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AMSTERDAM. — 1925.

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RESEARCHES WITH THE DROPPING MERCURY CATHODE.

PART I.

General introduction

BY

J. HEYROVSKÝ.

The electrolysis with the dropping cathode¹), as applied to the study of electrolytic processes by the present author, uses the mercury cell arrangement of B. Kučera, which is a modification of Lippmann's capillary electrometer method for the determination of the change of surface tension of polarised mercury.

If the solution in this cell be freed from air, and the current due to the polarising E. M. F. be measured, the initial "residual current" is found to be very small (of the order of 10^{-8} to 10^{-7} amp.) and the beginning of the electrolytic deposition is well marked.

Moreover, owing to certain favorable circumstances, such as the continuous renewal of the surface in the mercury drop at the cathode, the high over-potential on pure mercury and the constancy of the anodic potential of the large mercury layer, this electrolysis has been found to be highly "reversible" i. e. the potentials of polarised drops are in just as simple equilibrium with the ions of the solutions as electrodes of concentration cells are. This is evident from the shifts of the "current-voltage" curves proceeding with the dilution of the electrolyte, which shifts closely agree with those calculated from the ionic concentrations.

Since the apparatus and experimental arrangements have already been described in detail in previous communications²) and the recently introduced photographic auto-registration machine for recording the polarisation curves will be described in Part. II (following this), we may here discuss at once the theory of this kind of electrolysis.

The reduction and the deposition potentials.

Since the current density at the large mercury anode is very small, its potential is maintained constant throughout the electrolysis, especially when in solutions of a salt whose anions form insoluble mercury

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¹) This method has nothing in common with the "dropping electrode" introduced by Ostwald to serve as the so-called "absolute zero" electrode.

²) Chem. Listy **16**, 256 (1922), Phil. Mag. **45**, 303 (1923), Trans. Faraday Soc. **19**, 692 (1924), Compt. rend. **179**, 1044, 1267 (1924).

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Consider first the case of the electro
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$$Me^{n(+)} + n(-)$$

If the drop is polarised to the poter
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$$\pi = -\frac{RT}{nF}\log.$$

must hold, where K_{Me} is a specific co
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Secondly let us consider the electr
reaction

$$M^{n(+)} + r(-) \rightarrow$$

Denoting by $[M^{(n-r)+}]$ the co
accumulated at the mercury drop surfa
ion surrounding the drop, we must ha
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$$\pi = -\frac{RT}{r \, . \, F}\log.$$

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process a strict analogy to the meta
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is surrounded by the product of the c
of the ratio of the concentration of tl
the reducible matter being determined

The values of the two potentials, (r
reduction process and that of the met

salts. The whole polarising E. M. F. thus controls the process at the cathode, which may consist in the deposition of cations or in lowering their valency, or in general in the reduction of any substance capable of being chemically reduced.

If the process proceeds reversibly in all these cases, at every instant at each potential acquired by the polarised drop an equilibrium is established between the reducible substance in solution and the reduction products arising at the cathode — the equilibrium depending upon the potential of the drop.

Consider first the case of the electro-*deposition* of a n-valent metal Me, represented as

$$\mathrm{Me}^{n(+)} + n(-) \twoheadrightarrow \mathrm{Me}.$$

If the drop is polarised to the potential π, and the metal deposits onto mercury, accumulating there to a concentration C, then the expression

$$\pi = -\frac{RT}{nF}\log.\frac{C\,.\,K_{Me}}{[\mathrm{Me}^{n(+)}]} \quad . \; . \; . \; . \; . \; . \quad (1)$$

must hold, where K_{Me} is a specific constant of the metal, depending on the "solution tension" of its amalgam.

Secondly let us consider the electro-*reduction* represented by the reaction

$$\mathrm{M}^{n(+)} + r(-) \twoheadrightarrow \mathrm{M}^{(n-r)(+)}\,.$$

Denoting by $[\mathrm{M}^{(n-r)+}]$ the concentration of the reduced ions accumulated at the mercury drop surface, i. e. in the layer of the solution surrounding the drop, we must have at any reduction potential. π the ionic electrode equilibrium according to the formula

$$\pi = -\frac{RT}{r\,.\,F}\log.\frac{K\,[\mathrm{M}^{(n-r(+)}]}{[\mathrm{M}^{n(+)}]}, \quad . \; . \; . \; . \quad (2)$$

if the process proceeds rapidly enough to establish the equilibrium instantly. This is possible with very small currents (10^{-8} to 10^{-} amp.), which pass through the dropping cathode cell, before considerable electrodeposition sets in. At the beginning of the ionic reduction the concentration in the surface layer of the solution closely surrounding the drop becomes richer in the lower valency ions so that it contains both kinds of ions, the ratio of which at any instant of polarisation depends upon the potential of the mercury drop through the logarithmic ratio given in (2). We thus have in the accumulation of the lower valency ions round the cathode during the *reduction* process a strict analogy to the metallic *deposition* according to the process (1). In either instance the mercury drop serving as the cathode is surrounded by the product of the cathodic reduction, the logarithm of the ratio of the concentration of the reduction products to that of the reducible matter being determined by the potential applied.

The values of the two potentials, (namely, the potential of the ionic reduction process and that of the metal deposition), bear respectively a different relationship to the ordinary "reduction-electrode-potentials" and to the „electrolytic potentials" of metals, as measured in galvanic cells.

It has been shown previously by the present author[3]), that the dropping mercury cathode "deposition potential" series differs from the reversible "electrolytic potential" series by the affinity of the respective metals for mercury, which facilitate their deposition at the dropping cathode. Thus, for example, alkali metals, which have a very large affinity for mercury, come out at the mercury cathode at a potential of 1.2—1.4 volt less negative than their electrode potential. Metals possessing less affinity for mercury, e. g. zinc or lead, exhibit a difference of only ca. 0.15 v. between the two potentials whereas metals which have no tendency to form amalgams (e. g. iron) exhibit even "cathodic passivity" at the dropping cathode, being deposited at a more negative potential than their equilibrium "electrode potential".

However the "reduction potential" series of reducible ions, as observed at the dropping cathode, must run strictly parallel to the series of "reduction-electrode-potentials" as measured by a platinum electrode immersed in an equiconcentrated mixture of higher and lower-valency ions.

