We will not look in detail at the experimental evidence of the difficulties described in the foregoing, and we will now consider some of the fastest transients with smooth and regular shapes which we have obtained and which are given in numerical form in Table I. Figure 3 shows the recorded curves of the best experiments. The experiments of Table I have been chosen to give the same arithmetical mean value for the time needed to reach 60 percent deflection, as found for the entire set of the 50 well-shaped curves which we have recorded.

The most likely interpretation of these results is that the response of a glass electrode to a rectangular pH step is an exponential curve of type $e^{-\alpha t}$ with a time constant $1/\alpha$ of about 30 msec. As we know nothing about the shape of the experimental pH variations no absolute proof of this can be drawn from the data, but some arguments can be advanced.

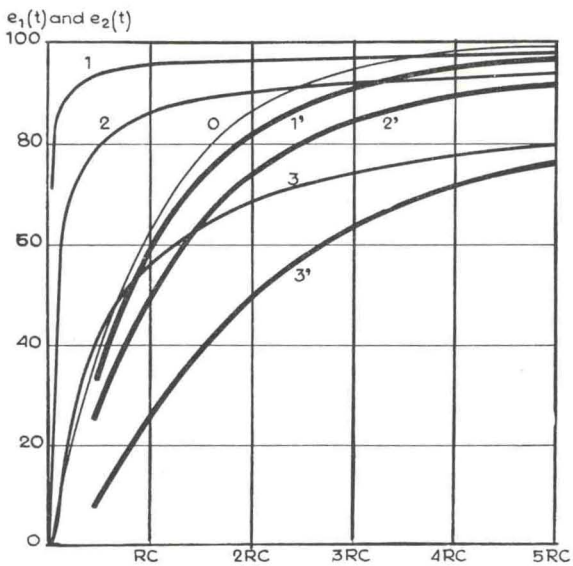

FIG. 6. Calculated response (curves 1′, 2′, 3′) of a glass electrode to a rectangular pH step transmitted to the electrode membrane by diffusion through a thin film of liquid of 0.3μ (curve 1), 1μ (curve 2), 3μ (curve 3). The diffusion curves are drawn after Hill (see reference 9). Curve 0 is the electrode response to a rectangular pH step undelayed by diffusion.

Above a certain value of flow rate, important variations of jet speed with obvious improvement of the washing efficiency have but little effect on the response: in over 200 experiments 60 percent deflections are attained in 60 msec to 28 msec (10 experiments give values ranging from 140 to 60 msec).

Figure 4 shows the theoretical electrode response to exponential pH variations of type $e^{-\beta t}$ of increasing speed, assuming that the electrode response to a rectangular pH step is represented by $e^{-\alpha t}$ with $1/\alpha = 30$ msec. Some experimental data from Table I have been plotted on the diagram. It is seen that $1/\beta$ decreases from 23 msec to 4–7 msec, whereas the time at 60 percent deflection decreases from 54 msec to 28 msec, when

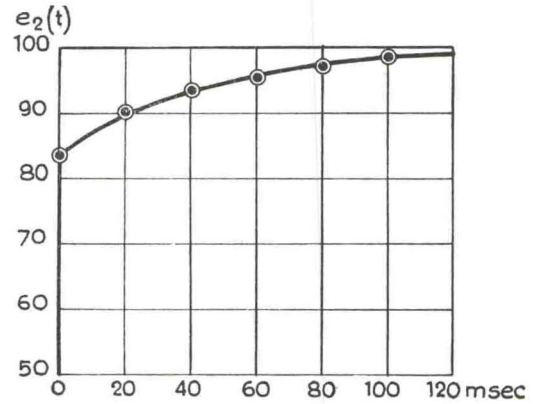

FIG. 7. Calculated (smooth curve) and experimental (0) response to a rectangular step voltage of the network of Fig. 9 with $r = 9.10^7$ ohms, $R = 10^5$ ohms, $C_1 = 400$ cm, $C_2 = 80$ cm.

the injection apparatus is used respectively with the channel method and the free-hanging drop arrangement. The value of 4–7 msec for $1/\beta$ is in agreement with the expected performance of the injection apparatus. The rate of the flow in the middle of the range used has been measured and found to be 20 cm³/sec. The volume of the droplet under the electrode is ~0.05 cm³. It can be calculated that in ideal conditions (cross section of the drop inscribed in the rectangular section of the jet), the droplet could be removed in 6 msec.

