed. Then they were both treated with 2 - 3 N hydro-
chloric acid and washed until free from chloride. The Zeo-karb
225 was then in the hydrogen form, and the De-acidite FF was in
the chloride form. Both were then ready for use.

**Measurement of pH.** - For the measurement of the hydrogen
ion concentration of solutions a Cambridge pH meter was used,
in conjunction with a standard glass electrode and a calomel
electrode, in the usual way. Before use, the instrument was
standardised by means of a standard buffer solution of pH 4.00
(0.05M potassium hydrogen phthalate). After the completion of
a titration, or series of measurements, the standardisation was
again checked to ensure that no change had occurred which would
invalidate the results.
(ii). Nature of nickel-coumarin solutions.

The ultraviolet absorption spectrum of coumarin in aqueous solution has been given in the literature (8,10). Values given for absorption coefficients, together with experimental values are shown in the following table:

<table>
<thead>
<tr>
<th>(\lambda, \mu)</th>
<th>(\varepsilon)</th>
<th>(\lambda, \mu)</th>
<th>(\varepsilon)</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>278</td>
<td>10,500</td>
<td>310</td>
<td>6,000</td>
<td>(8)</td>
</tr>
<tr>
<td>278</td>
<td>10,700</td>
<td>305</td>
<td>6,000</td>
<td>(10)</td>
</tr>
<tr>
<td>278</td>
<td>10,880</td>
<td>310</td>
<td>6,250</td>
<td>exp.</td>
</tr>
</tbody>
</table>

For a 0.10M solution of nickel sulphate the following results were obtained: \(\lambda_{\text{max}}\) = (i) 397, (ii) 715 \(\mu\); \(\varepsilon_{\text{max}}\) = (i) 5.02, (ii) 1.88. Below 310 \(\mu\) the absorption was very small.

The influence of concentration of nickel sulphate on the coumarin spectrum was investigated. No detectable change could be observed at nickel concentrations up to \(10^{-2}\)M, i.e. one hundred times as strong as the coumarin concentration. Addition of potassium chloride to a concentration of \(10^{-1}\)M also caused no change. It was concluded that complex-formation between nickel and coumarin does not occur to more than a very minor extent under these conditions, if at all.

* * * * * *

(iii). Nature of nickel-boric acid solutions.

Absorption spectra. - The absorption spectrum of the nickel ion in 0.10M nickel sulphate was determined in the presence of 0.05 and 0.25M boric acid solutions, respectively.
In neither case could any change be detected from the spectrum obtained in solutions free from boric acid.

Ion exchange. - Two exchange columns were prepared as previously described, one containing Zeo-karb 225 resin (hydrogen form), the other, De-acidite FF (chloride form).

The column containing Zeo-karb 225 was treated with a solution containing M/100 nickel nitrate and M/10 boric acid until the region of sorption of nickel ion had extended halfway down the column (green colouration). The resin was then washed with distilled water till free from impurities. It was then eluted with 1N hydrochloric acid. If the eluate contains boric acid the existence of a positively charged boric-nickel complex is signified. The presence of boric acid was sought by two methods, given by Vogel (111):

(a). A portion of the eluate was made alkaline with 2N sodium hydroxide, the precipitated nickel hydroxide was filtered off, and the filtrate re-acidified with dilute hydrochloric acid. A piece of turmeric paper was dipped into the solution and dried in an oven at 110°. If boric acid is present the paper becomes reddish-brown, and on moistening with dilute sodium hydroxide solution turns bluish- or greenish-black. The test was negative, a comparison test having been simultaneously performed on a solution known to contain boric acid.

(b). A portion of the eluate was made alkaline with 2N sodium hydroxide, the precipitated nickel hydroxide
was filtered off, and the filtrate evaporated to dryness in a porcelain crucible. The warm residue was then stirred with 2-3 drops of "Chromotrope 2B" reagent (a 0.005 per cent solution of "Chromotrope 2B" in concentrated sulphuric acid). If boric acid is present a greenish-blue colouration should be obtained on cooling, but again the test was negative.