This is evident from the thermodynamics of reversible electroreduction, where the electrode material does not enter into consideration, and the energy necessary to reduce the ion must thus be independent of the electrode material. With the dropping cathode the reduction of ions yielding in the solution layer round the drop a concentration of 10^{-6} gram-ions of the reduction product per litre is already observable by an increase of current. The position of the bend at which the increase of current occurs will differ, say in a deci-normal solution of higher-valency ions, from the "normal reduction-electrode-potential" by the amount $\frac{RT}{r\,.\,F}\,.\,\log.\,\frac{0.1}{10^{-6}}$, i. e. will be more positive by $\frac{0.058}{r}\,.\,5$ volt. Similarly for all concentrations the "normal-electro-reduction-potential" may be calculated from the potential derived from the polarisation curves obtained with the dropping cathode.

Under suitable conditions the deposition potential of a metal might be delayed — owing to small affinity for mercury — to such an extent, that the reduction to the lower valency-ions can commence before the deposition potential is reached, or vice versa, so that new electrode processes, observable only at this special mercury cathode, might be encountered, which could not take place at a cathode consisting of another metal (e. g. with nickel, see part VII of these researches).

Since reduction at the cathode gives rise to a mixture of higher and of lower-valency ions in the solution layer surrounding the drop, whereas deposition causes an increase in the metallic concentration in the mercury phase, (immiscible with water), the latter process must

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[3]) Phil. Mag., l.c.

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and in part XI (influence of anions)

The determination of the turning

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be compared. Consider two such p
two curves, obtained from the polar
ionic concentrations c and c′, have

Here $\frac{di}{dt} = \left(-\frac{n\,.\,F}{RT}\right).\,e^{-\frac{\pi n}{RT}}$

be much less affected by diffusion than the reduction process. Thus it is to be expected that the reversibility of the cathodic deposition of a metal will approach nearer the ideal state than that of reduction processes and that the polarisation curves in the former electrolysis will approximate more closely to the theoretical ones.

Finally there is the possibility at the dropping mercury cathode, as at all cathodes, of a secondary reduction being brought about by chemical action. Thus unionized substances are reduced by hydrogen in the nascent state, or even by molecular hydrogen diffusing through the solution and reducing matter which is not attracted to, or repelled from the cathode. The former process, represented by the equations:

$$H^{+} + \ominus \twoheadrightarrow H$$
$$H + \text{oxid.} \twoheadrightarrow \text{red.}$$

will by found fully discussed in M. Shikata's paper (read before the Far. Soc. 16. II. 1925), who investigated the reduction of nitrobenzene at the dropping cathode, whereas the second i. e. molecular reduction process will be mentioned in part V of this series (arsenic deposition) and in part XI (influence of anions).

The determination of the turning points of the polarisation curves.

Most characteristic of the polarisation curves obtained from electrolysis with the dropping cathode are the positions of the turning points, indicating a sudden increase in current due to the decomposition of the electrolyte. To understand their significance, let us consider the beginning of amalgam formation during electrolysis with this cathode. The current intensity, i, being equivalent to the amount decomposed in unit time, must be directly proportional to the amalgam concentration C in the continually renewed mercury surface of the drop.

$$\text{Thus } i = k \,.\, C$$

Substituing the value of C obtained from formula (1) the expression

$$i = e^{-\frac{\pi n F}{RT}} \,.\, \frac{[Me^{n+}]}{K_{Me}} \,.\, k$$

is derived, showing, that the curve indicating the dependence of the intensity upon the potential, i. e. the "current voltage" curve, should be an exponential.

There is, therefore, not a distinct "kink" or "break" but more or less sharp bends in the polarisation curves; thus to compare the shift of the curves due to the variable ionic concentration the abcissae (potentials), at which tangents to the curves have equal slopes, must be compared. Consider two such potentials. π and π', at which the two curves, obtained from the polarisation of the two solutions having ionic concentrations c and c′, have identical tangential slopes.

$$\text{Here} \quad \frac{di}{dt} = \left(-\frac{n \,.\, F}{RT}\right) . \, e^{-\frac{\pi n F}{RT}} \frac{c}{K_{Me}} \,.\, k$$
$$= \left(-\frac{nF}{RT}\right) . \, e^{-\frac{\pi' n F}{RT}} \,.\, \frac{c'}{K_{Me}} \,.\, k.$$

Hence $\pi - \pi' = \frac{RT}{nF} \log. c/c'$.

These points have to move with the ionic dilutions in the same way as the concentration cell potentials vary. (In the practical examples given below the tangent of 45 degrees was always used; in previous communications, before this theory was presented, the potential of the curves at which an increase of 0.001 volt effected an increase of 10^{-8} amp. were termed "deposition potentials", which do not differ practically from the demarcation now adopted).

This method thus gives a similar means for the determination of ionic concentrations as the potentiometric methods of concentration cells; the dropping cathode is, however, more widely applicable, since it might be extended to the magnesium and the other alkaline earths, including even the rare earths, metals of the iron group, zinc in alkaline solutions etc.; further to metals in non-aqueous solvents and inorganic as well as organic electro-reduction in different solvents. The sensitivity of the method, which allows most of the metals to be detected in a few ccms. of a solution when present as 10^{-6} moles per litre, promises applications to qualitative as well as quantitative micro-analysis.

"Waves" due to the saturation current.

If the concentration of a reducible substance which gives a well defined deposition potential, is made less than 10^{-4} gram-equivalents per litre, the polarisation curve, after rising to ca. 4/5 of the whole ordinate (i. e. indicating 10^{-6} amp.) becomes horizontal again, and the current remains constant with increasing polarisation until the potential of a new reduction is reached (compare the graphs part II fig. 3, 4, 5).

This change of the shape into such a "wave" is easily understood, when considering that at such dilutions the interfacial solution layer freshly surrounding newly formed drops of polarised mercury is exhausted of the reducible matter and further deposition can only proceed at the rate at which the reducible substance is diffusing to the surface of the drop. This, of course, is very small and is entirely independent of the polarisation potential.

When a wave of this height appears in a polarisation curve, it indicates that the substance is present in the concentration 10^{-4} equivalents per litre, and the potential at which the bend occurs, denotes the nature of this reducible matter. Diluting further, say 10 times, the "wave" is one tenth of the previous one, and at 10^{-6} the "wave" almost disappears (e. g. see graph fig. 3 part IX), so that impurities of that order are the smallest traces determinable by this method.

