Polarographic Cells with Fused-in Capillaries

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Synopsis—Two new types of all-glass polarographic cells with included capillaries and connections to reference electrodes are described. One type is designed to be specially suitable for operation in a thermostat bath.

The two polarographic cells, Types A and B, described in this paper were designed as units in which all the parts were to be permanently connected. Although they are quite different in design, each embodies a fused-in capillary, a connection through a liquid junction to a standard half-cell, provision for de-oxygenation of solutions by nitrogen gas in a delivery funnel fitted with a seal and not in the dropping electrode compartments, and means for washing the whole of the interior of the cell *in situ* and for withdrawing mercury drops for weighing.

The fused-in capillary was introduced to obviate the need for insertion and removal of a capillary each time a fresh solution was examined, and to protect the capillary from mechanical damage and contamination. The cells can, however, be used with capillaries inserted through small bungs or ground-glass connections by a minor modification of the design.

Type A

The apparatus shown in Fig. 1 depends on the use of a second mercury reservoir for filling and emptying the cell. It is simple to operate but the apparatus does not readily lend itself to insertion in a thermostat bath. The liquid junction between the polarographic cell and a calomel electrode is formed by Coates's method.[1] The mercury that passes through the capillary in a given time can be withdrawn from the bottom of the cell by a turn of the double-bored tap.

The dropping electrode vessel, A, with capillary, B, and stand tube, C, for accurate reading of the pressure of mercury at the capillary tip, has an internally-sealed nitrogen-inlet tube fitted with a tap, T_1, which can be turned so as to establish connection with nitrogen or with the atmosphere, and a double-bored tap, T_2, one outlet of which is joined with flexible tubing to a mercury reservoir, E, and the other can be used for withdrawing mercury drops for weighing.

At the top of A a side tube, G, so arranged that no dead space is left in the cell after filling, passes to the three-way tap, T_3, which is connected also to the delivery funnel, H, fitted with a stopper, preferably a ground-glass connection, carrying a bent tube and inverted funnel dipping into sodium sulphite solution (to prevent diffusion of oxygen through the seal), and to the double-bored tap, T_4, through the liquid junction tube, J. One outlet of tap T_4 is for draining off the waste liquid from the cell after use; the other outlet is connected by means of a ground-glass joint or a short rubber tube to the upturned delivery tube of the calomel electrode vessel, K, containing 3·5 *N* potassium chloride. The side arm of the stand tube, C, is connected by plastic tubing to the reservoir, F, containing pure mercury for the capillary electrode, B.

OPERATION—

By suitably turning taps T_3 and T_4, and tap T_5 of the potassium chloride reservoir of the calomel electrode, allow a little of the potassium chloride solution to flow into the junction tube, J. Then turn tap T_4 through 180° and allow the junction tube to empty. Raise the mercury reservoir, E, and turn taps T_2 and T_3 so that any electrolyte in the cell is driven into the delivery funnel, H, and then out to waste through tap T_4. Fill the funnel, H, with water, allowing some water to run to waste through T_4 before closing this tap. Lower the mercury reservoir, E, in order to fill the cell with water, and then expel the water by raising

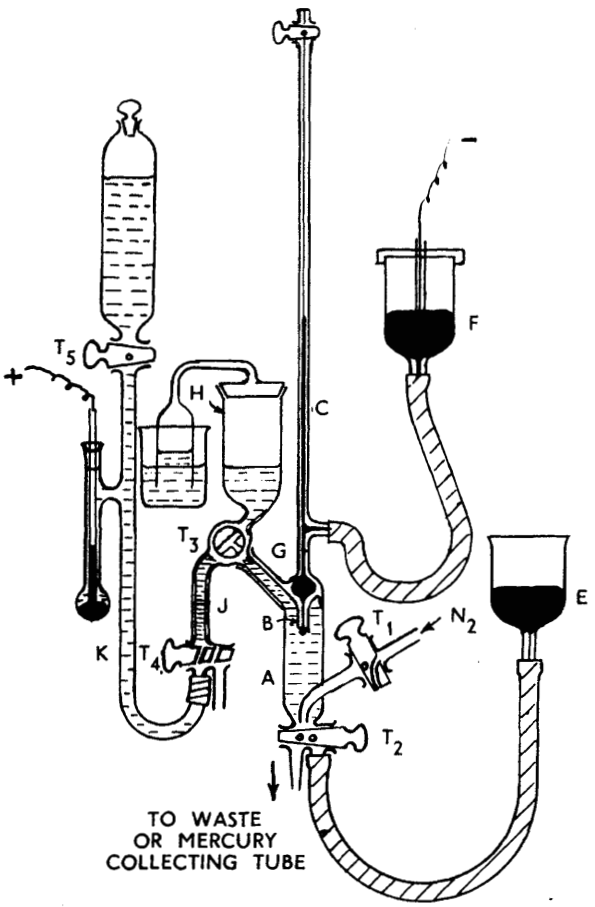

Fig. 1. Polarographic cell with fused-in capillary and mercury-operated filling.

