

Fig. 2. Schematic diagram of an apparatus to produce pH step variations under a glass electrode (see text).

solution 2 away. The liquid is collected in glass vessel *F*. The whole apparatus is carefully insulated from ground and shielded. Valve *a* is simply a soft rubber washer fitted in shaft *c* and held tight by hydrostatic pressure on the rim of a rigid rubber tube *b*. The valve is operated manually and opens by pushing button *d* (on top of shaft *c*) upwards to stop *f*. This movement simultaneously closes electrical switch *e* which starts the time base of the oscilloscope. The under part of shaft *c*, in the solution, is ebonite, the upper part is brass and earthed (parts *d*, *e*, *f*, and the guide through which *c* slides are fixed on a wooden block, represented by a dotted line, behind the plane of Fig. 2).

The flow is regulated by means of clamp *g*. Tube *y* is fitted with a removable flattened tip to obtain a ribbon-like jet. Its vertical branch serves to trap air bubbles which may appear at the tip when the flow is interrupted. Any orientation of tube *y* is possible. To fill the apparatus, the tube is removed from its clamp and leveled with bottle *A*, which is 50 cm above. The air bubble trap is filled up to the top.

The glass electrode *E*, and its top calomel electrode *G*, are fixed in a highly insulated ebonite clamp which can be oriented in any position. The whole electrode assembly can be moved smoothly along its vertical axis by screw action. The second calomel electrode *H* (in dotted line) is fixed to a separate insulated stand and is located behind tube *y* and electrode *E*. Contact with the droplet of solution 2 under the electrode is made through a thin agar-agar filled bridge *i* with a few millimeters of cotton thread sticking out of the tip. The bridge is fixed so as not to be blown away by the liquid jet, and only the cotton thread is in contact with the liquid.

The main difficulty with this apparatus is in aligning the electrode and jet so that proper grazing of the suspended droplet is obtained. To make this easier, experiments have been made with a slightly modified arrangement. A thin rectangular flat-bottomed celluloid channel is fitted horizontally under the tip of tube *y*. The drop of solution which has to be washed away is squeezed

between the electrode membrane and the dried celluloid plate, forming a liquid layer 1 or 2 mm thick, located at 2 mm from the tip end.

## Results

It soon became evident, after the first experiments, that the response of the glass electrode is so fast that it is very difficult to produce, mechanically, a pH change fast enough to approximate a rectangular step compared to the transient response of the electrode. The efficiency of the washing depends very much on the respective orientation of jet and electrode. The difficulty with the described apparatus is to direct the jet properly on the electrode to wash the droplet away as quickly and completely as possible. When the jet breaks on the electrode stem, there is much turbulence, the liquid creeps upwards, mixing occurs under the membrane before the droplet is removed. When the jet reaches only the droplet, part of it remains under the electrode. Diffusion complicates the process still further in both cases. Parallelism between membrane and jet, form and section of the injection tip, and flatness of the electrode membrane, are all factors of importance.

With the celluloid channel arrangement, alignment is more easy and reproducible, but much slower variations are obtained. The droplet squeezed between two planes is more difficult to remove. Much liquid flows around the electrode and produces turbulence of flow, which may result in stationary mixing under the electrode, as was discovered with dyed solutions.

For a given spatial arrangement the washing efficiency passes through a maximum range when the flow is increased. Higher flow rates are possible with the free-hanging drop method than with the channel method, before too much turbulence makes it illusory to increase the flow still further.

TABLE I. Milliseconds at percent total deflection.<sup>a</sup>

Experiment <i>n</i> <sup>o</sup>	20%	40%	60%	80%	90%	100%
<i>A</i> <sub>8</sub> 1	23	44	61	87	122	192
2	21	31	44	65	87	200
<i>A</i> <sub>17</sub>	21	38	61	105	166	350
<i>A</i> <sub>18</sub>	21	38	61	80	105	228
<i>A</i> <sub>19</sub>	21	35	58	87	114	280
<i>A</i> <sub>27</sub> 1	31	39	56	75	96	140
2	30	39	52	79	96	140
<i>A</i> <sub>40</sub> 1x	24	38	54	78	102	180
2x	20	36	52	72	92	180
3x	20	32	50	68	88	160
<i>A</i> <sub>48</sub> 2	16	25	39	52	70	175
9	18	25	44	87	122	350
<i>A</i> <sub>49</sub> 1x	12	20	28	44	64	160
2	18	26	37	44	70	260
7x	12	22	28	40	60	100
9x	18	22	32	45	68	140
10x	12	20	28	44	68	130
<i>A</i> <sub>50</sub> 8	18	26	39	52	122	260
9	18	26	39	61	140	350

<sup>a</sup> Remarks: *A*<sub>8</sub>–*A*<sub>27</sub> phosphate buffer; *A*<sub>40</sub>–*A*<sub>50</sub> acetate buffer; *A*<sub>8</sub>–*A*<sub>40</sub> channel method of injection; *A*<sub>40</sub>, flow rate increased from 1 to 3; *A*<sub>48</sub>–*A*<sub>50</sub> free hanging drop method of injection; *A*<sub>49</sub> different flow rates; *x*, values measured on enlarged records, the other values are measured directly on the film.

