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RESEARCHES WITH THE DROPPING MERCURY CATHODE

PART II.

The Polarograph

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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. 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]).

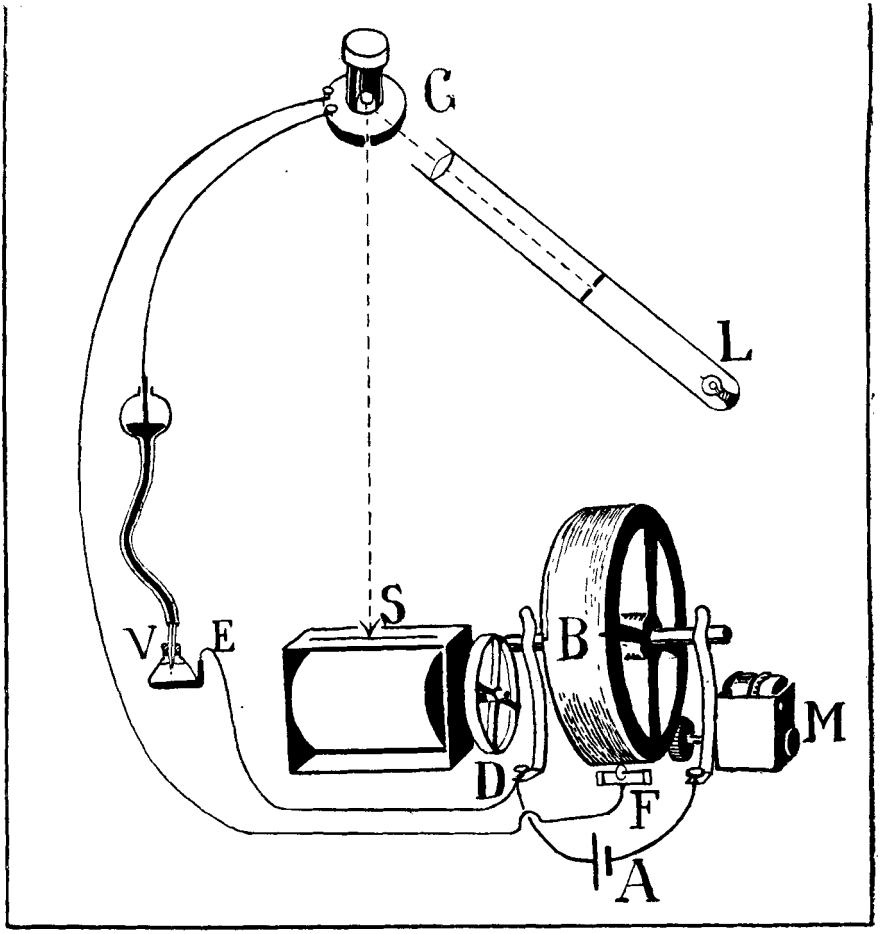

Fig. 1.

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.)

[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 $^0/_0$.

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.

