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PART I.

THE MEASUREMENT OF THE POTENTIAL OF THE ELECTRODES IN STATIONARY LIQUIDS. THE DETERMINATION OF CHANGES OF CONCENTRA- TION AT THE CATHODE DURING ELECTROLYSIS.

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MOLLWO PERKIN in the Chair.*)

In recent electrochemical investigations accurate data are, as a rule, to be found regarding current-density, voltage, temperature, and concentration of liquid taken, and very often also regarding the potential of one of the electrodes, defined as the drop of potential on the boundary between it and the electrolyte. The actual concentration of the electrolyte in contact with the electrode is, however, very often uncertain, owing to the removal of substance by electrolysis. Some years ago I was able to demonstrate the great importance of this factor in connection with the electrolysis of acid solutions of copper sulphate.* When small current-densities were employed in a stationary solution, it was possible to show with a fair amount of accuracy that evolution of hydrogen only took place after the complete removal of copper salt from the liquid in contact with the electrode. On the other hand, when large current-densities were employed, this local depletion took place so rapidly that even the most vigorous stirring could not prevent it. The result obtained in this research could be predicted theoretically when the assumption was made that the process occurring at the electrode itself was of a reversible nature; that is, that on the boundary between electrode and electrolyte, chemical equilibrium must be supposed to remain continually established. The matter may also be stated in the following manner corre-

* *Phil. Mag.*, 6th Series, i. 45.

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sponding to a form in which it has recently been put forward by Nernst* as a general principle : differences of chemical potential cannot exist for a finite period of time on the boundary of two phases, that is " between infinitely near points," as this would lead to infinitely great forces and reaction velocities. According to this assumption the actual velocities of electrochemical reactions, and of all others which occur on the boundary of two phases, are infinitely great as soon as conditions of equilibrium have been overstepped by a finite amount, the observed velocities being simply limited by the rate with which diffusion and convection renew the material removed by the reaction. As conditions of equilibrium in electrochemical reactions are determined by the electrode-potential, by which name I propose to indicate the drop of electromotive force on the boundary between electrode and electrolyte, and the rate of these reactions is proportional to the current strength, this may be expressed in the following manner : " When the electrode-potential at which a reaction begins has been exceeded by a finite amount, the current strength becomes independent of it, being only limited by the velocity of convection and diffusion. The instance just referred to of the deposition of copper conforms to this rule, for it seems very probable that when a sufficient drop of potential is maintained on the boundary between electrode and electrolyte, the rate of deposition of copper only depends on the rate of renewal of the metal-salt at the electrode. Examples of a similar kind have been studied by Brunner,† viz., the rate of reduction of iodine to hydriodic acid with definite cathode-potentials and the rate of liberation of hydrogen from weak solutions of acids under similar conditions.

As has already been indicated, Nernst and Brunner are plainly of opinion that all cases of electrochemical action may be ultimately considered from the same point of view. It is not the object of the present paper to enter very fully into a thermodynamical discussion of the principle involved. It will suffice to point out that the latter seems sufficiently invalidated for *à priori* application to actual cases owing to the impossibility of stating that the atoms chemically reacting on the boundary of two phases are in infinite proximity.‡ In fact the results of several recent researches, notably those of Haber,§ stand in opposition to conclusions drawn from the principle under discussion. The object of all these researches is the investigation of the dependence of electrode-potential as defined above on current-density. In Haber's work the reduction of nitrobenzene is examined but instead of finding the current-density to be independent of the potential of the cathode, his results point to a logarithmic dependence of the latter on the former. In fact he has partially explained his results, starting from the not improbable assumption that the variations of potential are brought about by the absorption in varying concentrations of hydrogen, or other reducing material, by the electrode. In the further elaboration of this view his results may all be foretold if we adopt as an empirical fact that the velocity of reduction at the electrode v depends on the concentration of hydrogen c in it according to the relation—

$$v = \kappa c^\gamma$$

in which κ and γ are constants depending on the conditions of the experiments. In contradiction to this, as will be understood from what has already

* *Ztschft. Phys. Chem.* xlvii. 52 (1904).

† *Ztschft. Phys. Chem.* xlvii. 56 (1904).

‡ Nernst himself points out that the boundary of two phases is not to be considered mathematically discontinuous, but apparently attaches little importance to this fact.

§ *Ztschft. Phys. Chem.* xxxii. 193 (1900), also Russ, *Ztschft. Phys. Chem.* div. 641 (1903).

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been said, Nernst's view would require that once the conditions of equilibrium have been overstepped, the above velocity should be infinitely great. As a matter of fact, Haber's results have been doubted by Brunner, who believes that changes of concentration in the liquid adjoining the electrode may be partly responsible for them. To this Haber and Russ have replied, stating reasons for the correctness of the results obtained by the former.* In view of the fact that the investigation of the dependence of electrode-potentials on current-density seems one of the most important problems of contemporary electrochemical research, it appears very desirable to have independent methods for the determination of the rate at which changes of concentration occur in the layer of electrolyte adjoining the electrode.