The important curvature at the start of the slower transients, the much increased steepness in the fast ones, and the fact that the deviations from an ideal exponential curve decrease progressively as the speed increases, show the approach towards a limit as exemplified in Fig. 4. It will be noticed however that the plotted data corresponding to the fastest experiments reveal a slight deviation from the calculated curves. Analysis by the graphical and numerical method of Hill[14] is given in Fig. 5, revealing an overshoot of 14 percent. An explanation for this phenomenon has been suggested earlier. The argument concerning the shape of the limit

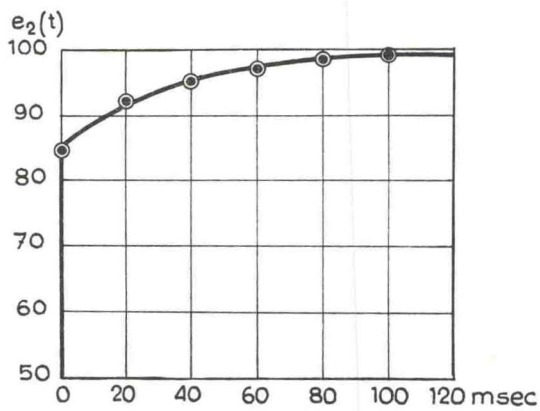

FIG. 8. Calculated (smooth curve) and experimental (0) response of a glass electrode ($n°$ 95a, see text) to a rectangular step voltage in series with the electrode.

[14] A. V. Hill, J. Sci. Instr. **26**, 56 (1949).

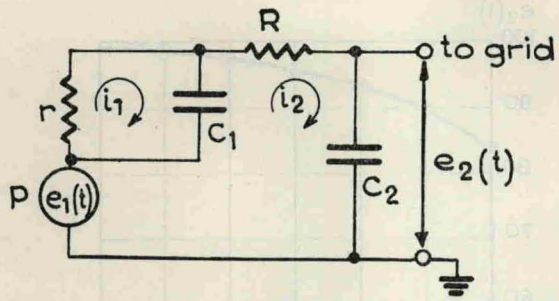

FIG. 9. Equivalent network for glass electrode and input connections to the electrometer, for responses to step voltages in series with the electrode.

transient is somewhat reduced by the fact that if the curves present great similitudes up to 80–90 percent deflection, important differences are observed in the last part of the deflection. The time required for full deflection ranges from 100 to 450 msec. The delaying factor is most likely diffusion, but we have no experimental evidence. If part of the *p*H variation is transmitted to the membrane by diffusion either through a film of liquid remaining on the membrane because of insufficient washing, or through a film of adsorbed dirt or impurities from the buffer solutions, the delay will be especially noticeable in the last 20 percent of the deflections because of the peculiar shape of the diffusion curves. This is shown in Fig. 6, which gives the theoretical transient response of the glass electrode to a rectangular *p*H step transmitted to the membrane by diffusion through a thin film of liquid. The response curves are calculated by numerical and graphical analysis,[14] again assuming $e^{-\alpha t}$ to represent the electrode response with $1/\alpha=30$ msec, when there is no diffusion. The diffusion curves are taken from Hill[9] (diffusion constant $=5.10^{-6}$). It is obvious that the electrode response is severely slowed by diffusion even with films of less than 0.3 μ, and comparison with Fig. 4 shows clearly that the delay is especially marked in the last 20 percent of the response curve.