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

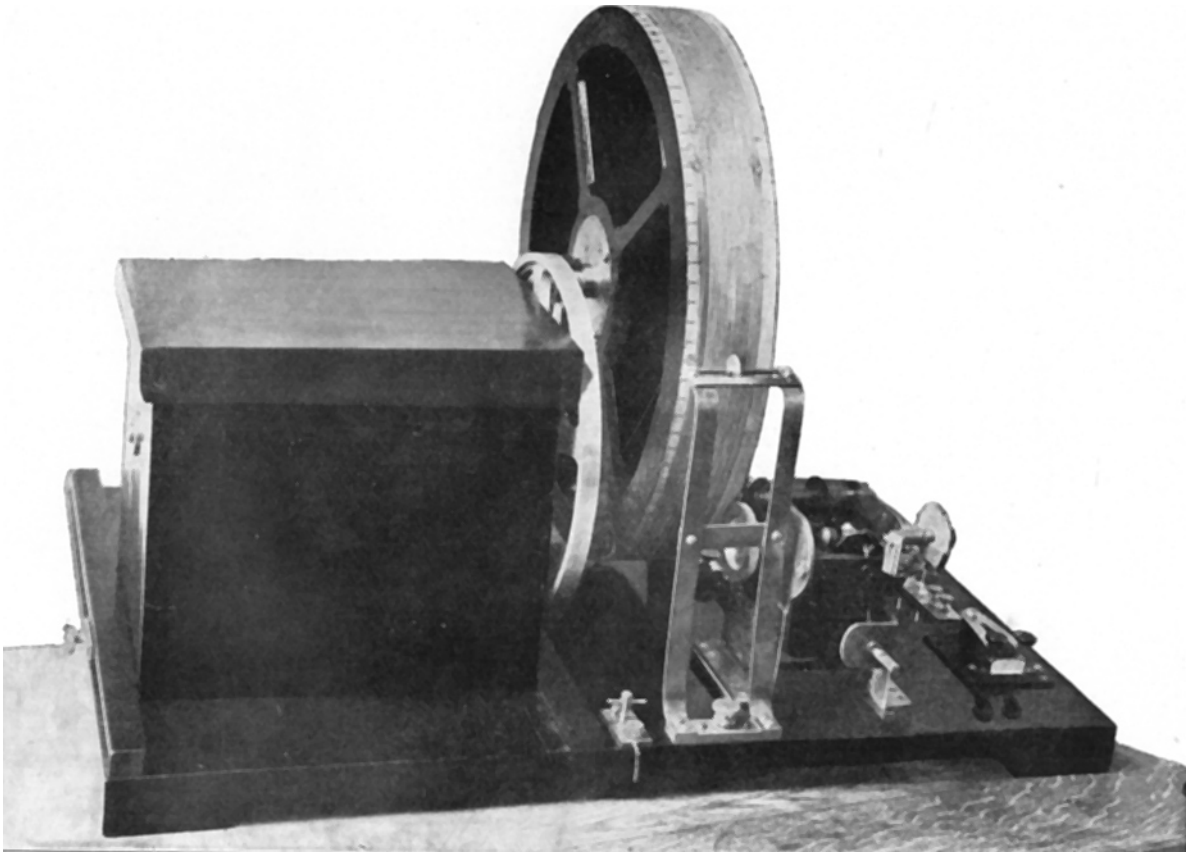

Plate 1.

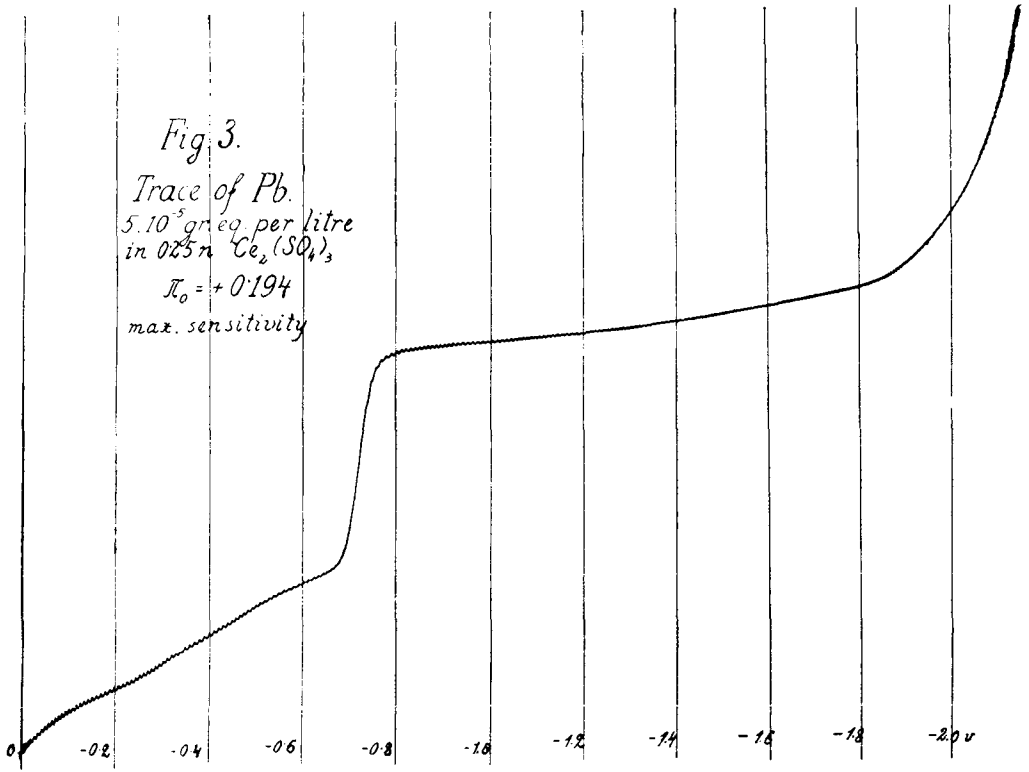
Fig. 3.
Trace of Pb.
5.10⁻⁵ gr. eq. per litre
in 0·25 n Ce₂(SO₄)₃
π₀ = + 0·194
max. sensitivity
0
-0·2
-0·4
-0·6
-0·8
-1·0
-1·2
-1·4
-1·6
-1·8
-2·0 v

