Section 4. Reference Electrodes

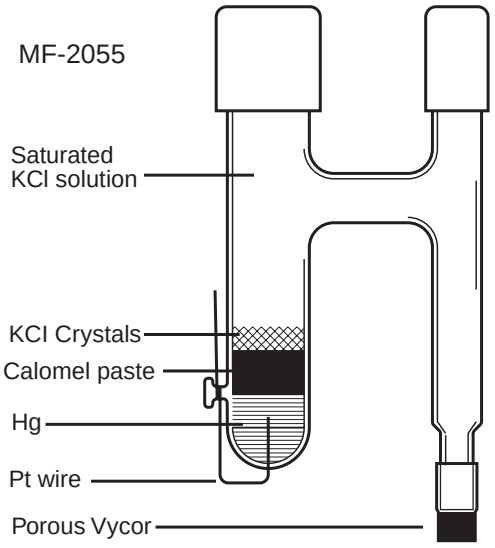
The purpose of the reference electrode is to provide a stable, reproducible voltage to which the working (detector) electrode potential may be referenced. A reference electrode may be considered a small battery whose voltage (potential) is determined by the chemistry taking place between a solid conductor (usually a metal salt) and the electrolytic solution around it. Ideally, if a small current is passed through the electrode, the potential change is negligible, and in any case, returns to the initial value when the current ceases. In addition, the potential value should not vary with time and should be reproducible from electrode to electrode. The most common reference electrodes meeting these criteria are the mercury/mercurous chloride (calomel) and the silver/silver chloride (Ag/AgCl) electrodes.

4.1 Assembling the RE-2 Calomel Reference Electrode

The calomel reference electrode is provided in kit form and is easily constructed. The essential components are the electrode body (an "H" glass design), mercurous chloride (calomel), and KCl. Figure 4.1 depicts an assembled RE-2.

NOTE: Mercury is also used in the RE-2; however, due to recent changes in U.S. Department of Transportation regulations, the mercury cannot be supplied by BAS. Many laboratory suppliers have appropriate licenses and can provide mercury. If you have any questions, please call BAS at 1-800-845-4246.

Figure 4.1. An assembled RE-2 calomel reference electrode.



CAUTION: Mercury and calomel are POISONOUS substances. They should be handled carefully, and waste material should be disposed of in accordance with accepted procedures. If the calomel vial has broken in shipping, DO NOT OPEN the protective outer plastic enclosures. Dispose of the vial and contents as a single unit. Call BAS (1-800-845-4246) for a replacement.

Kit Components

1. Glass electrode "H" body with a porous Vycor® junction, platinum wire, and two yellow caps
2. Calomel paste (labeled Vial B)
3. Saturated KCl solution (labeled Vial C)

Tools and Materials Required But Not Provided

1. Disposable pasteur pipettes
2. 1-mL pipette with bulb
3. Small beaker, or a small flask fitted with a one-hole rubber stopper that can accommodate the narrower arm of the glass body (fill the flask or beaker with saturated KCl solution, and clamp it to a ring stand for support)
4. Plastic tray to collect spills
5. Rubber gloves
6. Triple distilled mercury

Assembling the Calomel Reference Electrode

1. Place the electrode body upright, using the small flask of KCl solution for support. The narrow arm with the Vycor tip should fit comfortably into the hole in the stopper and the Vycor should be wetted by the solution.
2. Hold the reference electrode body and remove both yellow caps.
3. Carefully pour the mercury into the wide arm (the one with the platinum wire on it) and make sure none of the mercury crosses the bridge into the other arm.
4. Use the 1-mL pipette to dispense 0.5 mL of saturated KCl (Vial C) into the calomel paste (Vial B). Use the tip of a pasteur pipette to mix paste and solution into slurry.
5. Using the same pipette, transfer small aliquots of the slurry to the wide arm of the body and gently layer it on top of the mercury pool. Be careful not to allow any of this material to touch the connecting bridge or reach the other arm of the body.
6. Allow slurry to settle. Draw off excess KCl solution with the pasteur pipette and discard.
7. Repeat steps 5 and 6 until the calomel layer is 5 mm deep.

8. Using a new pipette, gently fill the other arm of the electrode with saturated KCl solution. Keep filling until the solution is within 5 mm of the top of the electrode and the connecting bridge is filled.

9. Replace the yellow caps and store the electrode in the stoppered flask of saturated KCl.

10. After at least 2 hours, the Vycor tip will be fully wetted and the RE-2 will be ready for use. A small bubble will have formed above the Vycor plug inside the electrode. Gently tap the electrode with your finger to dislodge the bubble prior to use.

RE-2 Usage

The RE-2 calomel reference electrode is relatively fragile. Avoid any jarring or other activity which would disrupt the mercury/calomel/saturated KCl solution interfaces. Disturbing these layers would necessitate rebuilding the electrode.

The Vycor tip, once wetted, must always be kept wet. When not in use, keep it immersed in saturated KCl solution.

The solution level in the electrode must always be kept above the connecting bridge. Remove the yellow caps periodically and add more KCl to the Vycor arm side of the electrode as needed.

If bubbles form, dislodge them by tapping the electrode with your finger to maintain contact of the Vycor with the solution.