When the diffusion coefficients required for calculating these changes of concentration are not known, it would seem that the most reliable method for arriving at an estimation of their rapidity is afforded by the investigation of the behaviour of stationary liquids free from convection currents. This was the method adopted by me for the examination of copper solutions. When hydrogen began to be evolved owing to complete depletion of the copper-salt at the electrode, a sudden, very large fall of cathode-potential took place, which caused a corresponding increase of voltage between the two electrodes that could be easily observed. This method is only applicable where very sharp breaks of potential occur, and the anode is not polarisable in the liquid employed. Another method has since been described by Cottrell.† In it a constant E.M.F. is maintained between the electrodes; the current, however, must remain so minute, or the resistance of the electrolyte be so small, that practically no E.M.F. is required to overcome it according to Ohm's law.

It is the object of the present paper to describe a method which will allow the electrode-potential in stationary liquids of the most varying kind to be measured, when very much larger currents are employed, than those which can be made use of according to Cottrell's method, and at the same time to indicate the nature and the scope of the conclusions that can be drawn from the results obtained.

DESCRIPTION OF APPARATUS AND ELECTRICAL ARRANGEMENTS.

It was necessary that the apparatus should fulfil the following conditions :

- (1) The electrode under examination must be placed horizontally either at the top or at the bottom of the apparatus. It should be readily interchangeable and accessible to observation during an experiment, and allow the current to have uniform density.
- (2) The electrode not under examination should be as non-polarisable as possible, and no gases must be evolved which might stir the liquid.
- (3) The difference of potential between the electrode and the layer of electrolyte in contact with it must be capable of continuous measurement during the course of an experiment.
- (4) It was found desirable to have the apparatus arranged so that several successive determinations could be carried out without taking it to pieces.

Figs. 1 and 2 serve to illustrate the apparatus that was designed to meet these requirements. For the sake of brevity we shall call the electrode under observation the cathode, the other electrode through which the working current enters or leaves the liquid the anode, although there is no reason why

* *Ztschft. Phys. Chem.* xlvii. 260 (1904).

† *Ztschft. Phys. Chem.* xlii. 385 (1903).

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Fig 1.

Fig. 2.

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our cathode should not be used as anode and *vice versa*. Making use of these abbreviations, Fig. 1 shows the apparatus with the cathode at the top, that is for liquids that become specifically lighter during electrolysis. In Fig. 2 the cathode is at the bottom as used for liquids that become specifically heavier during electrolysis. The positions of the anode are indicated in both figures by A. The current passes up the wide tube B, and then enters the long straight tube C of about 1 cm. bore. The cathode is approached through a hole D in the glass plate D, as shown in Fig. 1. The electromotive force between the cathode and the part of the electrolyte on the other side of the glass plate D is determined, a liquid connection being tapped off here through the annular space E and the tubes F to the non-polarisable standard electrode G. We shall indicate by T the place in the electrolyte between the glass plate D and the tube C, where the liquid connection is tapped off to the potentiometer. The electromotive force actually measured on the potentiometer is that between the cathode and the standard electrode, and this is composed of the following parts :—

Fig. 3.

(1) The drop of electromotive force due to polarisation between the cathode and the layer of liquid in contact with it.

(2) The difference of potential between the cathode and T calculated according to Ohm's law as the product of the resistance between the two and the current strength.

(3) Any small electromotive force brought about by contact of the electrolyte examined with the decinormal potassium chloride solution of the standard electrode.

(4) The constant E.M.F. of the standard electrode.

The first of these quantities is the one which it is desired to measure, the third was always assumed to be zero, as has been done by other investigators. The fourth may be taken according to Ostwald and Wilmore to be 0.615 volts for the standard so-called decinormal electrode composed of mercury in contact with a decinormal solution of potassium chloride saturated with mercurous chloride. Being constant for all experiments it need, however, not be taken into consideration. The second difference of potential mentioned, may as a rule be calculated when the specific

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resistance of the electrolyte is known. It is better, however, actually to determine the resistance between the cathode and T during the course of an experiment, more especially when there is a possibility of an increase of resistance at the electrode, owing to the formation of badly conducting deposits, gas-bubbles, etc. The electrical method required for this purpose had to be devised in such a manner that no false connections should be introduced and that it should at the same time be independent of the polarisation of the electrode. As far as I am aware the only method suitable for this purpose is one described several years ago by Nernst and Haagen.* It consists of a modification of the Wheatstone-bridge method for alternating currents, two resistances being replaced by standard condensers, and rough condensers being interposed wherever a false connection would otherwise be made. Its application to the present case is shown diagrammatically in Fig. 3. The two resistances compared are the resistance from the anode to T, and the resistance from T to the cathode, plus a known variable resistance M. These formed two arms of the Wheatstone bridge, the other two being the standard condensers A and B, Fig. 3. A special box was made up for this determination containing capacities varying from one-thousandth of a microfarad to half a microfarad. In order to form the bridge containing the telephone between the junction of the two condensers and T, a second auxiliary electrode P is required in the liquid contained in the annular space E, Fig. 1. It was found that an electrode of ordinary smooth platinum answered perfectly well for this purpose. The current for these measurements was derived from a small induction coil, a rough condenser being interposed between it and one of the junctions. The method of working consisted in giving the two standard condensers A and B suitable values, say 500 and 20 millemicrofarads, and finding the value m_1 of the variable resistance M taken from a dial-resistance-box that produced a minimum in the telephone. The smaller of the two condensers, B, *i.e.* the one on the anode side, was then altered to its r -fold value $20r$ millemicrofarads, the other condenser being left unaltered. The new resistance m_2 , which produced a minimum in the telephone, was now determined. The required resistance x from the cathode to T is then manifestly derived from the equation—

