

THE GLASS PARTS OF POLAROGRAPHIC APPARATUS

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The glass parts of polarographic apparatus — cells, capillaries, etc. — supplied with commercially available polarographs are not suitable enough. Even such an advanced apparatus as the Énergohermet TsLA recording polarograph [1] is provided with a cell with an internal (not isolated from the test solution) anode which does not have a jacket for thermostating the apparatus. The capillaries supplied with this polarograph for the dropping electrodes do not enable one to use the apparatus to its best advantage. Actually, the large dropping period of these electrodes compels one to damp the apparatus; this leads to a sharp increase in the inertia of the following system and to considerable distortion of the shape of the polarographic curves. This had led us to publish details of a considerably more convenient, in our opinion, design for the glass parts of the polarograph, a design which has been used in our Institute for several years.

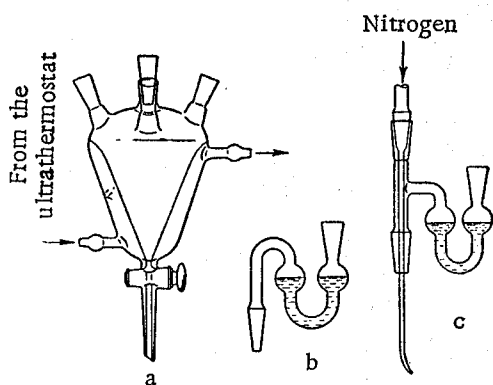


Fig. 1. Polarographic cell (a) and water seals (b and c).

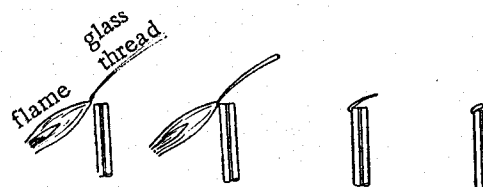


Fig. 2. The method used for fusing the blade onto the capillary tip.

The cell (Fig. 1a) is a conical vessel with a jacket which can be thermostatted by means of an ultrathermostat of the Heppler type or the TS-15 type. The lower, narrower end of the cell is provided with a tap for running off mercury or solution; the upper part of the cell has five inlets with normal ground-glass joints (NSh 10). The central inlet is for introducing the capillary of the dropping electrode, the two side inlets for the anode and the reference electrode, the other for a capillary through which nitrogen is supplied, and, finally, the last inlet is used for introducing the test solutions, and is usually sealed with a water-seal (Fig. 1b), through which the nitrogen escapes to the atmosphere.

Sometimes — with the aim of freeing one inlet, e.g., for connecting a buret so that there is no access to atmospheric oxygen — it is necessary to connect the inlet and outlet for the nitrogen into one. In such a case, the capillary for the nitrogen is placed in the cell through a socket provided with a water seal (Fig. 1c). The cell is supported on a stand by placing it in a rubber ring stretched over a metal ring, a small piece of the latter being sawed out so that it is possible to slip the rubber tubing over it. In order to fix the cell firmly in position, a rubber bung is fitted onto the stem of the cell, and this bung is clamped in a boss and clamp-fitted to the same stand.

Dropping electrode. The most convenient type of electrode, both for analytical and research purposes, is a dropping electrode in which the drop is forced to drop off by coming into contact with a small blade [2]. The capillary of the electrode is prepared by drawing out a thermometer tube so that the length of the working (narrow) part amounts to 40-80 mm, while the diameter of the canal is 30-60 μ . The blade is fused on as follows. Air or nitrogen is passed continuously through the canal. The capillary tip, that part to which the blade is to be fused, is introduced into the small sharp flame of a blowpipe; simultaneously, into the flame is introduced a capillary tube of the same glass, drawn out beforehand into a thread (diameter about 0.1 mm) (Fig. 2a). As the thread

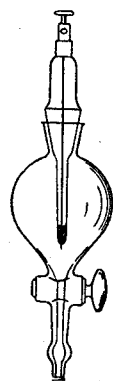


Fig. 3. Supply reservoir of mercury.