Maximum of the polarisation curves.

In certain cases, e. g. when traces of nitrobenzol are present in slightly acidic solutions a well defined maximum appears in the

polarisation curve (see part II grap
been thoroughly investigated by M.
Far. Soc. 16th Feb. 1925) and disc
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The influence of anions.

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immediately at the cathode.

The reason this splitting does not
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cannot be reached with the polarisa
fact that the presence of nitrates,
reversible reduction has been used

polarisation curve (see part II graph fig 6). This phenomenon has been thoroughly investigated by M. Shikata (a paper read before the Far. Soc. 16th Feb. 1925) and discussed in that communication; the explanation given being that the decrease of the current after the maximum is due to the desorption of reducible matter, whose adsorption potential is just overcome by the cathodic potential applied. At this instant the mercury drop is formed in a new concentration, considerably smaller than that before the potential corresponding to the maximum was reached, at which the adsorbable substance accumulated on the mercury. Thus the "saturation" current which follows the maximum is, owing to the overcoming of the adsorption, much smaller. This, of course, can only be so if surface active substances are in solution, which accumulate at the mercury-solution interface. A similar phenomenon appears in solutions of quinine (see part. X).

Another instance of the occurrence of maxima in the polarisation curves has been encountered in complex argenti-cyanide solutions, which again can only be explained satisfactorily by a change in adsorption caused through the overcoming of the adsorption potential of the surface active substance by the potential applied. This phenomenon has been investigated by E. B. Sanigar and will be dealt with in part VIII. No doubt, such maxima can be found useful as characterising impurities present and may yield information about the value of adsorption potentials of surface active substances.

The influence of anions.

. Experimental work on electrolysis with various reducible anions (see the communication of Gosman, Part XI), has shown, that even strongly oxidising ions such as nitrate or chlorate ions have very little influence upon the processes at the dropping cathode.

This is explained by their repulsion from the cathode, which suggests that owing to the negative potential of the mercury drop no negative particle can be electro-chemically acted upon at this cathode.

This explanation is certainly applicable for metalloid anions, such as NO_3', ClO_3', SO_4'', etc., but would not hold when considering the electrodeposition of zinc, lead or silver from their complex zincates, plumbites or alkali-cyanides. That these are not repelled from the mercury cathode, but deposited at well defined reversible deposition potentials, may be understood by imagining that at a certain cathodic potential the positively charged metallic ions are attracted out of the complex metallic anion, the negatively charged radicles being repelled from the cathode. In other words, at this potential the complex anions are torn into their simpler components, the metallic ions depositing immediately at the cathode.

The reason this splitting does not take place with ordinary metalloid anions, is that the energy to split these ions into simpler components cannot be reached with the polarisation of the dropping cathode. The fact that the presence of nitrates, sulphates etc. does not affect the reversible reduction has been used in practice in these investigations to extend the beginning of the polarisation to nearly + 0.300 v. from the potential of the normal calomel electrode, the value of the potential of the mercury in the electrolysis cell when the latter contains a solution of nitrates or sulphates.

The oscillations of the galvanometer.

Owing to the drop-formation during which the cathode surface increases to a maximum and then decreases instantly to a minimum, when each drop falls, the current intensity is not constant but oscillates synchronously with the dropping. When viewed under the microscope, it is observed that immediately the drop breaks off, the mercury is drawn back into the capillary, ca. 1 mm inside from the opening of the tip and then a new drop slowly begins to grow. The cathode thus has its minimal surface equal to the cross section of the capillary tips (ca. 0.04 mm in diameter). When fully grown, the drop has a diameter from ½ to 1 mm. This regular change of the electrode surface is the cause of regular (saw-like) undulations of the photographically registered polarisation curves (see graphs in the following part II). The extent of the galvanometric oscillations largely depends upon the sensitivity and damping of the galvanometer used. In these experiments D'Arsonval galvanometers, having a sensitivity of 10^{-8} amp., were used and the damping so adjusted that the period of swing was 2—3 seconds.

The form of the oscillations as represented by the polarograph, is often characteristic of the reduction or deposition process at the cathode. Thus when metals which readily form amalgams are deposited, the oscillations almost disappear (e. g. see graphs 4, 5 part II), whereas the evolution of hydrogen or reduction processes are always accompanied by large oscillations on the graph (compare the fig.in part IV). In amalgam formation the metal diffuses continually into the interior of the drop, causing thereby a large continuous increase of current, whereas when no amalgam is formed, the whole current depends upon the changeable electrode surface. Whether adsorption or desorption takes place at a certain potential, can be distinguished from the shape of the undulations which in one case become "inverted" to those of the other (see part VIII).

Besides this effect, the drops become further charged, to a certain extent, through their electrocapillarity, which induces an electric charge on every increasing mercury surface.

This effect is never great being always negligible in comparison with the 10^{-7} amp. of the residual current and stops entirely at the so called "absolute zero potential", ca. — 0.56 v. from the calomel zero. This is observable e. g. on the graph fig. 1 part VII.

Large oscillations appearing at the commencement of polarisation mean that the solution has not been reduced properly and still contains easily reducible matter.

This suffices for a general introduction to the researches with the dropping mercury cathode, which were all carried out in the physico-

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chemical laboratory of the Charles'
described in the following parts I—

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chemical laboratory of the Charles' University, Prague, and are described in the following parts I—XI.

All the authors are much indebted to Professor B. Brauner for his encouragement during their work, and for his generosity in placing at their disposal not only room in the Institute of Inorganic Chemistry but also his own private specimens. They also wish to place on record their thanks for his sympathetic and helpful advice given throughout the whole of the work.

Prague, *The Physico-Chemical Institute, Charles' University.*

(Reçu le 7 février 1925).

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RESEARCHES WITH THE DROPPING MERCURY CATHODE

PART II.

The Polarograph

BY

J. HEYROVSKÝ AND M. SHIKATA.

The polarisation method hitherto used of adjusting the resistances in rheostats and observing the corresponding galvanometer readings became considerably tedious for observers especially when several polarisation curves had to be determined per day and the readings afterwards graphically recorded. Moreover to follow in detail the whole polarisation right to the decomposition required sometimes more than an hour's time since after each resistance rearrangement one had to wait until the galvanometer became steady. To obviate all these difficulties and to eliminate the personal element in the method the authors have set up a photographic auto-registering machine, which by means of a kind of rotating Kohlrausch drum, automatically rotated, attached to a photographic cylinder records the polarisation curves, giving such "polarograms" in less than 20 minutes.

