# 24. *A Study of Liquid–Liquid Junctions with a View to eliminate the Potential Difference thereat.*

By Jamiat V. Lakhani.

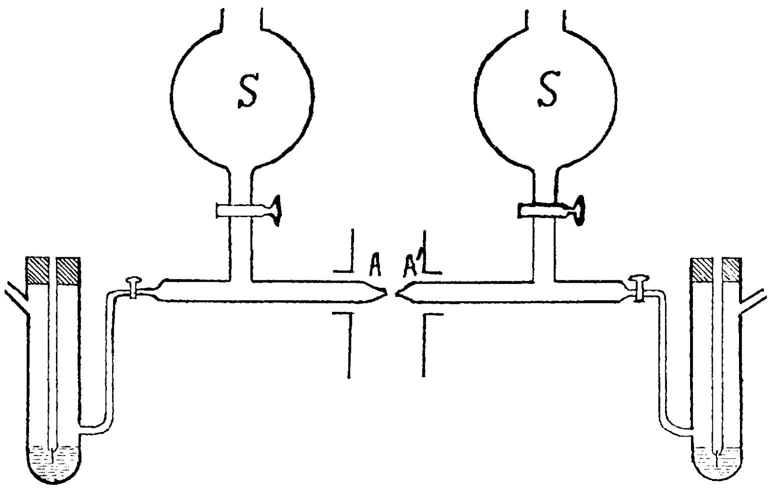
The object of this work was to devise experimental means by which to eliminate the liquid junction *P.D.* between two different solutions, in order to throw light on other fundamental problems of *E.M.F.* measurements of single electrodes and activity coefficients.

The researches of Lamb and Larson (*J. Amer. Chem. Soc.*, 1920, **42**, 229), Roberts and Fenwick (*ibid.*, 1927, **49**, 2787), and Guggenheim (*ibid.*, 1930, **52**, 1315) have been mainly directed towards producing constant and reproducible liquid–liquid junctions, Roberts and Fenwick suggesting the use of a mica plate with a small hole to establish contact between two electrolytes. Theoretical expressions for calculating the values of the *P.D.* at liquid junctions have been given by Nernst (*Z. physikal. Chem.*, 1889, **4**, 129) and Planck, who assume the formation of an initial sharp boundary at the junction of two electrolytes and then a process of natural diffusion, by Henderson (*ibid.*, 1907, **59**, 118; 1908, **63**, 325), who assumes the formation of a connecting layer, and by Lewis and Sargent (*J. Amer. Chem. Soc.*, 1909, **31**, 363).

If, as Nernst assumed, the junction *P.D.* between two solutions is due to the diffusion of ions of unequal mobilities, and the absolute velocities of ions are comparatively small, it was thought that the time required for the establishment of the *P.D.* might be appreciable, and that by allowing the two solutions in contact with the electrodes to flow out in the form of fine jets, making momentary contact before the mixed liquid falls as drops, it might be possible to eliminate or markedly to reduce the *P.D.* at the boundary.

In order to test this possibility, the apparatus shown in Fig. 1 was assembled. The separating funnels SS were of 250-c.c. capacity, and the electrode vessels were of the usual Ostwald type. The outlet tubes A A′ were each narrowed to a fine hole so as to permit fine jets of the liquids to come out and play upon each other. No rubber joint was employed, and the hydrochloric acid and potassium chloride used were both of analytically pure standard. Calomel was electrically prepared from pure distilled mercury. In starting

FIG. 1.




measurements, the stop-cocks of the separating funnels were turned on to such an extent as to allow regulated jets of electrolytes to be formed.

The following cell combinations were used :

| | | | | |
|---|---|---|---|---|
| (1) | Hg \| HgCl | *N*/10-KCl \| *N*-KCl | HgCl \| Hg | |
| (2) | Hg \| HgCl | *N*/10-KCl \| *N*/10-HCl | HgCl \| Hg | |
| (3) | Hg \| HgCl | *N*-KCl \| *N*/10-HCl | HgCl \| Hg | |

(The author is aware that the behaviour of calomel electrodes in hydrochloric acid is said to be unsatisfactory, but since the primary object was to test liquid junction *P.D.*, absolute *E.M.F.* values were not directly concerned. Actually, however, these combinations were found to be in good agreement with the calculated values.) *E.M.F.* Measurements were made with a potentiometer reading directly to 0·1 millivolt and by estimation to 0·01 millivolt. The high-resistance galvanometer was sensitive enough to give a deflection of about 0·5 cm. for 0·1 millivolt.