$$\frac{x + m_1}{x + m_2} = \frac{1}{r},$$

its value being

$$x = \frac{m_2 - r m_1}{r - 1}.$$

The following are details of the apparatus shown in Figs. 1 and 2 that must be specially referred to. The cathode and the glass plate it rests on are both ground perfectly flat. The latter is rectangular in shape, and the edges of the hole D, drilled in it, are perfectly even and free from chips. The plate is put in position in such a manner that the hole D exactly forms the continuation of the tube C; the way in which it is held on the flanged glass cylinder H and the electrode pressed against it by the specially designed clamp K will be understood from the Figs. 1 and 2, as also the manner in which electrical connection is made by means of thin copper foil bent round the rubber washer w (Fig. 2). Practically no leakage took place between the electrode and the glass plate, even when no grease was

* *Zeitschft. Phys. Chem.*, xxiii. 97.

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employed to make a joint. Nevertheless, a small amount of liquid always creeps up, and this seems to give rise to convection currents owing to evaporation, more especially when alcoholic solutions are employed. A very small amount of vaseline thickened with a little paraffin-wax was therefore spread round the edge of the electrode before it was placed in position. In order to guard against its being accidentally moved backwards and forwards over the plate, which would have caused the grease to spread over its surface, a cardboard ring *c* was fixed on the glass plate by means of paraffin-wax, and the electrode rotated inside this ring to place it in position. The electrode could easily be levelled both when used as in Fig. 1 and as in Fig. 2, by placing a small spirit-level on the glass plate (Fig. 2); the retort-stand, to which the apparatus was attached, being fixed on a levelling stand.

The tube *C*, the end of which was bevelled, was fixed centrally in the flanged cylinder *H*, and was held firmly in position with regard to the latter, not only by the rubber bung *L*, but also by means of the two clamps *M*₁ and *M*₂ (Fig. 2), both of which are fastened to a common short rod *n*. The clamp *M*₁ at the same time serves to support the apparatus on its retort-stand. The tube *C* ends about $\frac{1}{2}$ mm. below the glass plate, thus allowing sufficient room for a liquid connection between the auxiliary electrodes and the liquid through which the working current is passing.

The two auxiliary electrodes have already been referred to. The place where the junction between the electrolyte examined and the decinormal solution of KCl of the standard electrode is made, is indicated in both figures by *J*. The method of filling the tubes *P* and *O* and keeping the liquid in them by means of cotton-wool plugs before placing the tubes in position will need no further explanation.

Considerable difficulty was at first experienced in arranging the anode to satisfy condition 2 (p. 3). The method finally adopted consisted in the employment of electrodes of either copper or mercury, the electrolyte under examination being displaced in the vicinity of the electrode by a solution of metal-salt which was run in slowly through the capillary tap-funnel *U* (Figs. 1 and 2). The displaced electrolyte was generally removed through the tube *W* (Fig. 1). The anode solution, employed in conjunction with the copper electrode, when the electrolyte was an acid alcoholic solution, consisted of cuprous chloride dissolved in a mixture of alcohol and hydrochloric acid. When the electrolyte was an alkaline solution containing alcohol, and also in some experiments on alcoholic acid solutions, a mercury electrode was employed in contact with a solution of mercurous nitrate and a little nitric acid. As the latter, however, as a rule, produced a precipitate in contact with the electrolyte under examination, a solution of ammonium nitrate was interposed. The liquids in this case were run under the electrolyte in the following sequence: (1) ammonium nitrate solution; (2) mercurous nitrate solution; (3) mercury.

The requirement that the apparatus should allow several successive determinations to be performed without taking it to pieces, was only met satisfactorily when the cathode was at the top, as in Fig. 1. For this purpose it was necessary to renew the liquid at the cathode by stirring, without at the same time causing anode solution to come into the cathode compartment. As will be seen from Fig. 1, the rubber tube *R* with screw clips *YY* and the glass side-tube *S* were therefore introduced between the tubes *B* and *C*. The method of using them was the following: When a determination was finished, the side-tube *S*, which was generally left open during the experiment, was closed, about 5 cc. of air being left in it. The standard electrode was then removed

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by undoing the connection at J, and a rubber stopper with a tap-funnel-introduced in its place. The screw clips YY were then closed. A considerable amount of electrolyte was thus forced out of the rubber tube R, and was allowed to escape through one of the taps. The top part of the apparatus was then taken from the retort-stand and moved up and down, the rubber tube R being used as a hinge. Air-bubbles from the side-tube S could thus be admitted to stir the liquid and afterwards be returned to the tube S. When it was necessary to leave the apparatus overnight the anode solution was removed through the tube *u* of the tap-funnel U; being replaced by electrolyte run in through the funnel introduced at J. It was thus found possible to keep the cathode compartment perfectly free from anode solution, even when experiments were spread out over several days. The apparatus was also used

Fig 4

for single experiments, without the rather troublesome arrangements allowing a repetition.