The column containing De-acidite FF was treated with a solution containing M/10 nickel nitrate and M/100 boric acid. The extent of sorption of ions onto the column could not be followed in this case since no colouration of the resin occurred. Consequently, approximately the same volume of solution was used as had been used on the other column. The resin was then quickly washed with distilled water until free from nickel ions (dimethylglyoxime test), and was then eluted with 1N hydrochloric acid. The eluate was tested with ammoniacal dimethylglyoxime, the following results being obtained:

1st 10 ml. - no reaction
2nd 10 ml. - red precipitate
3rd 10 ml. - red precipitate
4th 10 ml. - red precipitate (fainter)
5th 10 ml. - no reaction

Thus, a small amount of nickel is present in the eluate. This can only be accounted for by assuming that it was sorbed on the resin in a negatively charged complex.

The ion-exchange results may be summarised as follows:
No evidence in favour of a positively charged boric-nickel complex was obtained. (Possibly the tests used for the detection of boric acid were not sufficiently sensitive). Evidence in favour of a negatively charged complex was obtained, however. A complex having a zero charge is not detectable by this method. The extent of complex formation, of any sort, is probably quite small, for a number of reasons. Firstly, the spectroscopic results were negative. Secondly, the amount of nickel sorbed on the anion-exchange column was insufficient to cause colouration and the amount of nickel eluted was small. Thirdly, the amount of boric acid involved in a postulated positively charged complex was insufficient for detection.

**pH titrations.** - In the introduction to this thesis doubt was cast upon the ability of boric acid to act as a buffer at around pH 5 since it behaves as a weak monobasic acid having a dissociation constant of $6 \times 10^{-10}$. It was decided to investigate the pH changes which occur when sodium hydroxide is added to solutions of boric acid containing various nickel salts. The experimental details were as follows: 50 ml. portions of the particular boric acid-nickel salt solution under investigation were pipetted into a 100 ml. beaker. The pH was adjusted to 3.0 by dropwise addition of dilute sulphuric acid. 1N sodium hydroxide was added dropwise, with constant stirring, from a 5 ml. burette graduated in 0.02 ml. divisions. Addition of each drop of sodium hydroxide
caused initial precipitation of nickel hydroxide and so it was necessary after each addition to wait for the nickel hydroxide to redissolve, i.e. to wait for the pH meter reading to come to equilibrium. This trouble could possibly have been minimised by using more dilute sodium hydroxide, but it was desired that the volume change produced by the additions should be kept as small as possible, i.e. that pH changes due to dilution of the solution should only be of minor importance. It was found that the interesting parts of the pH titration curves occurred within the first five ml. of added hydroxide solution; that is, a maximum volume change of only ten per cent. The titration curves obtained are shown in figure 57 for the addition of 1N sodium hydroxide to 50 ml. portions of the following solutions:

(a) 0.5M boric acid
(b) M nickel sulphate
(c) M nickel chloride
(d) M nickel nitrate
(e) M nickel sulphate + 0.5M boric acid
(f) M nickel chloride + 0.5M boric acid
(g) M nickel nitrate + 0.5M boric acid
(h) M nickel sulphate + 0.8M boric acid (saturated)
(i) Watts solution (0.85M nickel sulphate, 0.15M nickel chloride, 0.5M boric acid).

The titration curve for boric acid is much as would be expected. The curves for the nickel salts show buffer action between pH 6.0 - 6.5, the buffering being due to precipitation
Figure 57. pH titration curves for 50 ml portions of nickel-boric acid solutions.
of nickel hydroxide, with consequent removal of hydroxide ions from solution. The curves are influenced by the nature of the anion. Nitrate is a non-complexing anion with nickel ions (84) and so the nitrate curve should be solely due to interaction of hexaquo-nickel ions with hydroxide ions. Chloride and sulphate are both complexing anions and displace the titration curve to higher pH values. For chloride the displacement is quite small. For the titration curves of boric acid in presence of the nickel salts a marked displacement of the curves to lower pH values has occurred. Watts solution, which contains nickel mainly as the sulphate, gives a curve experimentally indistinguishable from the M nickel sulphate + 0.5M boric acid curve. For Watts solution there is little buffer action at pH 5, although the results indicate that in boric acid-nickel salt solutions an equilibrium is established which involves hydrogen ions. The nature of the equilibrium may be quite complicated as it has been shown (89) that in boric acid solutions stronger than 0.2M the following species, apart from boric acid, are present:- $\text{B}_3\text{O}_8^-$, $\text{B}_4\text{O}_7^-$ (or $\text{HB}_3\text{O}_7^-$) and monoborate $\text{H}_2\text{BO}_3^-$. The ion-exchange results have also given evidence in favour of a negatively charged nickel-boron complex.