The diagram of the complete instrument is given in fig. 1, whilst the photograph of the machine is reproduced in plate 1.

The current from a 2 or 4 volt accumulator, A, passes round the wooden drum B, about 40 cm. in diameter with 20 winds of about 0.6 mm. thick nickelin resistance wire, the contact being made through the axles. The polarising current is shunted from this drum by connecting the positive terminal of the drum D to the bottom layer E of the mercury in the polarising vessel V and joining the reservoir of the dropping electrode through the galvanometer G to a wheel F, which moves along the sliding resistance wire of the drum when set rotating by the clock-work M. The wheel contact thus continually moves from the first terminal D to the other end of the sliding wire increasing the polarising E.M.F. from 0 to 2 or 4 volts. The current, which is caused by this gradually increasing polarisation, moves the mirror of the galvanometer G, which sends a ray reflected from the source of light L to the slit S, through which it penetrates on to the photograpic paper fixed round a cylinder which is rotated 20 times more slowly than the drum, by pressing the circumference of its wheel

on the axle of the rotating drum.
shows after development the exact
reliably than the previous hand-mad
be obtained in 15—20 minutes [1]).

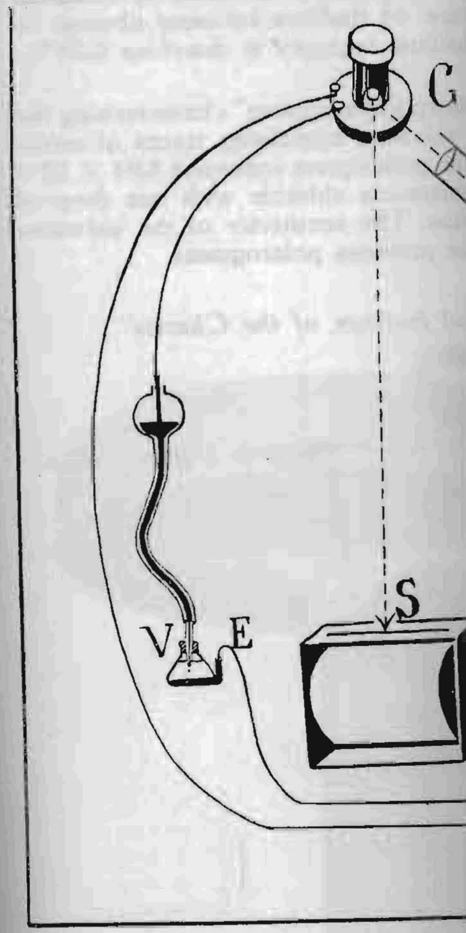

Fig.

Some of the characteristic curve
are shown in fig. 3—5 (plates 2, 3

Plate 2. is the polarogram of
sulphate, which evidently contains
per litre, i. e. 0.01 %. (The dim
20 × 40 cms.)

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[1] The machine excluding the galvanom
from the mechanic of the Chemical Instit
University, Prague — VI. Presslova ul. No.

on the axle of the rotating drum. The photographic paper then shows after development the exact polarogram more precisely and reliably than the previous hand-made graphs could show, and may be obtained in 15—20 minutes [1]).

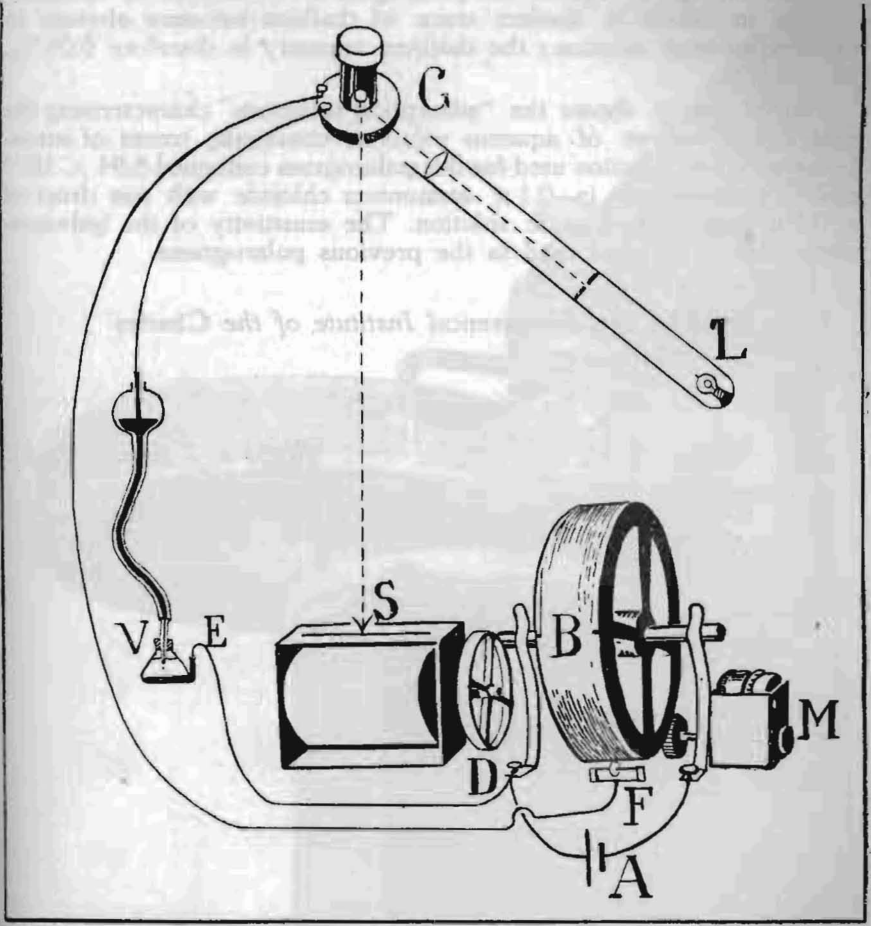

Fig. 1.

Some of the characteristic curves obtained with this polarograph are shown in fig. 3—5 (plates 2, 3).