For the purpose of filling the apparatus as illustrated in Fig. 1, both the funnels U and V must be employed, the top being inverted for filling the upper part through the funnel V. A vent-hole with tap (not shown in the figure) allows the air to escape through the bung L. The last air-bubbles are removed from the cathode through the side-tube S. When in use the apparatus was placed on a non-vibrating shelf.

The electrical arrangements are shown completely in Fig. 4. They comprise the main circuit, the condenser-bridge circuit already explained on p. 6, and the potentiometer circuit. The current was derived from a battery of small accumulators A, and was kept perfectly constant by variation within suitable limits of the original electromotive force employed as shown at B, Fig. 4. It passed through a known constant resistance C, then through a dial-box, provided for the purpose of introducing when required the resis-

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tance M referred to on p. 7. As a rule this box was however kept free from resistance. After this the current passed through the electrolytic cell E and finally through a rough resistance F of about the same magnitude as the latter.

For the purpose of determining the current-strength and the cathode-potential, the voltage between the ends γ and γ_2 of the known resistance C, and between g_2 and the standard auxiliary electrode, were measured on the same potentiometer circuit. The latter was composed primarily of a slidewire with a variable back resistance. As several points of the potentiometer had to be tapped simultaneously during an experiment, a system of wires along which mercury cups could be moved was arranged in parallel with the slidewire, and the required potentials tapped off from these mercury cups, the electrical position of the latter relative to points of the slidewire being arranged by separate determinations before an experiment.

The following manipulations and measurements were carried out during an experiment. The current was kept constant at a known value, the potentiometer regulated by occasional comparison with a Clark cell, and the resistance between the cathode and T measured now and again as explained on pp. 6 and 7. At the same time the cathode-potential had to be determined by measurement of the E.M.F. between γ_2 and the standard auxiliary electrode, and the time had to be read. In order to facilitate the last two determinations a chronograph was designed, which contained a slidewire that was shunted parallel to part of the potentiometer circuit. The slider on the latter was moved by hand so as to balance the difference of potential to be measured; its position, however, was automatically recorded on curve-paper moved past it by means of a drum rotated by clockwork.

With regard to the already explained measurement of the resistance from the cathode to T by means of the condenser-bridge circuit, it must be pointed out firstly that a false connection is introduced unless the galvanometer G, for measuring the current, is thrown out of circuit during a determination, and secondly that the rough resistance F is required in the main circuit on account of this measurement in order to prevent the greater part of the current from the induction coil from finding its way through the battery instead of through the electrolytic cell. The resistance taken from the dial resistance-box must be so small, that its effect on the current during the fraction of a minute it is in circuit, need not be considered.

All the points of the various circuits that were ever interchanged were connected by special wires to a central switchboard of mercury cups on which all the connections were conveniently and rapidly made. All such points are indicated in the figure by xx , other switches being indicated by S.

RESULTS OBTAINED WITH AQUEOUS SOLUTIONS OF COPPER SULPHATE, SILVER NITRATE AND ZINC SULPHATE.

The first series of experiments we have to refer to is one carried out with aqueous solutions of metal salts, the substances employed being solutions of copper sulphate, silver nitrate and zinc sulphate. As long as metal-salt is left in the layer of liquid touching the cathode, the metal is deposited from such solutions at a cathode-potential, probably either identical with or differing only slightly from the potential at which it is in equilibrium with the solution of its salt. But when the salt has been removed from the electrode by the current, a sudden drop of the potential of the electrode takes place. A marked difference is however observed in this connection between solutions of copper sulphate and silver nitrate. In the case of the former the cathode-potential

Fig. 5.
Aqueous Solutions of Silver Nitrate and Copper Sulphate.
Abscissae: Difference of Potential between Standard Electrode and Cathode.
Ordinates: Time.

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drops about one volt, and then becomes fairly constant again. At the same time the resistance of the layer of liquid around the cathode increases by about 175 ohms per sq. cm., the combined effect being that the difference of potential between the standard electrode and the cathode, as measured in the experiments, increases by 1.2 to 1.3 volts above its original value. The increase of resistance is found to be due to the formation of a deposit of copper hydroxide arising from hydrolysis of the copper sulphate at great dilutions. In the case of the silver nitrate, however, when depletion of the silver occurs a drop of the potential of the cathode amounting to only about 0.2 volt takes place, after which the potential approaches its former value again more or less rapidly. The cathode is then found to have become covered with a mass of silver crystals which grow into the solution. The curves in Fig. 5 show results obtained with a silver nitrate, and with a copper sulphate solution. As has been shown in the previous communication referred to, the diffusion coefficient of the salts experimented on may be calculated when the time is known which elapses until the concentration of the salt in the layer of liquid at the electrode becomes zero, and this time may be taken as that at which the break in the curve takes place. The actual points chosen on this break were 5 centivolts in the case of the silver nitrate, and 50 centivolts in the case of the copper sulphate solutions. The formula employed is—