* * * * * * *
Section VI

Summary and conclusion.
The experimental work has described the effect of coumarin on the reduction of the nickel ion in various electrolyte solutions at a dropping mercury electrode. The work was undertaken in an effort to gain information regarding the influence of coumarin on the electrodeposition of nickel on metal cathodes from a nickel plating solution of the Watts type. Although a mercury electrode, in many ways, behaves differently from a solid metal electrode certain factors are common to both and it was hoped that certain correlations could be made. In view of the experimental results it is believed that a number of facts can be justified for both mercury and solid electrodes.

The experimental results show that the phenomena which govern the levelling properties of coumarin in electroplating baths are confined to the boundary region at the electrode surface. No evidence could be obtained in favour of interaction between coumarin molecules and nickel ions, in the bulk of the solution, to form a complex compound. The levelling properties of the coumarin are probably due to adsorption of the compound at the cathode surface. There is strong evidence that adsorption occurs at a mercury cathode. Little is known of the nature of the adsorption, at the present stage, but it may well be a rapid physical adsorption requiring little activation energy, and involving weak van der Waals forces. One theory of levelling proposes that the levelling agent is preferentially adsorbed on the crests, or high parts, of an
electrode and the plating out occurs in the troughs, which are consequently filled in. Thus, the profile of the electrode surface becomes smoother. Such an explanation would be acceptable if the molecules of the addition agent were so large that they were unable to be adsorbed inside the pits of the electrode surface. In the case of coumarin, however, levelling occurs even if the surface has pits and troughs visible under a microscope. The pits must therefore be many thousands of times larger than the coumarin molecule, and it is difficult to see why levelling occurs on this comparatively macro scale. Another difficulty in this theory is that very little of the additive is incorporated in the nickel plate. To explain this it is necessary to assume that nickel ions can pass through the adsorbed additive layer without destroying its properties. It may well be that the potential of the electrode is an important factor and that the coumarin alters the potential at which the nickel is deposited. Evidence in favour of this is given by the polarographic results although it is a big step to say that a similar phenomenon is in operation at a nickel electrode.

In practical nickel plating complications arise from breakdown of the additive. There is evidence that breakdown occurs both by cathodic reduction and anodic oxidation. It was not possible to study the latter process in the present work as coumarin was found to be not oxidisable in the potential range accessible with a dropping mercury electrode (positive...
limit +0.4 volt vs. the S.C.E. in a nitrate supporting electrolyte). Coumarin is reducible at the dropping electrode and the reduction product is believed to be a mixture of dimeric isomers, namely meso and racemic tetrahydrodi-4,4'-coumarinyl. This compound is very insoluble in water and probably has a negligible influence on the plating results. In the reduction, hydroxide ions are formed which would cause precipitation of nickel hydroxide, which may well be incorporated in the nickel plate. The polarographic results also indicate the possibility of other interactions in the diffusion layer between nickel ions and coumarin reduction product, or products.

For a nickel cathode the reduction need not necessarily proceed in the same way as for the mercury cathode. However, even if the reduction does occur in a different way, it seems likely that hydroxide ions will still be produced. For example, if melilotic acid is the reduction product the net reaction, in unbuffered solution, can be formulated:

\[
\text{C}_{16}\text{H}_{10}\text{O}_2 + 2e + 3\text{H}_2\text{O} = \text{C}_{16}\text{H}_{12}\text{O}_3\text{CO}_2\text{H} + 2 \text{OH}^{-}
\]

In this case nickel hydroxide would be incorporated in the deposit as before.