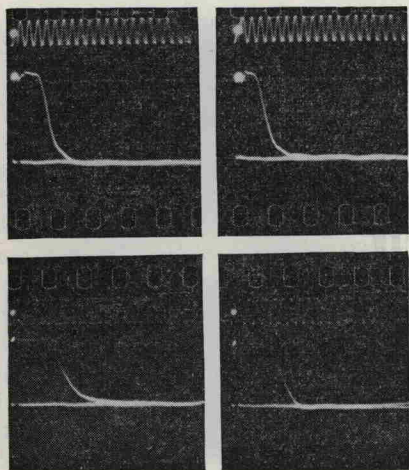


FIG. 3. Oscillographic records of fast pH step variations under a glass electrode (experiments  $n^{\circ}A_{40}$ , below, and  $A_{49}$ , above, from Table I). Time-scale: 50 c/sec sine wave.

The high dc resistance of the electrode also complicates the problem. Electrostatic disturbances and mechanical vibrations, due to the jet impact, are picked up and appear as spurious jumps, overshoot, and oscillations in the amplifier output. These effects become very large at high jet speeds, especially when the liquid reaches the paraffin wax coating of the electrode. At lower speeds, a slight overshoot or, sometimes, a potential drop at the beginning of the transient can still be detected in almost any experiments with free-hanging droplets, but is much less frequent when a channel is used. An explanation is that the insulated injection apparatus may have a different electrostatic charge than the glass electrode, whose tip

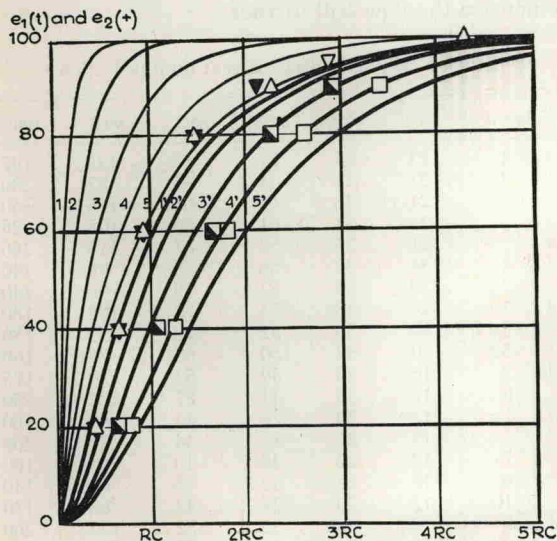


FIG. 4. Calculated responses (smooth curves 1' to 5') of a glass electrode to exponential pH step variations of type  $e^{-\beta t}$  for different values of  $\beta$  (smooth curves 1 to 5). Curve 5 represents also the response of the electrode to a rectangular pH step. The plotted data are taken from Table I ( $RC=30$  msec).

is earthed through the calomel electrode. In the free-hanging drop method, electrode and injection apparatus are separated by an air gap, whereas the celluloid channel provides a leakage path. If the conductivity of the more or less dried celluloid surface is increased by means of a wet cotton thread, fixed inside the injection tip and stretched across the channel so as to touch the bridge tip of the calomel electrode and to dip in the collecting vessel (see Fig. 2), the effects due to initial electrostatic charge difference between electrode and injection apparatus disappear almost completely. The thicker the membrane the more difficult it is to avoid electrical disturbances. As it soon appeared that *the membrane thickness has little or no effect on the response speed*, thin electrodes were prepared for most of the experiments.

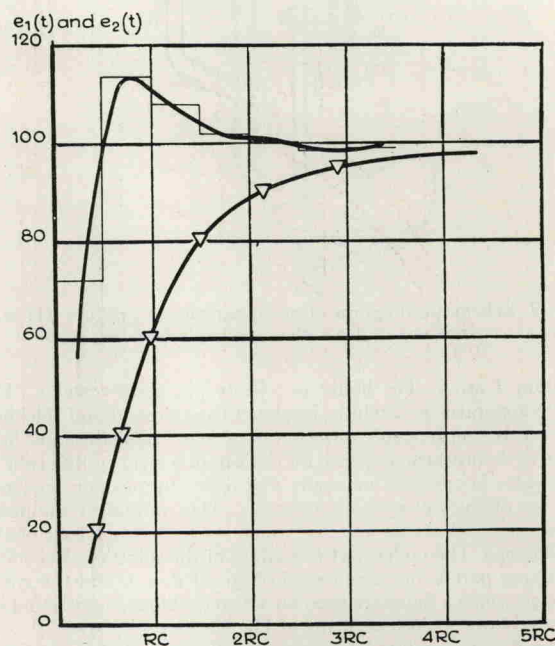


FIG. 5. Calculated pH variation (blocs) from the recorded response of a glass electrode (experiment  $n^{\circ} 49_1$  of Table I).

Perfect cleanliness and wettability of the electrode membrane are, of course essential to obtain quick responses, independently of the speed of the pH change. Unclean membranes slow the response considerably. Washing with organic solvents (to remove traces of paraffin wax, used to increase the resistivity of the glass stem), with concentrated  $\text{HNO}_3 + \text{H}_2\text{SO}_4$ , improves the response of unclean electrodes. It is difficult to keep the electrodes clean, even in distilled water, and we have used the electrodes as soon as they were made, after a few minutes soaking in the buffer solution. Better results are obtained with acetate buffer (0.1 N acetic acid + 0.1 N NaOH, pH 4.66) than with phosphate buffers (pH 7), because the latter prepared from crystallized Na and K salts, always contains grease which deposits on the membrane.