the reservoir and allowing the water to run to waste through T_4. Wash the cell in this manner two or three times and leave it empty. Pass a stream of nitrogen through tap T_1, place the solution to be examined in the funnel H, insert the stopper and de-oxygenate the solution in the funnel with tap T_3 turned so as to make connection only between the funnel and the cell. After a suitable time, close tap T_1 and turn tap T_2 so that any mercury above it flows to waste, and a little of the electrolyte from H washes out the cell. Then turn tap T_2 through 180°, turn T_1 to connect with nitrogen, raise the mercury reservoir, E, and allow the mercury to rise and make contact with the solution in the funnel, the nitrogen in the cell being forced out through the solution. Close tap T_1, leaving some mercury in the tube, lower the reservoir and bring the solution into the cell. Close tap T_2. When it is desired subsequently to weigh a number of mercury drops, allow the mercury in the side tube below T_1 to be replaced by electrolyte by forcing some of the electrolyte up the tube and then letting the mercury run down into the cell, and then out through T_2. Turn tap T_3 so that connection is made in three

directions, fill tube J, allowing a little of the de-oxygenated electrolyte to flow to waste through tap T_4, and then turn taps T_4 and T_5 so that the 3·5 *N* potassium chloride rises a centimetre or so in tube J. Leave taps T_1 and T_2 closed, while tap T_4 establishes contact between the calomel electrode and the liquid in J, and tap T_3 establishes contact between the liquid in J and that in the funnel and in the cell. The apparatus is now ready for the recording of a polarogram.

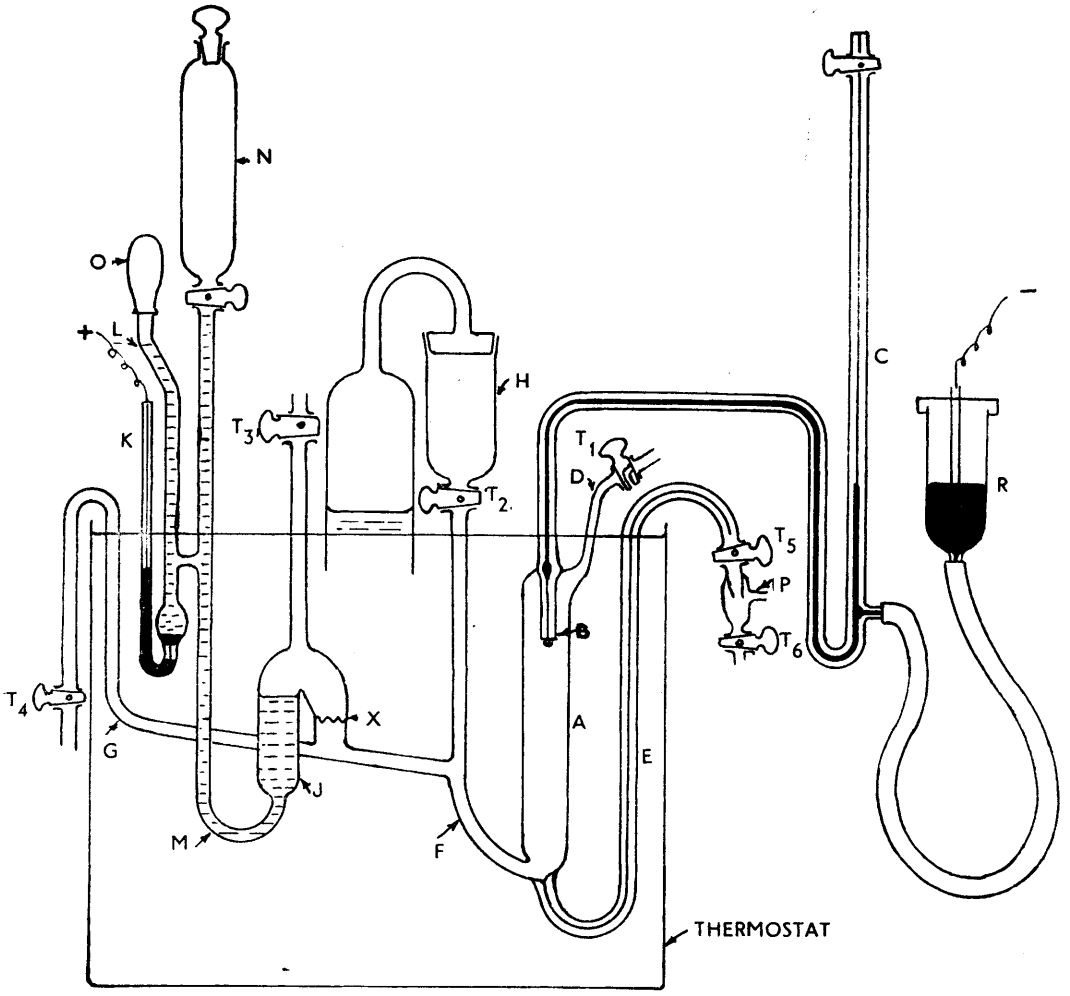

Fig. 2. Polarographic cell with fused-in capillary designed for use in a thermostat.