$$k = \frac{1.1284^2}{96540^2} \frac{i^2 t n_a^2}{c^2}$$

k being the diffusion coefficient of the salt in $\frac{\text{cm.}^2}{\text{sec.}}$, when c is the concentration of the solution in $\frac{\text{mg.-equiv.}}{\text{cm.}^3}$, i the current strength in $\frac{\text{milamps.}}{\text{cm.}^2}$, t the time in seconds, and n_a the transport value of the anion. Details of the experiments and results are arranged in the following table.

TABLE I.

A. Copper sulphate solution concentration 0.204 $\frac{\text{mg.-equiv.}}{\text{cc.}}$. Electrode : Platinum-iridium of available surface 0.7589 cm.² $n_a = 0.63$.

Current-density in $\frac{\text{milamps.}}{\text{cm.}^2}$	Time in Seconds.	Temperature T in °C.	Diffusion Coefficient at T° in $\frac{\text{cm.}^2}{\text{sec.}}$	Diffusion Coefficient at 18° by Formula $k_{18} = \frac{k\tau}{1 + 0.026(T - 18)}$
2.109	790	15½	4.58×10^{-6}	4.86×10^{-6}
1.757	1,053	16	4.24×10^{-6}	4.45×10^{-6}
1.506	1,566	16	4.63×10^{-6}	4.86×10^{-6}
1.042	3,297	16¾	4.66×10^{-6}	4.81×10^{-6}

B. Silver nitrate solution concentration 0.1 $\frac{\text{mg.-equiv.}}{\text{cc.}}$. Electrode as above, $n_a = 0.528$.

1.757	580	18½	6.82×10^{-6}	6.73×10^{-6}
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According to Wiedeburg* the diffusion coefficient of CuSO_4 at 18° is 4.479×10^{-6} for the concentration 0, and 4.226×10^{-6} for the original concentration of the preceding table. The values in the table thus appear somewhat high. The value found for the diffusion coefficient of silver nitrate is very much too low if we take as correct the number $k_{18} = 12.5 \times 10^{-6} \frac{\text{cm.}^2}{\text{sec.}}$,

which has been calculated by Nernst from the migration velocities of the Ag^+ and the NO_3^- ion,† and which agrees with values extrapolated from Scheffer's determinations of diffusion coefficients.‡ This fact seems to point to the break in the curve occurring before complete depletion of the silver at the electrode has taken place. The matter is, however, undergoing further investigation. See also remarks below regarding deposition-potential of copper.

The numbers given in Table II. may be taken as typical results for the determination of the resistance of the copper sulphate solution between the cathode and the junction T described on p. 7. The experiments 1, *a*, *b*, *c*, *d*, were carried out before the current passed through the solution; experiments 2, *a* and *b*, after the break in the potential of the cathode had taken place.

TABLE II.

No. of Experiment.	Ratio of Condensers.	Resistance in Dial-box.	Resistance calculated by Formula on p. 7.
1	<i>a</i> 500 : 20	65	} From 1 ^a and 1 ^b 77 ohms
	<i>b</i> : 40	207	
	<i>c</i> : 50	278	From 1 ^a and 1 ^c 77 ohms
	<i>d</i> : 70	425	From 1 ^a and 1 ^d 79 ohms
2	<i>a</i> 500 : 50	122	From 2 ^a and 2 ^b 218 ohms
	<i>b</i> : 100	462	

The potential of the cathode, after allowance had been made for the drop according to Ohm's law between the cathode and the junction T, was, in the majority of experiments on copper sulphate solutions, found to lie about 10 to 20 millivolts below the potential of equilibrium. This matter, as well as the slight retrogression of potential at the beginning of the experiments which is visible in the copper sulphate curves (Fig. 5), similarly the conditions on which the crystallisation of the silver depends, is undergoing further investigation. Some of the results referred to, if corroborated, would lead to the conclusion that the deposition of metals from solutions like copper sulphate is not an absolutely reversible process, and this again would prove of importance in its bearing on the different nature of metal deposits obtained from different solutions. In a series of experiments on a decinormal zinc sulphate solution with an amalgamated copper electrode similar curves resulted to those obtained with the copper sulphate. Owing, no

* *Wied. Ann.*, 41, 675, 1890.

† *Ztschft. Phys. Chem.* II., 400 (1888).

‡ *Ztschft. Phys. Chem.* II., 628 (1888).

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Fig. 6.

Alcoholic Solution of Cuprous Chloride.

Abscissae: Difference of Potential between Standard Electrode and Cathode.

Ordinates: Time.