It is found empirically that large concentrations of
boric acid in a plating bath greatly improve the quality of the nickel plate. It is suggested that its function is to prevent formation of nickel hydroxide which might otherwise be incorporated in the deposit. It has been shown that a plating bath of the Watts type has little buffer capacity at pH 5, but the pH in the boundary region at the electrode surface is probably higher than this due to production of hydroxide ions. If this is the case, then boric acid could have adequate buffer capacity to remove the hydroxide ions. The polarographic results are in favour of this suggestion.

The greatest objection to the conclusions here outlined is the fact that it has been attempted to assign to a nickel electrode results obtained at a mercury electrode. It is suggested that the work could be repeated, in part, using a rotating or vibrating nickel wire microelectrode. The results obtained at the dropping mercury electrode could be used as a guide for this work. Another advantage of using a nickel microelectrode is that it might be possible to study anodic oxidation of coumarin by a polarographic method. Disadvantages would be those inherent in an electrode of this type, but if the electrode is suitably calibrated it may be possible to obtain quantitative, as well as qualitative, results. Another disadvantage is that it is not possible to study adsorption phenomena at a solid electrode by electrocapillary methods.

* * * * * *
Appendices.
Appendix I

Preparation of coumarin derivatives and purification of solvents.

(i). Preparation of coumarin derivatives.

**Coumarin.** - B.D.H. coumarin was purified by recrystallisation from aqueous ethanol. It had m.p. 68-69°.

**6-aminocoumarin.** - This was prepared by the method of Morgan and Micklethwaite (112). Coumarin (100 grams) was dissolved in 120 ccs. of glacial acetic acid and treated with a mixture of 56 ccs. of fuming nitric acid (sp. gr. 1.5) and 40 ccs. of glacial acetic acid; no appreciable rise of temperature was observed, but, on adding 100 ccs. of concentrated sulphuric acid, a vigorous reaction took place; the mixture was therefore cooled at first, and finally heated for a short time on the water bath. A portion of the nitrocoumarin crystallised, and the remainder was precipitated by pouring the acid mother liquor into ice water. The nitro compound (two parts) was then suspended in 50 parts of hot water acidified with one part of concentrated sulphuric acid, and reduced by the gradual addition of 4 parts of iron filings; the mixture was finally heated on the sand-bath, rendered alkaline with sodium bicarbonate, and rapidly filtered at the pump. The filtrate, on cooling, yielded 1.2 - 1.4 parts of 6-aminocoumarin, which separated from the solution in long, olive-yellow needles. It was then crystallised once from
alcohol, and then twice from benzene, and was obtained in the
form of clear, straw-yellow needles melting at 165 - 165.5°.
(Morgan and Micklethwaite gave its m.p. as 163-4° after three
recrystallisations from benzene).

6-acetamidocoumarin. - This can be prepared by the
method of Gattermann (113) by heating 6-aminocoumarin with
acetic anhydride. When crystallised from water it formed
slightly brownish crystals, m.p. 216-7°.

6-sulphamylcoumarin. - This was prepared by the method
of Rubtsov and Fedosova (114). 10 grams of coumarin were
added, with cooling, to 40 grams of chlorosulphonic acid. The
mixture was then heated to 100° for four hours, cooled, and
poured on ice, to yield 10 grams of 6-chlorosulphonylcoumarin.
Treatment of this with a 15 per cent ammonia solution at 35°
gave 6-sulphamylcoumarin, m.p. 186-7°, after two
recrystallisations from water. (Rubtsov and Fedosova gave its
m.p. as 189°).

* * * * * *

(ii). Purification of solvents.

Dioxane. - The method used was that of Eigenberger (115).  
B.D.H. "Laboratory Reagent" dioxane was refluxed for 8 hours
in a stream of nitrogen with 12 per cent of its volume of N
hydrochloric acid acid to hydrolyse any glycol acetal present.
It was then allowed to stand over solid potassium hydroxide
to remove hydrochloric acid and water. The separated
supernatant dioxane was refluxed with sodium metal for 24
hours when the latter remained as bright balls without further action. The dioxane was then distilled off, fractionally frozen twice, again refluxed with sodium until the latter remained bright (about 5 hours) and fractionated. Owing to its very hygroscopic nature it was stored in special vessels fitted with protector caps, containing phosphorus pentoxide.