After use wash out the cell with water as described above. Raise the reservoir, E, so as to cover the capillary tip with mercury, and turn a tap (not shown) at the bottom of the other reservoir, F, to stop the flow of mercury through the capillary. By this means water does not get sucked into the capillary, as frequently occurs when the mercury reservoir attached to a capillary dipping into water is lowered to stop the flow of mercury.

Polarography with a mercury pool anode instead of the calomel electrode may be carried out with this apparatus if an electrical connection is made to E and tap T_2 is suitably turned.

Type B

The apparatus shown in Fig. 2 was designed to facilitate the measurement or control, or both, of all important factors in polarographic work, *e.g.*, constancy of temperature, de-oxygenation in absence of mercury, accurate establishment of potential *versus* a standard

reference electrode, freedom from contamination by substances extracted from rubber stoppers, and so on, and measurement of rate of flow of mercury under the actual conditions of an experiment, coupled with simple means for filling, emptying, and washing out the cell, and for making liquid connection with a reference electrode. The apparatus can be accommodated in a 600- or 1000-ml. beaker. The method of forming the liquid junction follows that described recently elsewhere.[2] The dropping and calomel electrodes are immersed in the bath liquid, but all the operating taps are outside.

The dropping electrode vessel, A, contains the fused-in capillary, B, connected to a stand tube, C. To it are joined the nitrogen-inlet tube, D, fitted with a tap, T_1, which can be turned so as to establish contact either with nitrogen or the atmosphere, the narrow bore tube, E, used for removal of the mercury that collects at the bottom of the cell, and the tube F which provides connection through tap T_2 to the delivery funnel, H, and also to the liquid junction tube, J, and to waste, G. The waste tube, G, terminates in a siphon tube with tap T_4 to which slight suction can be applied when necessary. The narrow bore tube, E, leads to tap T_5 with delivery into a wider tube fitted with a side tube, P, for application of suction, and a tap, T_6. The calomel electrode, K, consists of a tube, L, holding the calomel electrode proper, joined to the delivery tube, M, of a tap-funnel, N, containing 3·5 *N* potassium chloride. The delivery tube, M, is bent upwards and joined to a somewhat wider tube, J, which has a sharp downward bend near the top for connection at X by means of a fused joint, ground-glass joint, or rubber tubing to a short tube fused on to the waste tube, G. The upper part of tube J carries a tube terminating in a tap T_3. The top of tube L is closed by means of a rubber teat, O. The delivery funnel, H, is fitted with a stopper, preferably with a ground-glass joint, carrying a bent tube connected to an inverted funnel dipping into sodium sulphite solution. The side arm of the stand tube, C, is connected by plastic tubing to the reservoir, R, containing pure mercury.

OPERATION—

Allow potassium chloride solution to run into tube J from N until the level of liquid is just below the bend, as shown in Fig. 2. Remove air from A and the connecting tubes by passing nitrogen gas through tap T_1 and out through taps T_2, T_3 and T_4, and then close these taps. Place the solution to be examined in the delivery funnel, H, and de-oxygenate it by passing nitrogen gas through the empty cell A and up through tap T_2. After passage of gas for a few minutes, allow the vessel A to fill by turning tap T_1 so that the nitrogen in A is forced out through the barrel of this tap. Then turn tap T_1 again so that the cell is closed at the tap. With tap T_2 still open, cautiously open tap T_3 to allow the electrolyte to pass along tube G and flow gently into tube J on top of the more dense 3·5 *N* potassium chloride. Connection has now been established between the dropping electrode vessel and the calomel electrode, and the apparatus is ready for the taking of a polarogram.

To withdraw mercury drops for weighing, apply suction at P with tap T_5 open and tap T_6 closed. A convenient method of applying suction is by connecting P to a partially evacuated vessel. The mercury that collects above tap T_6 can be run off into a vessel such as that described previously,[3] and then washed and weighed.

After use close tap T_2, apply gentle suction at T_4, open tap T_3, flush out the junction liquid with potassium chloride solution from the reservoir N, close the reservoir tap, and finally squeeze the teat so that the level in tube J is left just below the bend. Open tap T_2 and let the electrolyte in H flow away through T_4. Open tap T_1 so that the electrolyte in A is driven through G to T_4 by the pressure of nitrogen. Then wash out the cell two or three times by placing water in H, filling and emptying A, etc., as described above. Provided that tap T_3 is kept closed, the liquid used for washing cannot come into contact with the potassium chloride solution in J. Finally de-oxygenate some water in H and allow it to flow into A and cover the orifice of the capillary, and lower the mercury reservoir until dropping stops.

With a second connection similar to that at X on tube G it would be possible to have alternative reference electrodes. Both could be left permanently in position, but only the one required for any particular purpose would be brought into operation. Thus, if polarography in a medium of concentrated calcium chloride solution were necessary, a *N* calomel electrode might be used and the liquid junction formed by flowing the lighter liquid from the calomel electrode reservoir on to the top of the calcium chloride which had been allowed to go no further than the bend on the right-hand side of tube J.

This paper is published by permission of the Ministry of Supply. The apparatus described as Type B forms part of the subject-matter of Patent Specification No. 14306/49, dated May 27th, 1949.

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