II. ELECTRICAL CHARACTERISTICS OF THE GLASS ELECTRODE

Sending a step-voltage of a few millivolts through the electrode assembly (by closing a key across the terminals of an auxiliary potentiometer in series with compensating potentiometer of Fig. 1) gives a response curve like the one shown in Fig. 8. Figure 7 shows a similar curve obtained with the circuit[15] of Fig. 9, with $r=90\cdot10^6$ ohm, $R=10^5$ ohm, $C_1=400$ cm, $C_2=80$ cm (input capacity of electrometer). Both curves correspond to the equation:

$$e_2(t)=V[1-C_2/(C_1+C_2)e^{-t/r(C_1+C_2)} - C_1/(C_1+C_2)e^{-t(C_1+C_2)/C_1C_2R}]. \quad (1)$$

[15] A similar equivalent circuit for the glass electrode has been suggested by D. A. Mac Innes and D. Belcher, J. Am. Chem. Soc. **53**, 3315 (1931).

In the case of the glass electrode, C_2 and R (calomel electrodes+salt bridges+potentiometer=30 000 ohm) being known, C_1 and r (capacity and internal resistance of the glass membrane) can be calculated as follows:

Electrode $n°$	C_1 cm	$r10^6$ ohm	Eq. (1)
95*a*	460	65	$e_2(t)=V(1-0.15e^{-28t}-0.85e^{-5\cdot10^5t})$
95*b*	600	45	$e_2(t)=V(1-0.12e^{-33t}-0.88e^{-47\cdot10^5t})$.

Direct measurement of C_1 and r with capacimeter and megohmmeter gives the following values: 95*a*: $C_1=460$ cm, $r=300\cdot10^6$ ohm, $rC_1=138$ msec; 95*b*: $C_1=600$ cm, $r=240\cdot10^6$ ohm, $rC_1=133$ msec; other electrodes give respectively: $C_1=460$, 380, 610, 510 cm $-r=300$, 350, 240, $290\cdot10^6$ ohm$-rC_1=146$, 148, 138, 144 msec.

The discrepancy between the calculated and measured values of r is difficult to explain, but may be the result of polarization in the latter case.[15]

In Fig. 10, we have rearranged the circuit of Fig. 9 to represent the electrode transmitting a *p*H step, the electrode being taken as an emf source, without taking into account the internal mechanism for the conversion of the *p*H change into the corresponding step voltage. The response of this circuit where $r\gg R$, $C_1>C_2$ is given by equation:

$$e_2(t)=V[1-e^{-t/r(C_1+C_2)}]. \quad (2)$$

Using for r and C_1 the values calculated from Eq. (1), the recorded time constant of the electrode $r(C_1+C_2)$ can be expected to be 36 msec and 30 msec for electrodes 95*a* and 95*b*, the true time constant rC_1 being, respectively, 30 and 27 msec. This picture of the electrode transmitting the voltage corresponding to a *p*H step as a low-pass RC circuit fits well with our experimental conclusions, e.g., 1° the speed of the electrode tends towards a finite limit as the speed of the *p*H change increases; 2° the form of the transient of the fastest records is very near to an exponential curve of type $e^{-\alpha t}$ with $1/\alpha\simeq30$ msec; 3° the response is independant of the electrode thickness.

REMARKS. (1) If the band width of the electrode transmitting *p*H oscillations (sine wave) is 5 c/sec, it is interesting to notice that *p*H oscillations at 14 c/sec and 50 c/sec will be attenuated to $\frac{1}{3}$ and $\frac{1}{9}$ of their real amplitude. Discrimination between *p*H step

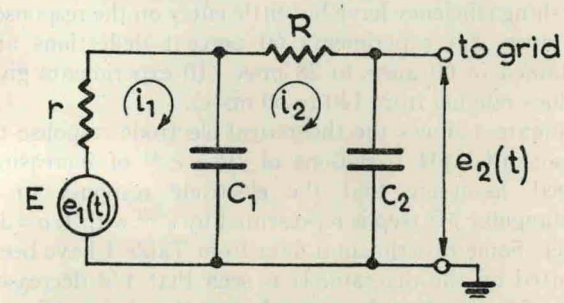

FIG. 10. Equivalent network for glass electrode and input connections to the electrometer, for responses to *p*H step variations.