**Benzene.** - B.D.H. "Analar" benzene was shaken with several portions of concentrated sulphuric acid, washed with water, 10 per cent sodium hydroxide solution, water, and dried over calcium chloride. It was fractionally frozen until a glassy mass was obtained, as distinct from feathery crystals. It was finally dried over two portions of phosphorus pentoxide and fractionated from fresh phosphorus pentoxide.

**Carbon disulphide.** - B.D.H. "Analar" carbon disulphide was shaken with solid potassium permanganate for 16 hours, and then with pure mercury for 6 hours. It was then distilled off, leaving a little black residue, and again shaken for 6 hours with mercury. No further blackening occurred and it was then shaken for 3 hours with mercuric sulphate. It was dried with phosphorus pentoxide and fractionated from fresh phosphorus pentoxide.
Appendix II

Derivation of some of the mathematical relationships given in section II.

(i). Derivation of equation (28).

The fundamental differential equation for diffusion to the dropping mercury electrode has been given by equation (27), namely

\[ \frac{\partial C(r,t)}{\partial t} = D \left( \frac{4}{3} \left( \frac{\partial^2 C(r,t)}{\partial \epsilon^2} - 2 \frac{\partial C(r,t)}{\partial \epsilon} \right) \right) \quad \ldots \quad (A-1) \]

It is required to obtain a solution to this equation for the initial and boundary conditions:

\[ C(r,0) = C \]
\[ C(r_0, t) = 0 \quad \text{for} \quad t > 0 \]
\[ C(r, t) \rightarrow C \quad \text{as} \quad r \rightarrow \infty \]

It is convenient to perform a substitution of variables to simplify the algebra. The necessary substitutions are

\[ x = \epsilon^3 \quad \text{and} \quad y = t^{4/3} \]

Thus

\[ \frac{dx}{d\epsilon} = 3\epsilon^2 \quad \text{and} \quad \frac{dy}{dt} = \frac{7}{3} t^{4/3} \]

also

\[ \frac{d^2 x}{d\epsilon^2} = 6\epsilon \]

In terms of these new variables

\[ \frac{\partial C(r,t)}{\partial t} = \frac{\partial C(r,t)}{\partial y} \cdot \frac{dy}{dt} = \frac{7}{3} t^{4/3} \cdot \frac{\partial C(r,t)}{\partial y} \quad \ldots \quad (A-2) \]
\[
\frac{\partial C(r, t)}{\partial \xi} = \frac{\partial C(r, t)}{\partial x} \frac{dx}{d\xi} = 3\xi^2 \frac{\partial C(r, t)}{\partial x} \quad \ldots \ldots \quad (A-3)
\]

\[
\frac{\partial^2 C(r, t)}{\partial \xi^2} = \frac{\partial C(r, t)}{\partial x} \frac{d^2 x}{d\xi^2} + \frac{\partial^2 C(r, t)}{\partial x^2} \left( \frac{dx}{d\xi} \right)^2
\]

\[
= 6\xi \frac{\partial C(r, t)}{\partial x} + 9\xi^4 \frac{\partial^2 C(r, t)}{\partial x^2} \quad \ldots \ldots \quad (A-4)
\]

Substituting equations (A-2, A-3, and A-4) into (A-1) and simplifying gives

\[
\frac{\partial C(r, t)}{\partial \gamma} = \frac{27}{7} \gamma^{4/3} \frac{D}{\partial x} \frac{\partial^2 C(r, t)}{\partial x^2} = m \frac{\partial^2 C(r, t)}{\partial x^2} \quad \ldots \quad (A-5)
\]

where

\[
m = \frac{27}{7} \gamma^{4/3} D \quad \ldots \ldots \quad (A-6)
\]

A solution of equation (A-5) is

\[
C(r_0, t) = K + B \int_0^{x/(2\sqrt{m\gamma})} \exp(-q^2) \, dq \quad \ldots \quad (A-7)
\]

where \(K\) and \(B\) are constants and \(q\) is an integration variable.