Plate 2. is the polarogram of a 0.25 normal solution of cero-sulphate, which evidently contains 3×10^{-5} gram-molecules of lead per litre, i. e. 0.01 %. (The dimensions of the polarograms are 20×40 cms.)

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[1]) The machine excluding the galvanometer and source of light can be obtained from the mechanic of the Chemical Institute, Mr. Petak, for about £ 10. (Charle's University, Prague — VI. Presslova ul. No. 1).

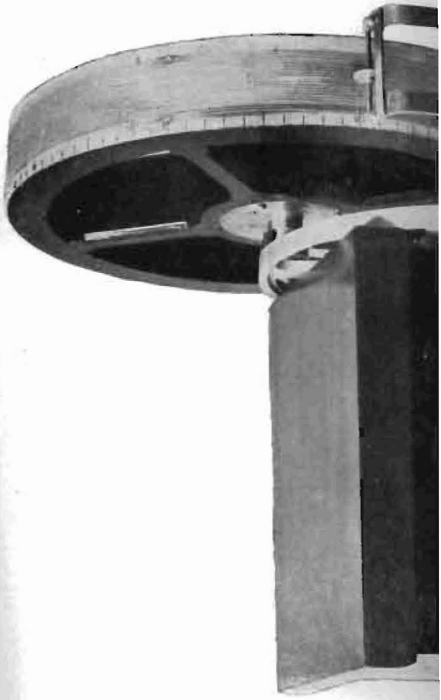
Plate 3. fig. 4. contains polarisation curves of solutions containing 10^{-3}, 10^{-4}, 10^{-5} and 10^{-6} gram equiv. of zinc-chloride per litre.

Plate 3. fig. 5. shows the polarograms of solutions of cadmium nitrate, in which a distinct trace of thallium becomes obvious in the deci-normal solution; the thallium impurity is therefore 0.06 %.

Plate 4. fig. 6. shows the "adsorption maximum" characterising the polarisation curves of aqueous solutions containing traces of nitrobenzene [2]). The solution used for this polarogram contained 8.94×10^{-5} molar nitrobenzene in 0.1 n ammonium chloride with one drop of a 0.1 n sodium hydroxide solution. The sensitivity of the galvanometer was $^1/_3$ of that used in the previous polarograms.

Prague, *The Physico-chemical Institute of the Charles' University.*

(Reçu le 7 févr. 1925.)



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[2]) see M. Shikata, a paper read before the Faraday Soc. 16, Feb. 1925.

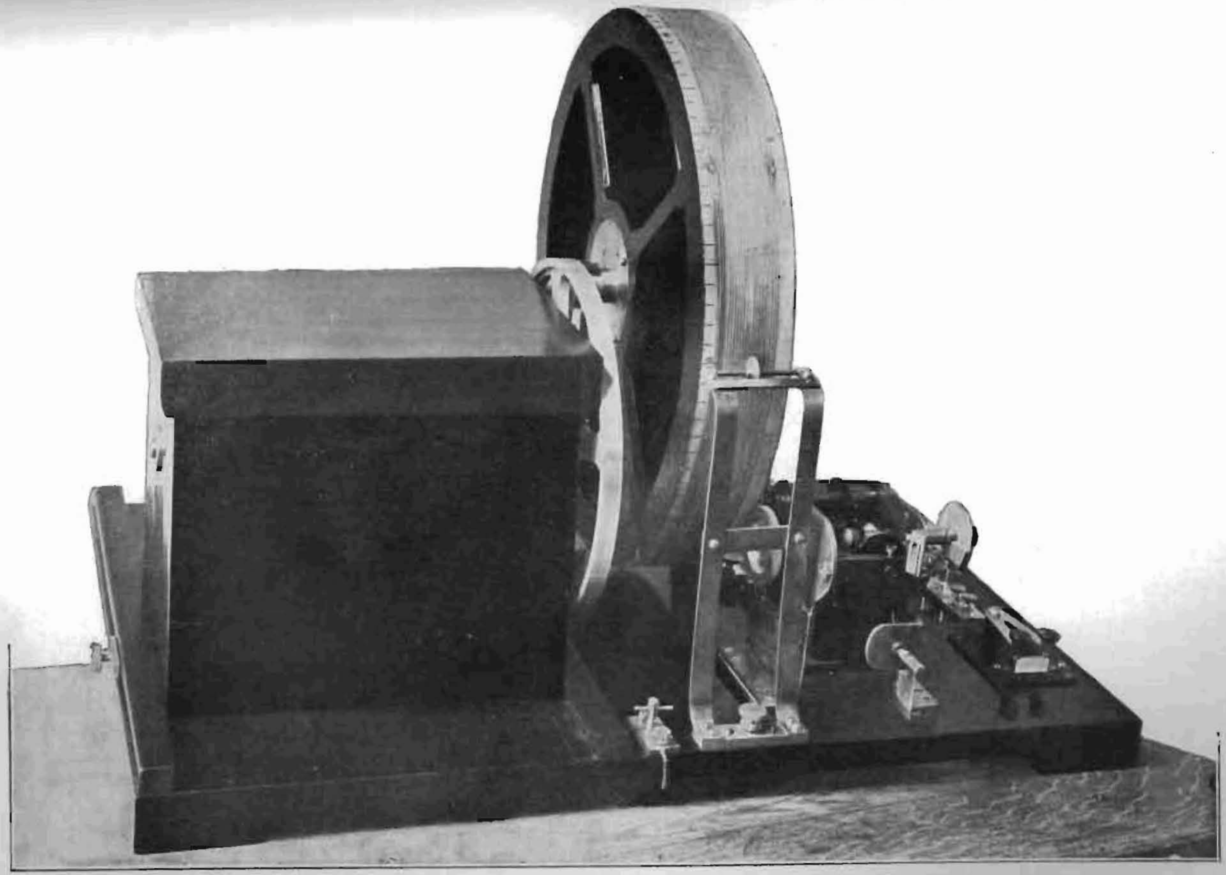

Plate 1.

