





potential whether fed to the grid through a 100-megohm resistor or directly.

As this instrument is intended to record continuous  $pH$  changes to within 0.01  $pH$  unit and less, great care has to be taken to eliminate the zero drift. It can be shown experimentally that with carefully matched tubes, there is always a setting of potentiometer  $P_1$  (heater current balance), for which one is able to find a setting of potentiometer  $P_5$  (plate load balance) which suppresses the zero drift between plates, or reduces it to a very small value. Once this equilibrium is reached, a slight change to the right or to the left in the setting of potentiometer  $P_5$  starts the drift in one or the other direction. The equilibration is carried out with a sensitive galvanometer with suitable shunt, plugged in between plates. To shift the zero  $P_3$  and  $P_4$  are used. At minimum drift point, provided the total filament current is always adjusted to the same value and the filament supply battery is maintained in the flat portion of its discharge curve, the H.T. battery can be used down  $\frac{2}{3}$  of its discharge curve without drift trouble. The minimum drift reached this way is always continuous. Spurious drifts and jumps indicate defective batteries, poor connections, insufficient insulation (input grid circuit, grid switch, electrode assembly, moisture, or dirt on the electrometer valves), sudden temperature changes, etc. The usual precautions against such sources of disturbance have been taken.

The major trouble when the output of the ET1 and ET3 electrometer valves is amplified and displayed on the oscilloscope screen, the amplification factor being as high as  $\times 190\,000$ , is their very marked microphony. To eliminate vibrations and sound pick-up, the valves have to be mounted in an electrically shielded sound-proof cabinet, on a spring suspension of the type designed by Hill<sup>10</sup> for vibrationless galvanometer mountings, and similar to the system described by Frankenhaeuser and Mac Donald.<sup>11</sup> The chassis with the circuit parts and controls, including the highly insulated grid switch, is fixed externally on the cabinet, which is firmly secured to the room-wall. The grid lead from the electrode assembly is a rigid high-insulated shielded cable of the coaxial

type, and care is taken to avoid having vibrations transmitted to this cable.

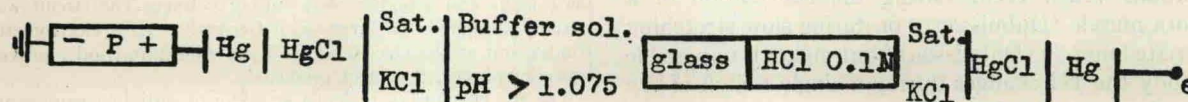
The electrometer stage is followed by a battery operated dc preamplifier. Its gain is  $\times 300$ , and it is similar to that described by Copeland.<sup>12</sup> It has four valves: two type E37A, operating as a long tailed-pair whose outputs are converted to a single-sided signal by a 6SC7 valve and fed at earth level to the oscilloscope amplifier by a cathode follower (6J5). The oscilloscope dc amplifier is the high gain channel ( $\times 900$ ) of the Cossor model 1049 double-beam oscilloscope with camera attachment.

The gain of the electrometer stage being  $\times 0.7$ , the over-all full voltage gain of the whole instrument is  $\times 190\,000$ . The tube sensitivity is  $160\ \mu\text{v}/\text{cm}$  ( $\approx 0.003\ pH/\text{cm}$ ). The oscilloscope attenuator is used for different gain settings. The signal acceptance at full gain without distortion is 50 mv. The over-all drift, after a 1 hr warmup, at full amplification, is about  $300\ \mu\text{v}/\text{hr}$  ( $\approx 0.005\ pH$  unit). The drift is continuous, without sudden jumps. The noise level is about  $50\ \mu\text{v}$  peak to peak (band width reduced to dc-4.6 kc/sec, input grid earthed or connected to the electrode assembly). Stepwise reduction of the band width is provided for, down to dc-50 c/sec, the peak to peak noise decreasing to less than  $20\ \mu\text{v}$ .

### B. Glass Electrodes, Calomel Electrodes, and Cell Assembly

The glass electrodes are of the Mac Innes and Dole type,<sup>13</sup> and made by sealing a thin membrane of 015 Corning glass onto an ordinary glass tube (inner  $\phi$  6.5 mm, outer  $\phi$  8 mm). The extremity of the glass tubes is ground flat and perpendicular to the stem axis. The tubes are 10 or 12 cm long, and coated with paraffin wax up to 2 or 3 cm from the membrane. Electrodes with skew, rippled, or sucked-in membranes are discarded.

The inside of the electrode is filled with 0.1 N HCl, and the electrode is connected in the following cell assembly:



( $P$  is the compensating potentiometer;  $e$  is connected to the input grid of the electrometer.)

The calomel electrodes are of the conventional type and care is taken to connect them in opposition during 48 hrs after filling with saturated KCl, to eliminate any potential difference. The salt bridges are filled with agar-agar jelly saturated with KCl.

The glass electrodes are checked by measuring their potential in an acetate buffer  $pH$  4.66. The electrodes giving stable potentials between 205 and 215 mv are retained.

The membrane thickness of the electrodes ranges from 5 to  $10\ \mu$ . These values have been found by comparing the edge thickness of about 100 glass flakes taken from the bulbs blown to make electrodes, to a calibrated wire gauge under a microscope with micrometer scale.

### C. Equipment to Produce a Step $pH$ Change Under the Electrodes

To measure the distortion introduced by the glass electrode in the recording of fast  $pH$  changes, the shape of the  $pH$  step variation has to be known. As the response of other electrodes, sensitive to  $H^+$  ions or other ions, is unknown,\* there is no direct

way to solve this problem. An indirect way is to produce a  $pH$  change so fast compared to the delay due to the electrode, that it can safely be assumed to approximate a rectangular step.

Fast  $pH$  changes can be produced mechanically, either by mixing solutions of different  $pH$  under the electrode, or by quickly displacing one solution by another. The shape of the  $pH$  variation will depend on the mechanical arrangement and may be affected by diffusion, adsorption, viscosity, and surface wetting. The faster the  $pH$  variation, the less its shape will depend on the first two of these factors, the last three appearing as speed limiting factors for a given solution.

Mixing was first tried, but soon proved to give irregular and too-slow  $pH$  changes, however vigorous the stirring.

The quick displacement of one solution by another of different  $pH$  gave much better results from the start. After much trial, the apparatus shown in Fig. 2 was built.

The inverted glass bottle  $A$ , the rubber tube  $B$ , the Y-shaped glass tube  $y$ , are filled with solution 1. The liquid does not flow as long as valve  $a$  is closed. A droplet of solution 2 ( $pH_1 - pH_2 = 0.3$ ) is suspended under the electrode  $E$ . When valve  $a$  is opened, solution 1 bursts out of the flattened tip of tube  $y$  and washes

depends very much on the degree of polish of the metallic surface. With the specimens tried, the response has been found much slower than that of a glass electrode. Only a few experiments have been made, and no conclusions can be safely drawn.

<sup>10</sup> A. V. Hill, *J. Sci. Instr.* **25**, 225 (1948).

<sup>11</sup> B. Frankenhaeuser and D. K. C. Mac Donald, *J. Sci. Instr.* **26**, 145 (1949).

\* Some experiments have been tried with a platinum electrode and quinhydrone, and with a  $\text{Cu}/\text{CuSO}_4$  electrode of the same shape as the glass-electrode. The response of these electrodes

<sup>12</sup> K. Copeland, *J. of Physiol. (London)* **117**, 15 P (1952).

<sup>13</sup> D. A. Mac Innes and M. Dole, *J. Am. Chem. Soc.* **52**, 29 (1930).