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doubt, to the fact that hydrogen is evolved sometimes after all the zinc has been removed from the solution and sometimes before, according to slight differences in the nature of the electrode, the results were somewhat irregular, and have therefore not been reproduced as curves. The values obtained for the diffusion coefficient of zinc sulphate varied between 3.5×10^{-6} and $4.5 \times 10^{-6} \frac{\text{cm.}^2}{\text{sec.}}$. They point to an increase of the diffusion coefficient of zinc sulphate at great dilutions, the value obtained by Weber* for solutions of 2.114 per cent., *i.e.*, $0.26 \frac{\text{mg.-equiv.}}{\text{cc.}}$ being $2.78 \times 10^{-6} \frac{\text{cm.}^2}{\text{sec.}}$. In agreement with this we should expect the diffusion coefficient of zinc sulphate not to differ greatly from that of copper sulphate at great dilution, owing to the fact that the mobilities of the zinc and the copper ion are nearly equal at great dilution.

ALCOHOLIC SOLUTIONS OF CUPROUS CHLORIDE.

The next series of determinations was carried out with the object of testing whether the method was suitable for alcoholic solutions. The solution chosen was one of cuprous chloride in a mixture of hydrochloric acid, alcohol, and water, its composition being 1 g. Cu_2Cl_2 , 25 cc. strong hydrochloric acid, 45 cc. 95 per cent. alcohol, 30 cc. water. Owing to contact with the air, part of the cuprous chloride became oxidised to cupric chloride. The curves on Fig. 6 show the degree of coincidence obtained in three successive experiments, determinations having been carried out with the current-density $1.054 \frac{\text{milamps.}}{\text{cm.}^2}$, and two with the current-density $1.318 \frac{\text{milamps.}}{\text{cm.}^2}$. The curves obtained are of interest inasmuch as they show plainly that two successive processes take place: firstly, the reduction of the cupric chloride to cuprous chloride, which begins at potentials lower than those registered in the figure, and goes on to about 45 centivolts; and secondly, the deposition of copper from the cuprous chloride beginning at about 45 centivolts and going on until the break in the curve is completed, when the potential becomes fairly constant at about 65 to 70 centivolts, and hydrogen comes off.

ACID SOLUTIONS OF NITROBENZENE.

We now come to the discussion of curves obtained when the solution of an organic substance, namely, nitrobenzene, was reduced under varying conditions. Two solutions were experimented upon with different electrodes and current-densities, other conditions remaining unchanged as nearly as possible. Stock solutions of accurately known composition were mixed in known proportion, the composition of the resulting liquids working out as follows:—

1 litre acid solution used for experiments of Figs. 7, 8, 9, 10, contains	$\left\{ \begin{array}{l} 5 \text{ g. nitrobenzene.} \\ 107 \text{ g. H}_2\text{SO}_4. \\ 425 \text{ cc. ethylalcohol.} \\ \text{Remainder water.} \end{array} \right.$
1 litre alkaline solution used for experiments of Fig. 11 contains... ..	$\left\{ \begin{array}{l} 5 \text{ g. nitrobenzene.} \\ 82 \text{ g. NaOH.} \\ 425 \text{ cc. ethylalcohol.} \\ \text{Remainder water.} \end{array} \right.$

* *Weid. Ann.*, 7, 536 (1879).

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Fig 7.

Acid Solution of Nitrobenzene.

Abscissae: Difference of Potential between Standard Electrode and Cathode.

Ordinates: Time.

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Fig. 8.

Acid Solution of Nitrobenzene.

Abscissae: Difference of Potential between Standard Electrode and Cathode.

Ordinates: Time.

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Fig. 9.

Acid Solution of Nitrobenzene.

Abscissae: Difference of Potential between Standard Electrode and Cathode.

Ordinates: Time.

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Fig. 10.

Curves to show change in Platinum Cathode brought about by use.

Abscissae: Difference of Potential between Standard Electrode and Cathode.

Ordinates: Time.

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Fig. 11.

Alkaline Solutions of Nitrobenzene.

Abscissae: Difference of Potential between Standard Electrode and Cathode.

Ordinates: Time.

70

80

90

100

110

120

130

140

150

160

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The anode for the experiments on acid solutions was, as a rule, one of copper in contact with a solution of 30 g. cuprous chloride in 200 cc. strong hydrochloric acid and 100 cc. 95 per cent. alcohol. For the experiments on the alkaline solution the anode was mercury in contact with a solution of 100 g. mercurous nitrate and 35 cc. strong nitric acid in 500 cc. water, the solution interposed (see p. 8) containing 125 g. ammonium nitrate in 500 cc.