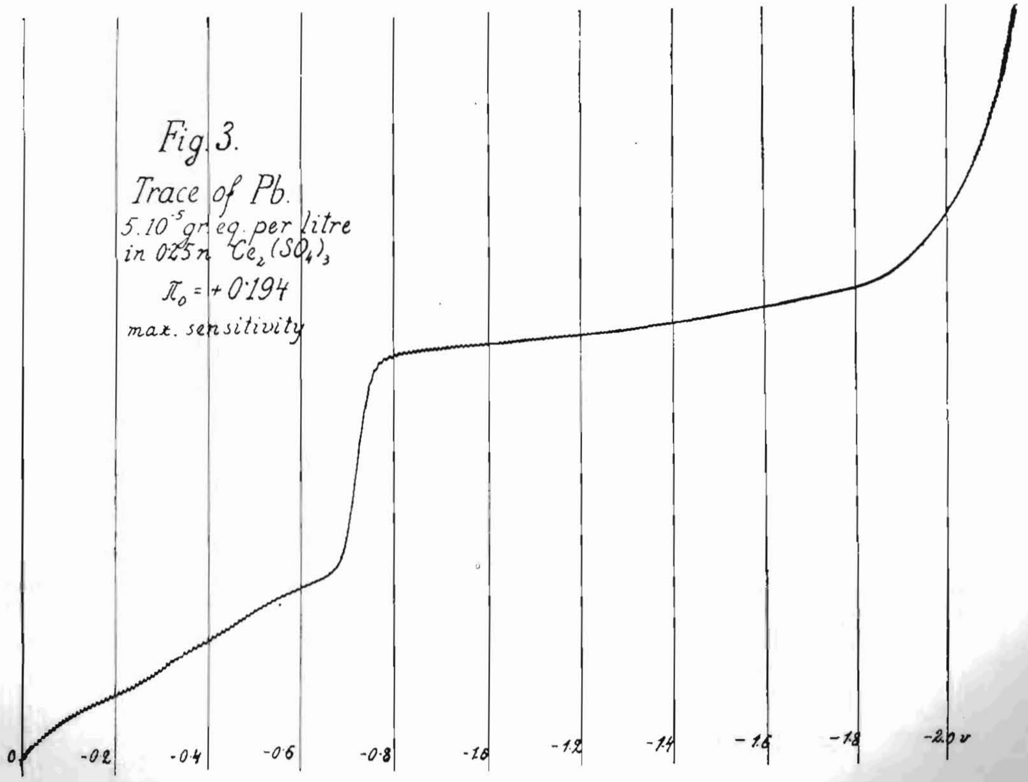

Fig. 3.

Trace of Pb.

5.10^{-5} gr. eq. per litre
in 0·25 n $Ce_2(SO_4)_3$

$\pi_0 = +0{\cdot}194$

max. sensitivity

Plate 2.

Fig. 4.

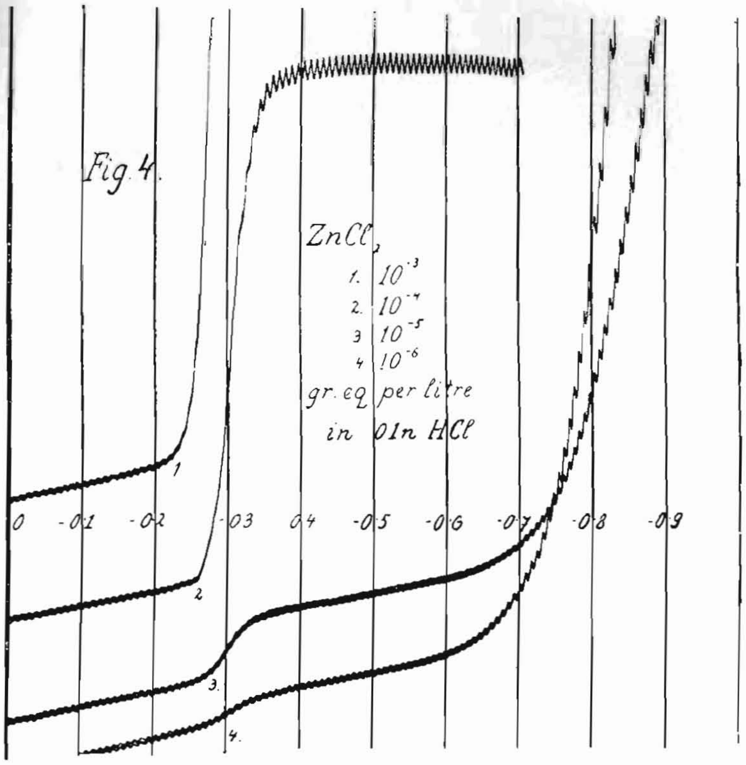

Fig. 5

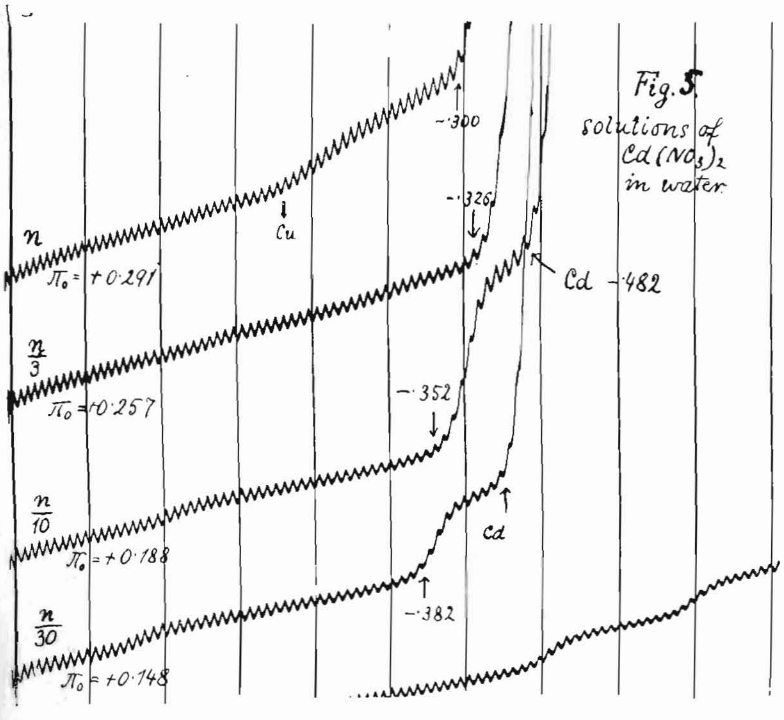

Plate 3.

