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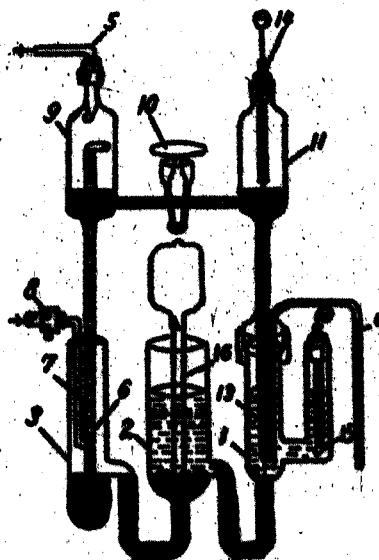
A Streaming Mercury Cathode

Mercury cathodes in the form of a jet are used for preparative purposes in electrochemistry, for preparing metal amalgams [1] for the electro-reduction of organic compounds [2], for studying the mechanism of cation discharge [3] and in oscillographic polarography [4].

The set-up which we have constructed, which includes a streaming mercury cathode, is depicted in Fig. 1. Chemically pure mercury is contained on the bottoms of the three connected vessels 1, 2 and 3.¹⁾ 11 is connected via a tap 10 to 9; 9 can be evacuated by means of a water jet pump, connected to tube 5. Mercury from the

Fig. 1. Set up for streaming mercury cathode.

1) electrolyzer; 2) partition for decomposition of the amalgam; 3) mercury receiver; 6) tube for leading mercury into 9; 7) T-piece with valve 8 for leading in nitrogen; 5) connecting tube to water pump; 10) tap; 11) bulb for passing mercury to the electrolyzer; 13) capillary tube; 15) anode; 4) electrolytic switch for electrode comparison.



bottom of 3 rises in tube 6 up to the T-piece junction at 7. By the action of a stream of nitrogen, sucked through valve 8, the mercury column in tube 6 breaks up into separate parts and is sucked into 9. After filling 9 with sufficient mercury, the vacuum is switched off and tap 10 is opened; the mercury flows in 11 and from there along capillary tube 13 in a jet into 2 (the electrolyzer).

The set-up subsequently works automatically by switching on the vacuum. The amalgam formed by cathodic polarization of the mercury jet flows from 1 into 2, where it is decomposed by means of acid and is mechanically stirred with a glass stirrer 16. The mercury goes from 2 to 3, from which it again rises into 9, etc.

Thus in the apparatus described the same mercury is used over and over again for obtaining a continuous jet of mercury, which serves as a cathode for an indefinite time.

¹⁾ For methods of purifying mercury see [5].

The negative pole of the current supply source is connected to the platinum contact 14, while the platinum anode is fixed in the side tube 15. The potential of the streaming cathode is measured during polarization by reference to a saturated calomel electrode by the usual compensating system. The distance of the end of the electrolytic switch from the mercury surface is fixed because the switch and the capillary tube 13 are fused into the cover.



Fig. 2
Restriction
of the lower
end of the
jet.

It was observed that with increasing current density the jet does not remain constant but increases. Under the action of the current the jet breaks up into small drops, the place at which the break up occurs however cannot be established even under strong magnification. In some essential cases (e.g. for calculating current density) the lower end of the jet can be confined with the help of a little shaft, fused into the cell wall (Fig.2)¹⁾.

An Apparatus with a Renewable Flat Cathode

Of all the apparatuses described hitherto which have a renewable mercury cathode [5,8], the Hildebrand cell is the most often used in electroanalysis [9]. We found that during the electrolysis of weak solutions of metals which can form amalgams, this apparatus does not always ensure good results in the sense that the separation of the metal is complete and pure.

This can be explained by a) an insufficiently intense exchange of mercury between the two separation cells, which leads to a change in the deposition potential of the metal as the result of an increase in its concentration in the amalgam located in the cathode compartment; b) the penetration of undecomposed electrolyte into the compartment used for the decomposition of the amalgam.

These drawbacks have been eliminated in the apparatus depicted in Fig. 3. The mercury is located at the bottom of the two vessels 1,2 which are doubly connected, 2 serves as the electrolyzer in which the mercury on the bottom serves as a cathode; the anode is separated from the catholyte by a porous diaphragm 5. When the stirrer 6 in the form of a corkscrew is rotated, the mercury in tube 7 is pumped up into 1, in which its level becomes higher than that in 2, so that there is a flow from 1 into 2 via 8. The renewal of the cathode surface in 2 is also assisted by stirrer 9 driven by the motor 12 by a pulley attachment. The length of the vertical parts of tubes 7 and 8 is sufficient to hinder the penetration of the electrolyte from 2 into 1, where the amalgam is decomposed. The decomposition velocity of the amalgam can be increased by anodic polarization from an independent D.C. supply (e.g. a dry 1.5-2 volt battery); a platinum-tin electrode immersed in the electrolyte in 1 serves as the cathode in this case.