The curves obtained show, firstly, the degree of coincidence yielded by a repetition of experiments, and, secondly, they exhibit both interesting similarities independent of the material of the electrode and characteristic differences due to it. The abscissæ again denote the experimentally found values of the potential of the standard electrode, the potential of the cathode being taken as zero. A small correction may be made for the difference of potential due to the resistance overcome by the current between the cathode and the junction T (p. 6), by taking the value $3\frac{1}{2}$ ohms for this resistance in the case of the acid solution, and 6 ohms for the alkaline solution. All the curves representing the results of experiments on acid solutions exhibit first a rise of potential. After this it recedes, or becomes almost stationary, then increases once more, and finally becomes stationary again. Bubbles of hydrogen may now be observed on the cathode. It may perhaps be premature to attempt to explain definitely the first retrogression of potential in the curves. The most probable cause seems to be a temporary change in the nature of the electrode, resulting from electrolysis. Such changes have been recently shown to occur frequently by Russ,* Luther, and Brislee,† and others. As a rule they tend to make cathodes more efficient, *i.e.*, they enable them to accomplish reduction with the expenditure of a smaller amount of energy. The electrodes are also certainly permanently changed under certain conditions in such a manner that they become less efficient. This is very notable with the cathode of smooth platinum when small current-densities are employed. If an electrode is used which has been freshly cleaned with ligroin, boiling strong nitric acid and boiling caustic soda solution, the potential of the standard electrode shows a comparatively low value throughout the experiment, the results being similar to those obtained with a cathode of platinum coated with platinum black. On repetition (p. 10) the cathode is, however, found to have become less efficient, the potential being considerably higher than in the first experiment. Further repetitions yield curves almost identical with the second, the potential, however, still becoming slightly higher. When the cathode is cleaned after this, as before the first experiment, it again yields a curve similar to the first. In Fig. 10 the first curve and one of its repetitions are shown.

Fig. 7 illustrates results obtained with a copper and a platinum cathode respectively. The experiments with the copper cathode were stopped after the first retrogression of potential. It will be seen that the latter occurs approximately at the same time in the experiments with the copper as in those with the platinum electrode. The difference between the actual values of the potentials is, however, very marked, the standard electrode at the beginning of the copper experiments showing a lower value than at the beginning of the platinum experiments. This corresponds to a greater efficiency, *i.e.*, a smaller expenditure of energy in the case of the copper than in that of the platinum electrode. In accordance, however, with the greater E.M.F. required for the liberation of hydrogen on a copper cathode

* Russ, *Ztschft. Phys. Chem.* xliv. 641 (1903).

† Luther and Brislee, *Ztschft. Phys. Chem.* xlv. 216 (1903).

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than on one of platinum,* the copper curves attain higher values of potential than the platinum curves at the end of the experiment.

Fig. 9 represents experiments with a copper cathode carried out until evolution of hydrogen takes place.

In Fig. 8 results are shown obtained with an electrode of platinum thickly coated with platinum black, the current-density being the same as in the experiments of Fig. 7. The low values of the potential represent the most conspicuous feature of these experiments. As the electrode is not smooth, the time values are not comparable with those of Fig. 7.

ALKALINE SOLUTIONS OF NITROBENZENE.

Fig. 11 represents results obtained with the alkaline solution of nitrobenzene. As the solution at the cathode becomes heavier during electrolysis in an alkaline electrolyte, owing to accumulation of alkali, the cathode was placed horizontally at the foot of the cell in these experiments (Fig. 2). At the points of maximum voltage hydrogen begins to be evolved. The differences between the experiments with copper and platinum electrodes are similar to those observed in acid solution. The time which elapses until hydrogen is evolved by a current of given density is considerably smaller than in acid solution. This points to the conclusion that the diffusion coefficient of nitrobenzene is considerably smaller in alkaline than in acid solution, and possibly also that the reduction does not proceed quite so far before hydrogen is evolved.

EXAMPLE OF APPLICATION OF RESULTS.

In conclusion, we have to show how experiments carried out according to the method described may be employed in order to arrive at an estimate whether results that have been obtained in electrochemical investigations are due simply to concentration changes at the electrode that take place so rapidly that they cannot be neutralised by stirring, or whether they are really properties of the solution originally made up by the experimenter. As an example, we shall investigate whether concentration changes can have taken place during the experiments by Haber, referred to in the introduction, with sufficient rapidity to explain his results.

We may approach such questions from two points of view. Firstly, we may make an arbitrary assumption regarding the time that must elapse until artificial stirring can completely renew the layer of liquid touching the electrode. For example, we might assume that such a renewal takes place completely after the lapse of one second, or of one minute, and then calculate what is the maximum change of concentration that can have taken place. Secondly, we may assume that owing to stirring the concentration of the electrolyte is always left unaltered at some definite distance, say $\frac{1}{10}$ mm. from the electrode, and then calculate the maximum change of concentration that is conceivable on this assumption.

Proceeding on the first plan, we have the equation †—

$$C = C_0 - 2F \sqrt{\frac{t}{\pi k}} \quad (1)$$

in which C_0 is the original concentration of the substance electrolysed, C its concentration after the time t , k its diffusion coefficient, and F the amount removed by electrolysis at the electrode per unit of surface and time.

* Caspari, *Ztschft. Phys. Chem.* xxx. 89 (1899).

† Sand, *loc. cit.*, p. 53.