The value of the integral in this equation is not a function of \(q\) but depends only on the numerical value of the upper limit. Values of this function, which is known as the "error function", have been given in Table 1 (p. 42).

The constants \(K\) and \(B\) can be evaluated by a consideration of the initial and boundary conditions. When \(t > 0\), \(C = 0\) at the electrode surface, and since \(x = \xi^3\) then \(x = 0\). Hence, when \(t > 0\) the value of the integral in equation (A-7) becomes zero (see Table 1). Since \(C(r_0, t)\) is also equal to zero when \(t > 0\) then \(K\) is also zero. On the other hand, when \(t = 0\), since
\( y = t^{7/3} \), the upper limit of the integral becomes infinity, and the value of the error function becomes equal to unity (see Table 1). Since \( C(C_0, 0) = C \), it follows that the constant \( B \) is simply equal to \( C \). Hence, equation (A-7) becomes

\[
C(r_0, t) = \frac{2C}{\pi^{3/2}} \int_0^{x/(2\sqrt{my})} \exp(-q^2) dq \quad \ldots \ldots \quad (A-8)
\]

Since \( x = \frac{3}{2} \), and \( m = \frac{27}{7} \sqrt[4]{3D} \),

\[
\frac{x}{2\sqrt{my}} = \frac{1}{6} \sqrt{\frac{27}{3D}} \cdot \frac{3^2}{(8t)^{1/6}} = s \quad \ldots \ldots \quad (A-9)
\]

and hence, equation (A-7) may be written

\[
C(r_0, t) = \frac{2C}{\pi^{3/2}} \int_0^s \exp(-q^2) dq \quad \ldots \ldots \quad (A-10)
\]

which is the required result.

(ii). Derivation of equation (103).

It is required to find an expression for the value of \( \frac{d}{dt} \log \left( \frac{1}{1 - \Phi(x)} \right) \). From equation (100) this is given by

\[
\frac{d}{dt} \log \left( \frac{1}{1 - \Phi(x)} \right) = \log e \cdot \frac{d}{dx} \ln \left( \frac{\Phi(x)}{1 - \Phi(x)} \right) \quad \ldots \quad (A-11)
\]

Now

\[
\frac{d}{dx} \ln \left( \frac{\Phi(x)}{1 - \Phi(x)} \right) = \frac{d\Phi(x)}{dx} \cdot \frac{d}{dx} \Phi(x) \left\{ \ln \Phi(x) - \ln (1 - \Phi(x)) \right\}
\]

\[= \frac{d\Phi(x)}{dx} \cdot \Phi(x) \frac{1}{1 - \Phi(x)} \]

\[= \frac{d\Phi(x)}{dx} \cdot \Phi(x) \frac{dx}{d\Phi(x)} \cdot \Phi(x) \frac{1}{1 - \Phi(x)} \quad \ldots \quad (A-12)
\]
Also, from equation (100)

\[
\frac{d\Theta(X)}{dX} = \pi^{\frac{1}{2}} \left\{ \exp(X^2) \text{erfc}(X) + 2X^2 \exp(X^2) \text{erfc}(X) + \right.
\]

\[
\left. X \exp(X^2) \frac{d}{dX} \text{erfc}(X) \right\} \ldots \ldots \ldots (A-13)
\]

\[
\frac{d}{dX} \text{erfc}(X) = \frac{d}{dX} \left\{ 1 - \frac{2}{\pi^{\frac{1}{2}}} \int_0^X \exp(-y^2) \, dy \right\}
\]

\[
= -\frac{2}{\pi^{\frac{1}{2}}} \exp(-X^2) \ldots \ldots \ldots \ldots (A-14)
\]

Therefore

\[
\frac{d\Theta(X)}{dX} = \pi^{\frac{1}{2}} X \exp(X^2) \text{erfc}(X) \left\{ \frac{1}{X} + 2X - \frac{2}{\pi^{\frac{1}{2}} \exp(X^2) \text{erfc}(X)} \right\}
\]

\[
= \Theta(X) \left\{ \frac{1}{X} + 2X - \frac{2X}{\Theta(X)} \right\} \ldots \ldots \ldots \ldots (A-15)
\]