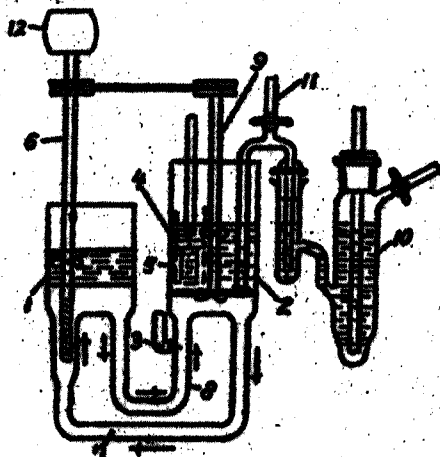


Fig. 3. An apparatus with a renewable flat cathode. 2) electrolyzer; 3) platinum contact; 4) anode; 5) porous diaphragm; 1) compartment for decomposition of amalgam; 6) corkscrew stirrer; 7-8) tubes for mercury flow and amalgam; 9) glass stirrer; 11) electrolytic switch; 10) standard electrode; 12) motor.

1) The streaming mercury cathode has the following advantages over a flat cathode a) the possibility of polarizing with a large current strength without appreciable heating of the solution as a result of Joule heating; b) lower concentration polarization because of the vigorous stirring of the solution by the mercury jet [7].

The cathode potential is standardized against an electrode suitable for any particular set of experimental conditions. A suitable form is shown in Fig. 3.

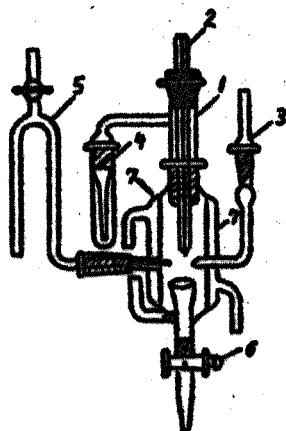


Fig. 4. Cell for polarographic analysis. 1) tube on a rod for strengthening the capillary electrode; 2,3,4) inlet and outlet tubes for hydrogen; 5) electrolytic switch; 6) outlet tap for mercury; 7) water jacket

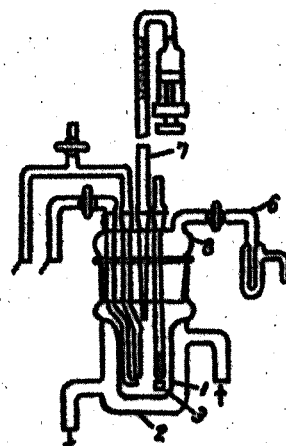
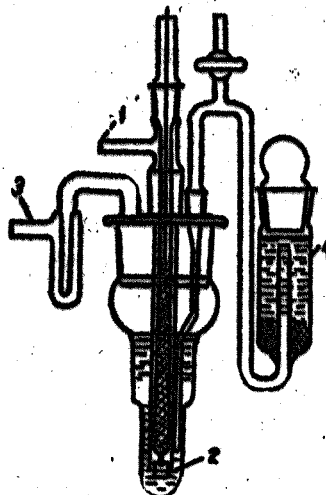


Fig. 5. Cell for potentiometric titration. 1) working volume (constricted part); 2) water jacket; 8) ground glass cover with tubes; 4,6 inlet and outlet tubes for nitrogen; 3) reference electrode; 5) electrolytic switch; 7) microburette.

Fig. 6. A cell for pH determination by means of a hydrogen electrode. 1,3) inlet and outlet tubes for hydrogen; 2) platinum electrode; 4) saturated calomel electrode



Apparatus for Polarographic and Potentiometric Analysis 1

a) A cell is shown in Fig. 4 which can be used for polarographic analyses with both external and internal anodes. In the latter case the potential of the mercury drop is measured by reference to a saturated calomel (or some other reference electrode) by means of the electrolytic switch 5. Capillary 2 is fixed on to a rubber cork, which is separated adequately from the solution in the cell. This separation is important in order to avoid contamination of the solution and deformation of the polarograph wave by the action of surface active materials. [10]. The cell is thermostated by means of a jacket fused on to it, through which water heated to the required temperature in a Heppler thermostat is circulated.

b) Normally for potentiometric titration in an inert atmosphere all the details are mounted on the cork on a support [11]. Such a method is extremely inconvenient, particularly when working with very small volumes of solution, since it leads to accidents to some of the parts, and also to contamination from rubber connections, etc., when working with heated solutions, etc.

An apparatus is depicted in Fig. 5 in which all the details are mounted on a ground glass cover. 1-2 ml solution can be dealt with in the constricted lower part of the cell. In order to measure the potential accurately, two platinum electrodes are fixed into the cover, from the readings of which the average values are taken.

The apparatus is thermostated in the same way as described in apparatus (a).

c) When a pH is determined by means of a hydrogen electrode (Fig. 6) there is no need to thermostat the apparatus since the temperature corrections can be calculated from a well known formula [12].

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