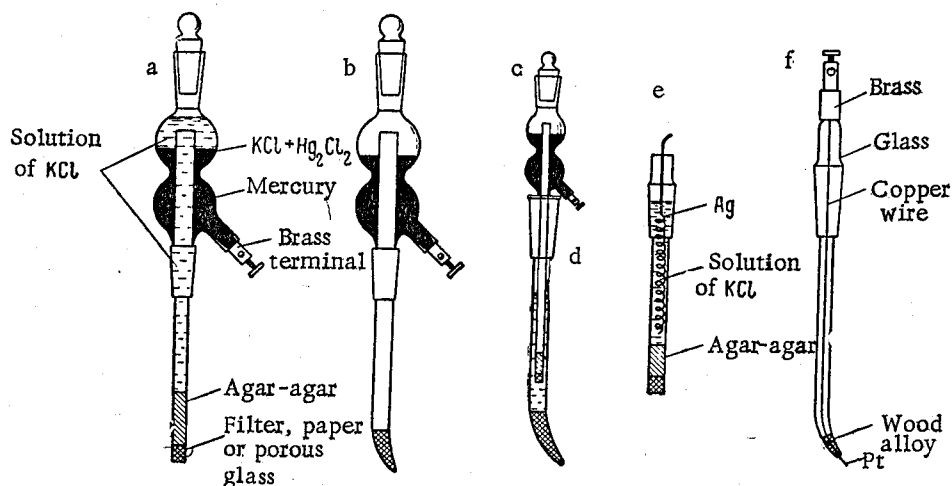


Fig. 4. Nonpolarizable electrodes and intermediate salt bridges.

softens (its tip starts to thicken) its tip is allowed to touch the heated cylindrical part of the capillary right at its end; the thread then sticks to the capillary. Without withdrawing the joint from the flame, the thread is bent; it is then drawn out, and finally fused (Fig. 2). By placing the blade in the flame it is thickened, and by means of a tungsten needle it is arranged that there is a gap of 0.5-1.5 mm (depending on size of drop required) between the blade and the mouth of the capillary. The core of a normal No. 10 ground-glass joint is fitted to the top of the capillary. The upper end of the joint being connected to a supply reservoir of mercury (Fig. 3); it is best that this reservoir should be provided with a tap.

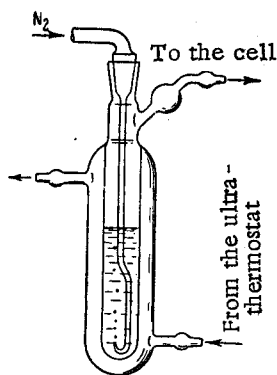


Fig. 5. Vessel for saturating the nitrogen with solvent vapor.

Nonpolarizable electrodes. As external anodes and reference electrodes, it is most convenient to use calomel electrodes, similar in form to electrodes prepared by the "Moskip" factory for the P-4 potentiometer (Fig. 4). Contact with the mercury is effected through a platinum wire fused into the glass; the wire is connected on the outside to a brass terminal (Fig. 4a), which is fused to the glass. The tip of the electrode siphon is sealed with a tightly rolled piece of filter paper and is filled with agar-agar gel and potassium chloride. In the reference electrodes the siphon is drawn out into a capillary, the end of which is placed close to the dropping electrode during measurements (Fig. 4b). On top, in the wide part of the electrode, calomel and KCl crystals are placed on top of the mercury. When it is desirable that the test solution should be free from chloride ions (e.g., when polarograms are taken at potentials more positive than that of the calomel electrode [3]) or potassium ions (when work is being carried out in the strongly negative potential region), then the nonpolarizable electrode is filled with mer-

cury sulfate and potassium sulfate [3] or with tetrasubstituted ammonium salts. For potentiometric measurement of the potential of the dropping electrode with respect to the calomel electrode, or during work in such solutions, it is expedient to have a special calomel electrode with a narrow siphon (Fig. 4c), which is not placed directly in the cell, but through an intermediate salt bridge (Fig. 4d) of agar-agar, containing potassium sulfate (or nitrate) or tetrasubstituted ammonium salts, respectively. A bridge of this type can be used for preparing an external silver chloride electrode. For this purpose, a silver spiral or foil is inserted into it and the bridge filled with a potassium chloride solution (Fig. 4e).

When it is desirable to use a mercury pool as the nonpolarizable electrode, then a special electrode (Fig. 4f) is inserted into the cell instead of the external electrode, in order to establish contact with the mercury pool.

Vessel for saturating nitrogen with solvent vapor. Before the nitrogen is passed into the cell, it is necessary to saturate it with the vapors of the solvent used in the test solution at the experimental temperature. The vessel shown in Fig. 5 is suitable for this purpose. The nitrogen is bubbled through the solvent which is kept at the same temperature as the test solution. The jacket of the vessel is connected in series with the cell jacket, so that the vessel and cell are both thermostatted by means of the same ultrathermostat.

LITERATURE CITED

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