Two of each of the electrodes were prepared and found to be in excellent agreement with each other. In order to test whether streaming potential differences were set up by the jets, two identical electrodes were measured with one jet in action and the other stationary: the result was negative.

The values obtained at 13° are shown in the table.

| Electrolyte junction. | Rate of flow at each jet. | *E.M.F.* (volts). Obs. | Calc., or previously observed. |
|---|---|---|---|
| *N*/10-KCl \| *N*-KCl | 30—35 c.c. per min. | 0·0519 | 0·0516 (18°) |
| *N*/10-KCl \| *N*/10-HCl | (1) No flow—mere contact at the jets. | 0·0277 | 0·028* |
| | | 0·0278 | 0·027† |
| | (2) 2 C.c. per min. | 0·0277 | |
| | | 0·0276 | |
| | (3) 16 C.c. per min. | 0·0278 | |
| | (4) (*a*) 35 C.c. per min. | 0·0278 | |
| | (*b*) Jets placed 3 cm. apart | 0·0278 | |
| | (*c*) Jets placed 6 cm. apart | 0·0278 | |
| | (5) 160 C.c. per min., by applying pressure. | 0·0279 | |
| | | 0·0278 | |
| | | 0·0279 | |
| *N*-KCl \| *N*/10-HCl | (1) 30—32 C.c. per min., jets 1—3 cm. apart. | 0·0429 | 0·0405 |
| | | 0·0430 | |
| | (2) Under pressure. | 0·0429 | |

* Compare Roberts and Fenwick (*J. Amer. Chem. Soc.*, 1927, **49**, 2787).
† Henderson's calculated value.

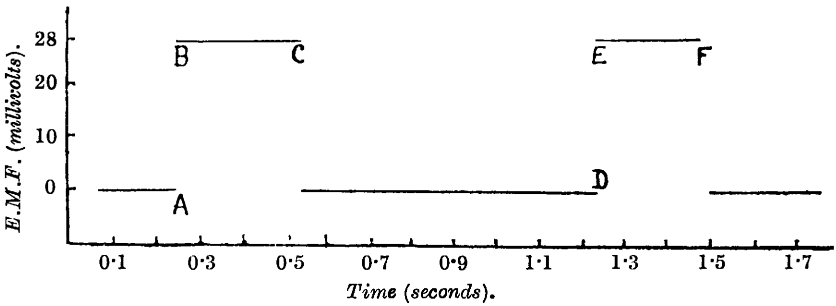
It was found that extremely constant and reproducible values were obtained when the jets were separated by more than 0·5 cm., and that this was independent of the rate of flow within the limits examined. Moreover, the values obtained are in excellent agreement with those obtained with Lamb and Larson's flowing junction and with Roberts and Fenwick's arrangement in which contact between two solutions took place at a small aperture in a mica plate, over the two sides of which the solutions were flowing.

The results indicate that the rate of flow has no appreciable effect on the *E.M.F.* of the cells examined, and that the *P.D.* at the junction is established very quickly.

To estimate the time taken to establish the *P.D.*, observations were made with a highly sensitive string galvanometer. The electrodes in *N*/10-potassium chloride and hydrogen chloride were connected directly with the terminals of the galvanometer, and momentary contacts between the flowing jets were made and broken by movements of one of the electrodes. The sensitivity of the galvanometer was such that an *E.M.F.* of 30 millivolts produced a displacement of the image of the string of about 1 cm. The image of the fibre was recorded on a moving strip of photographic paper. Fig. 2 gives a reproduction of part of the record. The contact between the jets was established at points A and D and broken at points C and F. The time taken to establish the *P.D.*, as measured by the time interval between A and B or D and E, was scarcely measurable and certainly less than $5 \times 10^{-3}$ sec. The horizontal portions BC and EF show that the *P.D.* also remains constant during contacts of short duration.

It seems, therefore, unlikely that increasing the speed of flow to any extent suitable for practical use would be effective in eliminating the junction potential; but the device appears to give a useful and

FIG. 2.




simple method of obtaining constant and reproducible values of the *P.D.* under conditions in which natural diffusion of the solutions into each other is prevented.

*Summary.*

(1) The *E.M.F.* equilibrium at the junction of two electrolytes takes place instantaneously, and it has not been possible to alter or reduce the *E.M.F.* value even when the junction is formed by rapidly flowing electrolytes.

(2) A simple, practical, and reproducible type of flowing junction by jets has been suggested which has the advantage of doing away with the mica plate as used by Roberts and Fenwick.

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