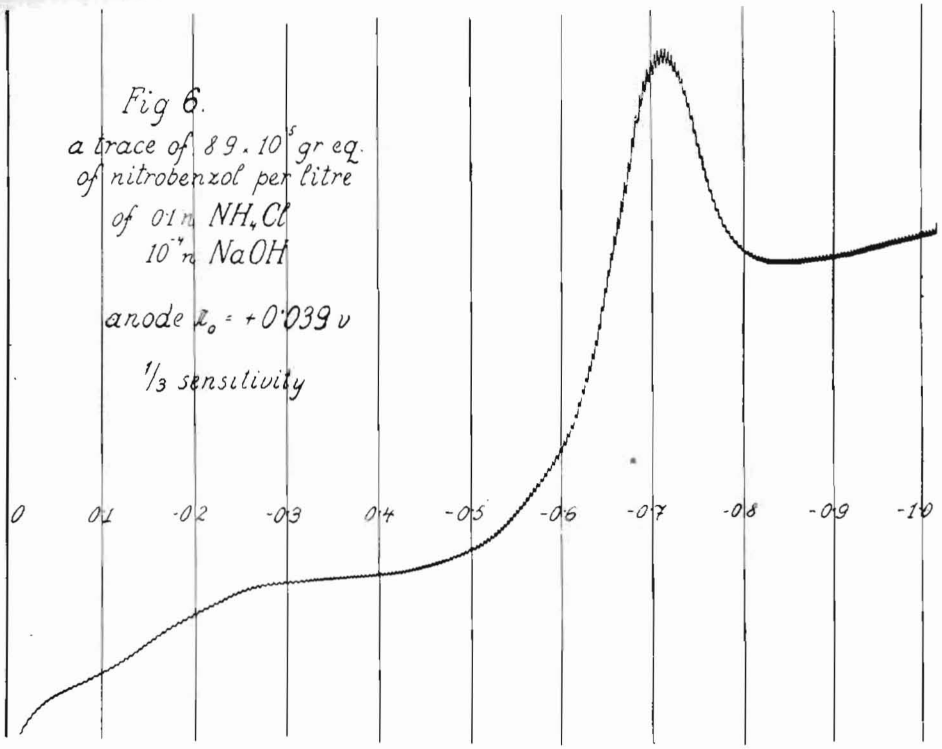

Fig 6.

a trace of $8\ 9 \cdot 10^{5}$ gr eq.
of nitrobenzol per litre
of $0{\cdot}1\,n$ NH_4Cl
$10^{-4}\,n$ $NaOH$

anode $\pi_0 = +0{\cdot}039\ v$

$1/3$ sensitivity

Plate 4.

537.33 : 541.13

RESEARCHES WITH THE DROPPING MERCURY CATHODE

BY

J. HEYROVSKÝ.

PART III.

A Theory of Over-potential.

The reason why the most positive metals, like the alkali metals, can be deposited at the mercury cathode without being attacked by water yielding hydrogen is certainly due to the high over-potential [1]), at which hydrogen is evolved at a fresh surface of pure mercury. Thus a fundamental phenomenon which has to be discussed in the dropping cathode processes and is conveniently studied in this arrangement, is the change of the overpotential with the hydrion concentration.

The natural and most widely accepted explanation of the hydrogen over-potential, which seems to be a specific hindrance of metals to the gas-bubble formation, is that metals catalyse to very different extents the joining of the hydrogen atoms into molecules.

Such a process, if proceeding in the simplest manner, i. e. as

$$2\ H \twoheadrightarrow H_2,$$

would lead to a change of hydrogen deposition potentials with the concentration of hydrions according to the formula:

$$\pi - \pi' = \frac{RT}{F} \log \frac{c}{c'}$$

if c and c′ are the different hydrion concentrations. This can be deduced by assuming the velocity with which molecular hydrogen is formed from the atoms to be proportional to the square of the pressure of atomic hydrogen, P_H, at the cathode and that this reaction velocity determines the current intensity, i; thus $i = K \, . \, P_H^2$.

The pressure of atomic hydrogen at the electrode is connected with the potential of the polarised drop, π, and the hydrogen concentration, c, by the formula

$$\pi = -\frac{TR}{F} \log \frac{P_H}{c};$$

---

[1]) Overpotential here means the difference between the potential at which hydrogen begins to evolve and the potential of the reversible hydrogen electrode in the same solution.

substituting the value of P_H from this formula in the expression for i and differentiating, the equation

$$\frac{di}{d\pi} = \left(-\frac{2\,F}{RT}\right) . \, e^{-\frac{2\pi F}{RT}} . \, c^2 . \, K$$

is obtained. From this relationship it can be deduced (in a similar manner to the deduction in part I) that when the hydrion concentration changes from the concentration c to c′, the deposition bend will be displaced by

$$\pi - \pi' = \frac{RT}{F} \log \frac{c}{c'},$$

i. e. by 58 millivolts for a ten-fold dilution. At the dropping mercury cathode, however, the hydrogen deposition potential has always been found to be displaced by twice that amount, namely by 116 millivolts for a tenfold dilution [2]). Hence another mechanism of the molecular formation of hydrogen must be postulated in order to explain these abnormally large deposition shifts. Consider the process

$$H^+ + H' \longrightarrow H_2,$$

which also gives rise to neutral (gaseous) hydrogen molecules and, as will be shown leads to deposition potential displacements which are twice those calculated from the older theory.

The process can be imagined to proceed so that some of the hydrogen atoms deposited associate with electrons at the negatively charged mercury cathode, forming a negatively charged hydrogen atom, i. e. the ion H′. At the mercury surface these H′ particles join immediately the hydrions of the solution forming molecular hydrogen much more rapidly than is possible from two uncharged hydrogen atoms.

The idea of H′ particles is by no means novel; the evidence for their existence being furnished by canal ray analysis and by the electrolysis of fuzed lithium hydride [3]).

Thus the increase of hydrions in the solution not only facilitates the deposition of atomic hydrogen but also favours the velocity of formation of the molecular hydrogen, so that the total effect of the hydrion increase is a double one, leading to deposition potential shifts

$$\pi - \pi' = \frac{2\,RT}{F} \log \; c/c'.$$

This may be deduced from the velocity of the reaction

$$H^+ + H' \longrightarrow H_2,$$

which determines the rate of the evolution of hydrogen, i. e. the current intensity; this gives

$$i = K . [H'] . c$$

where c is the concentration of hydrions in solution at the mercury-

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[2]) Comp. the following paper of P. Herasymenko, part IV.