Plate 2.

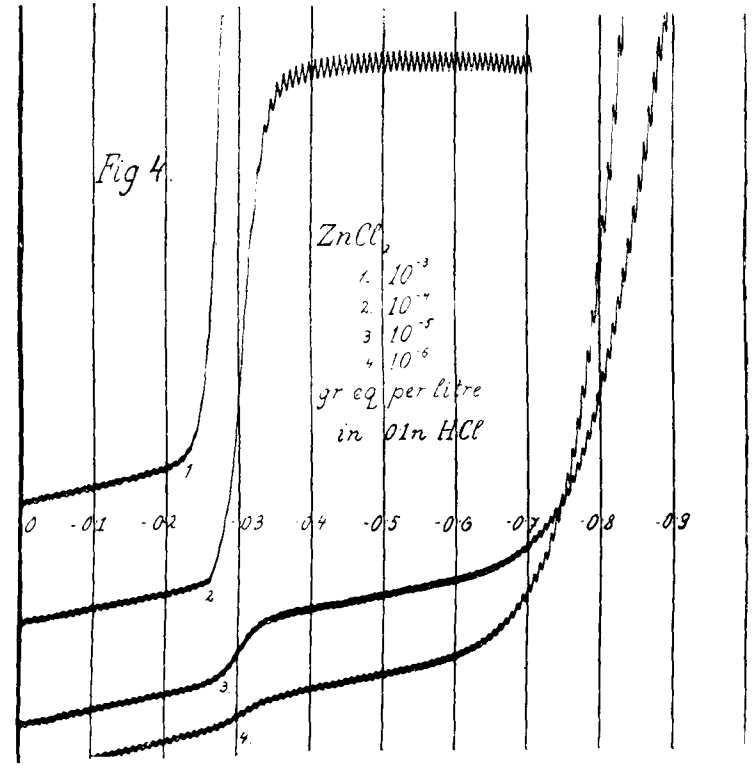
Fig 4.
$ZnCl_2$
1. 10^{-3}
2. 10^{-4}
3. 10^{-5}
4. 10^{-6}
gr eq per litre
in 01n HCl
0 -01 -02 -03 -04 -05 -06 -07 -08 -09
1
2
3
4