From equation (102)

\[
\frac{1}{X} \frac{dX}{dE} = -\frac{\alpha n_a F}{RT} \ldots \ldots \ldots \ldots \ldots (A-16)
\]

Combining equations (A-11, A-12, A-15, and A-16) we have

\[
\frac{d}{dE} \log \frac{1}{1-d-1} = -\frac{\alpha n_a F}{RT} \log e \left\{ \frac{1}{1-\Theta(X)} - \frac{2X^2}{\Theta(X)} \right\}
\]

\[
\ldots \ldots \ldots \ldots (A-17)
\]

which is the desired result.

(iii). Limits of equation (103).

It is required to evaluate \( \left\{ \frac{1}{1-\Theta(X)} - \frac{2X^2}{\Theta(X)} \right\} \)

for limiting values of \( X \).

As \( X \to 0, \Theta(X) \to 0 \) (see Table 3, p.66)

Now

\[
\frac{X^2}{\Theta(X)} = \frac{X}{\pi^{\frac{1}{2}} \exp(X^2) \text{erfc}(X)} \ldots \ldots \ldots \ldots (A-18)
\]
As \( X \to 0 \), \( \exp(X^2) \to 1 \), \( \text{erf}(X) \to 0 \) (Table 1, p.42), so that \( \text{erfc}(X) \to 1 \).

Therefore
\[
\left\{ \frac{1}{1 - \Theta(X)} - \frac{2x^2}{\Theta(X)} \right\} \bigg|_{X \to 0} = 1 \quad \ldots \ldots (A-19)
\]

From equation (80), for values of \( X \) greater than unity,
\[
\Theta(X) = \left\{ 1 - \frac{1}{2x^2} + \frac{1x3}{(2x^2)^2} - \frac{1x3x5}{(2x^2)^3} + \ldots \right\}
\]

Thus
\[
\left\{ \frac{1}{1 - \Theta(X)} - \frac{2x^2}{\Theta(X)} \right\} = \\
\left\{ 1 - \frac{1}{2x^2} + \frac{1x3}{(2x^2)^2} - \frac{1x3x5}{(2x^2)^3} + \ldots \right\} - 2x^2 \left\{ \frac{1}{2x^2} - \frac{1x3}{(2x^2)^2} + \frac{1x3x5}{(2x^2)^3} \right\} = \\
\left\{ 1 - \frac{1}{2x^2} + \frac{1x3}{(2x^2)^2} + \ldots \right\} \left\{ \frac{1}{2x^2} - \frac{1x3}{(2x^2)^2} + \ldots \right\} = \\
\ldots \ldots (A-20)
\]

Multiplying top and bottom of the R.H.S. of this equation by \( 2x^2 \), we obtain
\[
\left\{ \frac{1}{1 - \Theta(X)} - \frac{2x^2}{\Theta(X)} \right\} = \\
2x^2 \left\{ \frac{1}{2x^2} + \frac{3}{2x^2} + \frac{3}{(2x^2)^2} - (1 + 2x^2) \frac{1x3x5}{(2x^2)^3} - \ldots \right\} = \\
\left\{ 1 - \frac{1}{2x^2} + \frac{1x3}{(2x^2)^2} + \ldots \right\} \left\{ 1 - \frac{1x3}{2x^2} + \ldots \right\} = \\
2 + \frac{3}{2x^2} - (1 + 2x^2) \left\{ \frac{1x3x5}{(2x^2)^3} \ldots \right\} = \\
\left\{ 1 - \frac{1}{2x^2} + \frac{1x3}{(2x^2)^2} \ldots \right\} \left\{ 1 - \frac{3}{2x^2} \ldots \right\} = \\
\ldots \ldots (A-21)
\]

which equals 2, for large values of \( X \).
Therefore,
\[
\left\{ \frac{1}{1 - \Theta(X)} - \frac{2X^2}{\Theta(X)} \right\} \xrightarrow{X \to \infty} = 2 \quad \ldots \ldots \ldots \ldots (A-22)
\]

Thus, the value of \( \left\{ \frac{1}{1 - \Theta(X)} - \frac{2X^2}{\Theta(X)} \right\} \) approaches unity as \( X \) becomes small, and approaches 2 as \( X \) becomes very large.