[3]) Moers, Z. anorg. allgem. Chem. 113, 179 (1920).

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solution interface, and [H′] the
charged hydrogen atoms, which ar
surface from the atomic hydrogen
of the negatively charged electr
union of the atoms of hydrogen in
of the process here discused is re
tials — as negligible. To find the
consider them as being in equilibri
which form them according to the
the law of mass-action to electr
their active mass has to be taken
equivalent, which follows from th
H. Lorentz and A. D. Fokker [4])
energy of one Faraday of the gas

$$[H'] = K' .$$

The concentration of the electron
in the drop surface and this can b
negative potential, π, of the drop.

Then $$[H'] = K' .$$

During the range of the overpot
between the limits 0.9—1.8 volts
$\pi^{0.04}$ can be regarded as practicall
the "absolute zero" of the poten
normal calomel electrode potential.

Writing for $\pi^{0.04} . K'$ simply

and substituting P_H from the rel

$$[H'] = k . c$$

so that $$i = K . c . [H'] =$$

This gives the increase of curren
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solution, having a concentration c
tangent of a certain slope, $\frac{di}{d\pi}$, to t

$$\frac{di}{d\pi} = k' . c^2 . \Big(-$$

In another solution (concentrati
slope corresponds to a potential

$$\frac{di}{d\pi} = k' . c'^2 . \Big(-$$

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[4]) Bericht Solvay, 1911; Abh. Bunsen.
Sci. [3] 4, 394 (1918).

solution interface, and $[H']$ the concentration of the negatively charged hydrogen atoms, which are formed on the mercury cathode surface from the atomic hydrogen in contact with the free electrons of the negatively charged electrode. The reaction velocity of the union of the atoms of hydrogen into molecules against the velocity of the process here discused is regarded — in mercury overpotentials — as negligible. To find the concentration of the particles H′ consider them as being in equilibrium with the atoms and electrons which form them according to the law of mass action. In applying the law of mass-action to electrons it must be remembered that their active mass has to be taken as 1/25th that of their chemical equivalent, which follows from the "electron gas" treatment of A. H. Lorentz and A. D. Fokker 4) according to whom the volume energy of one Faraday of the gas is 0.0417 RT. Thus

$$[H'] = K' . P_H . [\varepsilon]^{0.04}.$$

The concentration of the electrons at the cathode is their density in the drop surface and this can be regarded as proportional to the negative potential, π, of the drop.

Then
$$[H'] = K' . P_H . \pi^{0.04}$$

During the range of the overpotential measurements, which varies between the limits 0.9—1.8 volts from the calomel zero, the term $\pi^{0.04}$ can be regarded as practically constant, even when admitting the "absolute zero" of the potentials to be at —0.56 v. from the normal calomel electrode potential.

Writing for $\pi^{0.04} . K'$ simply k, $[H'] = k . P_H$

and substituting P_H from the relationship $\pi = -\frac{RT}{F} \log \frac{P_H}{c}$,

$$[H'] = k . c . e^{-\frac{\pi . F}{RT}}$$

so that
$$i = K . c . [H'] = k' . c^2 . e^{-\frac{\pi F}{RT}}.$$

This gives the increase of current due to the evolution of hydrogen at the potential π. The turning point of the polarisation curve of a solution, having a concentration c of hydrions, is determined by the tangent of a certain slope, $\frac{di}{d\pi}$, to the polarisation curve;

$$\frac{di}{d\pi} = k' . c^2 . \left(-\frac{F}{RT}\right) . e^{-\frac{\pi F}{RT}}.$$

In another solution (concentration c′) the tangent of the same slope corresponds to a potential π', given by the relationship

$$\frac{di}{d\pi} = k' . c'^2 . \left(-\frac{F}{RT}\right) . e^{-\frac{\pi' . F}{RT}}.$$

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4) Bericht Solvay, 1911; Abh. Bunsen. Ges. No. 7, 32 (1914); Arch. Néerland. Sci. [3] 4, 394 (1918).

Hence $\left(\frac{c}{c'}\right)^2 = e^{\frac{(\pi-\pi')\,F}{RT}}$ or $\pi-\pi' = \frac{2\;RT}{F}\log c/c'$.

Thus, as has been stated above, the displacement of the deposition potential is twice that calculated from the older conception of the reaction mechanism.

It has to be remembered, that the mechanism of the formation of hydrogen molecules, such as proposed here, will lead at cathodes of a material having a small overpotential to a smaller velocity than that of the union of atomic hydrogen to molecules. Under such conditions (of small overpotential) the decisive reaction for the evolution of hydrogen will be the joining of neutral atoms, which will lead to the ordinary RT/F log c/c′ shifts of the deposition potentials, as required from simple reversible concentration cells.

The theory here given thus applies only to the hydrogen evolution on metals with high overpotentials such as zinc, lead, tin, thallium, besides mercury.

SUMMARY.

From the conception that the mechanism of the formation of molecular hydrogen is the union of H^+ with H′, it is deduced, that the change of the potential, at which hydrogen begins to be evolved, should increase with dilution according to the expression 2 RT/F log c_1/c_2, in other words that the *overpotential* increases with dilution by RT/F log c_1/c_2.

(Reçu le 7 févr. 1925.)

RESEARCHES WITH TH
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Changes in overvoltage with

B

P. HERAS

In the previous paper (part III
assumed that the abnormally large d
observed with dilution of acids at
the hydrogen formation according
. Making this assumption the fo
hydrogen deposition potentials wa
displacements should be equal to

$$\frac{2\,RT}{F}\ \text{lo}$$

In connection with the electroly
“overvoltage” or “overpotential”
this term different significations.
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which hydrogen begins to be evol
the electrode potential of the rev
in the same solution. The value o
the polarisation curve shows a tu
“deposition potential”.

For the changes of overvoltag

$$\omega_1 - \omega_2 =$$

follows evidently from the previo
The present investigation furnis
the formulae for the dropping me
The study of electrolytic proces
following advantages which have sp
of overvoltage:

1. the concentration polarisatio
2. the processes are observed

This cannot be reached in the or

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[1] J. Heyrovsky′, Trans. Faraday Soc.