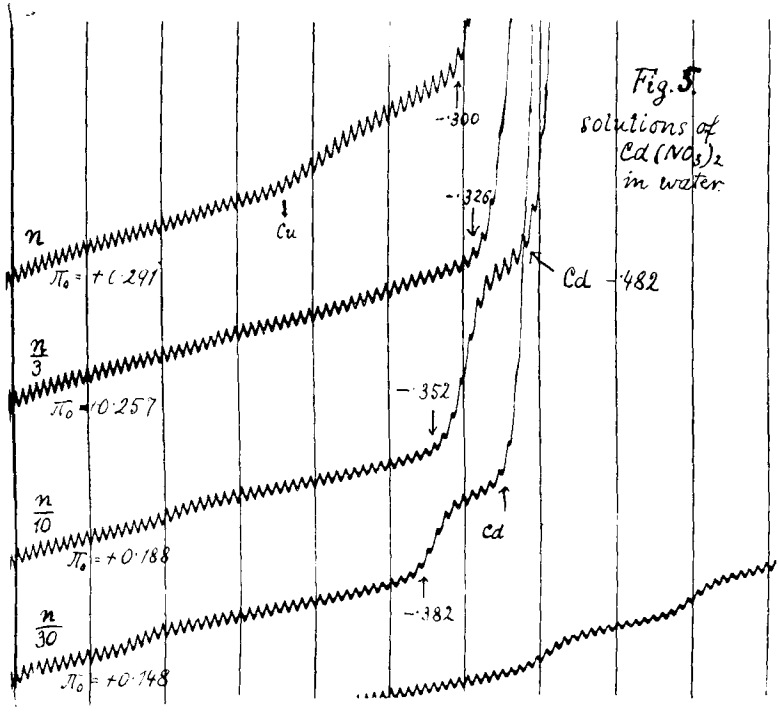
Fig. 5.
solutions of
$Cd(NO_3)_2$
in water
n
π_0 = +0·291
$\frac{n}{3}$
π_0 = 0·257
$\frac{n}{10}$
π_0 = +0·188
$\frac{n}{30}$
π_0 = +0·148
Cu
Cd
cd
-·300
-·326
-·352
-·382
-·482

Plate 3.

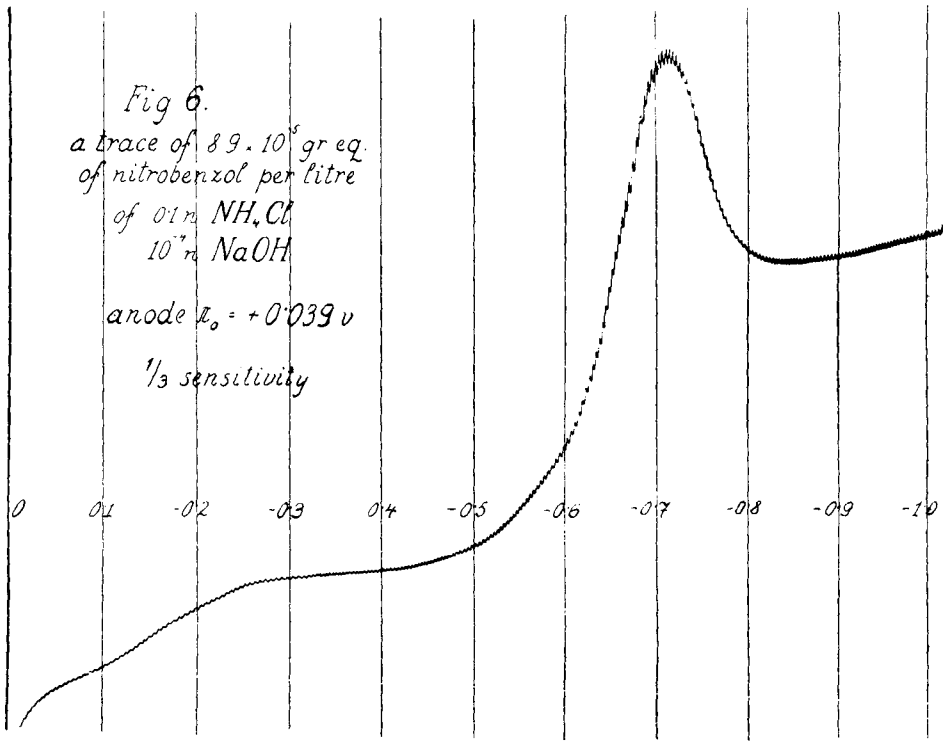
Fig 6.
a trace of 8·9 . 10⁻⁵ gr eq.
of nitrobenzol per litre
of 0·1 n NH₄Cl
10⁻⁷ n NaOH
anode E₀ = + 0·039 v
1/3 sensitivity
0
-0·1
-0·2
-0·3
-0·4
-0·5
-0·6
-0·7
-0·8
-0·9
-1·0

Plate 4.