(iii). *Derivation of equations (106) and (107).*

It is first of all required to find an expression for the value of \( \frac{d}{d\theta} \log \frac{\Gamma}{\Gamma_d} \).

This is given by
\[
\frac{d}{d\theta} \log \frac{\Gamma}{\Gamma_d} = \log e \cdot \frac{d}{d\theta} \ln \frac{\varphi(H)}{1 - \varphi(H)} \quad \ldots \ldots \ldots (A-23)
\]

From equations (86), (87), (44) and (94) it is seen that
\[
\varphi(H) = \frac{\Gamma}{\Gamma_d} = \frac{\tau^{1/2}}{\pi^{1/2}} \gamma_{k_f, h} \frac{1}{\sqrt{D_0 - \frac{1}{2}}} \exp\left(k_f^2, h \tau D_0^{-1}\right) \text{erfc}\left(k_f, h \tau D_0^{-1/2}\right) \quad \ldots \ldots (A-24)
\]

For \( t = \tau \), from equation (99), we also have
\[
\Theta(H) = \frac{1}{\Gamma_d} = \tau^{1/2} k_f, h \frac{1}{\sqrt{D_0 - \frac{1}{2}}} \exp\left(k_f^2, h \tau D_0^{-1}\right) \text{erfc}\left(k_f, h \tau D_0^{-1/2}\right) \quad \ldots \ldots (A-25)
\]

and so
\[
\varphi(H) = \frac{7}{6} \gamma \cdot \Theta(H) \quad \ldots \ldots \ldots \ldots (A-26)
\]

Thus, equation (A-23) becomes
\[
\frac{d}{d\Theta} \log \frac{\Gamma}{\Gamma_d} = \log e \cdot \frac{d\Theta(H)}{dH} \cdot \frac{dH}{d\Theta} \cdot \ln \frac{\Theta(H)}{\frac{7}{6} \gamma - \Theta(H)} \quad \ldots \ldots (A-27)
\]

Now
\[
\frac{d}{d\Theta(H)} \ln \frac{\Theta(H)}{\frac{7}{6} \gamma - \Theta(H)} = \frac{1}{\Theta(H) \left(1 - \frac{7}{6} \gamma \cdot \Theta(H)\right)}
\]
Thus, from equations (A-27) and (A-28), and using equations (A-15) and (A-16) (with $X = H$), we have

$$\frac{d}{dE} \log \frac{I}{I_0} = -\frac{\alpha n_a F \log e}{RT} \left\{ \frac{\Theta(H) - H^2 (1 - \Theta(H))}{\Theta(H)(1 - \Theta(H))} \right\}$$

$$\ldots \ldots \ldots (A-29)$$

The limiting values of this expression may now be obtained. At the foot of the wave, as $H \to 0$, $\Theta(H) \to 0$ and $\Theta(H) \to 0$ (see Table 3). Thus

$$\lim_{H \to 0} \left\{ \frac{d}{dE} \log \frac{I}{I_0} \right\} = -\frac{\alpha n_a F \log e}{RT} \left\{ \frac{1 - \frac{H^2}{\Theta(H)}}{\Theta(H)} \right\} \ldots (A-30)$$

It has already been shown that $\lim_{H \to 0} \frac{H^2}{\Theta(H)} = 0$. Hence

$$\lim_{H \to 0} \left\{ \frac{d}{dE} \log \frac{I}{I_0} \right\} = -\frac{\alpha n_a F \log e}{RT} \ldots (A-31)$$

At the head of the wave, $\Theta(H) \to \Theta(H)$ and so equation (A-29) becomes identical to equation (A-17) and the value of the upper limit becomes $-2\alpha n_a F \log e / RT$.

Thus,

$$\lim_{H \to \infty} \left\{ \frac{d}{dE} \log \frac{I}{I_0} \right\} = -\frac{2\alpha n_a F \log e}{RT} \ldots (A-32)$$

Equations (A-31) and (A-32) are the desired results.

* * * * * *
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