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From this equation we find the following value for the relative change of concentration at the electrode :—

$$\frac{C_o - C}{C_o} = \frac{2F}{C_o} \sqrt{\frac{i}{\pi k}} \quad \dots \dots \dots (2)$$

Proceeding according to the second plan and indicating the distance from the electrode at which no change of concentration takes place by δ , we have the following relation according to Fick's diffusion law :—

$$F = k \frac{C_o - C}{\delta},$$

from which we obtain for the relative change of concentration at the electrode the value—

$$\frac{C_o - C}{C_o} = \frac{\delta F}{k C_o} \quad \dots \dots \dots (3)$$

When the current is employed solely for reduction we have—

$$F = \frac{i}{96540} \quad \dots \dots \dots (4)$$

concentrations being expressed in g.-equivalents or mg.-equivalents per cc., and current-densities in amperes per sq. cm. or milamps. per sq. cm., respectively.

In order to eliminate k from these equations we may calculate its value from the experiments we have described in the present paper. For this purpose we must assume that nitrobenzene has been completely removed from the electrode by reduction to azoxybenzene when hydrogen is evolved. We then find k by applying equations (1) and (4) to our experiments. We thus obtain—

$$k = \left(\frac{2i'}{96540 C_o} \right)^2 \frac{l'}{\pi} \quad \dots \dots \dots (5)$$

quantities referring to our experiments being distinguished by dashes. The values for k derived from this equation are no doubt often vitiated by the fact that hydrogen may come off before complete reduction of the nitrobenzene has taken place, so that the values found for k are too small, and those for $\frac{C_o - C}{C_o}$ too large. This does not matter seriously, however, as we only desire to find an upper limit for the latter quantity. Eliminating F and partly k from the equations (2), (3), (4), (5), we find the following relations :—

$$\frac{C_o - C}{C_o} = \frac{i}{i'} \frac{C_o'}{C_o} \sqrt{\frac{l'}{l}} \quad \dots \dots \dots (6)$$

and

$$\frac{C_o - C}{C_o} = \frac{i}{96540} \frac{\delta}{k C_o} \quad \dots \dots \dots (7)$$

As an example, by which to test whether concentration changes played an important part in Haber's results, we take numbers from the paper recently published by him in conjunction with Russ.* According to Table II., p. 279, when a current of density $\frac{4.5}{1.5 \times 10} \frac{\text{milamps.}}{\text{cm.}^2}$ was passed through

* *Loc. cit.*

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a vigorously stirred alkaline solution of nitrobenzene of the concentration $0.8 \frac{\text{mg-equiv.}}{\text{cc.}}$, an absolute potential of 0.0737 volts was observed; whereas when the current had a density of $\frac{36}{1.5 \times 10} \frac{\text{milamps.}}{\text{cm.}^2}$, the potential was 0.1171 volts, the difference being 0.0434 volts. Now, according to the Table VIIa. on p. 285, when a current of the density $\frac{5}{1.5 \times 10} \frac{\text{milamps.}}{\text{cm.}^2}$ was employed in a solution of the concentration $0.8 \frac{\text{mg-equiv.}}{\text{cc.}}$, the potential 0.0993 volts was recorded. In order to obtain a rise of potential of 0.0434 volts by reduction of the concentration of nitrobenzene, the current strength being left unchanged, we can infer by interpolation from numbers given in the same table that the concentration must be reduced to $0.115 \frac{\text{mg-equiv.}}{\text{cc.}}$, i.e. to 14 per cent. of its former value. If the first experiments are to be explained as a result of local reduction of concentration at the cathode, such reduction must therefore amount to at least 86 per cent.

Now, in order to obtain an estimate of the magnitude of depletion at the cathode that actually took place, we refer to one of our experiments represented in Fig. 11. Taking, for example, curve 4, we have $i' = 1.184 \frac{\text{milamps.}}{\text{cm.}^2}$
 $i' = 460'$, $C' = \frac{5 \times 3}{123} \frac{\text{mg-equiv.}}{\text{cc.}}$. Employing equation (6), we find that if the

liquid touching the cathode is renewed completely after every second by stirring, the lowering of concentration could never go below 14 per cent. I have shown formerly* that under more unfavourable circumstances, viz., when the cathode was mercury contained in a cup, it is possible to prevent depletion, which would require 0.4 sec. if the liquid were stationary; it seems improbable, therefore, that the lowering of concentration in Haber's experiment went below the above value.

By employing equations (5) and (7), we find that if the concentration of the liquid be maintained continually at its original value by stirring at $\frac{1}{10}$ mm. distance from the cathode, the utmost lowering that could take place would amount to $5\frac{1}{4}$ per cent. Brunner† calculates the distance from the electrode to which he was able to keep the concentration unchanged in his experiments to have been $\frac{1}{30}$ to $\frac{1}{20}$ mm., so that, adopting his values, we should conclude that the lowering of concentration did not amount to more than about $1\frac{1}{2}$ per cent. Starting from other curves on Fig. 11, we obtain similar values. In any case the results show that we cannot assume changes of concentration amounting to 86 per cent. to have taken place in Haber's experiments, and that the variations of electrode-potential with current-density observed by him can therefore not be explained as the result of concentration changes at the cathode.

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* *Loc. cit.*, p. 77.

† *Zeitschrift. Phys. Chem.*, xlvii, 99 (1904).