APPENDIX II (continued).

| Degrees C. | 0. | 1. | 2. | 3. | 4. | 5. | 6. | 7. | 8. | 9. |
|---|---|---|---|---|---|---|---|---|---|---|
| + 0 | 120.35 | 123.90 | 127.55 | 131.25 | 135.00 | 138.80 | 142.70 | 146.70 | 150.75 | 154.90 |
| 10 | 159.10 | 163.40 | 167.75 | 172.20 | 176.70 | 181.30 | 186.00 | 190.75 | 195.45 | 200.50 |
| 20 | 205.50 | 210.55 | 215.70 | 220.95 | 226.30 | 231.70 | 237.20 | 242.80 | 248.50 | 254.25 |
| 30 | 260.1 | 266.0 | 272.0 | 278.1 | 284.3 | 290.6 | 297.0 | 303.5 | 310.0 | 316.6 |
| 40 | 323.3 | 330.1 | 337.0 | 344.0 | 351.1 | 358.3 | 365.6 | 373.0 | 380.5 | 388.1 |
| 50 | 395.8 | 403.6 | 411.4 | 419.4 | 427.5 | 435.7 | 444.0 | 452.3 | 460.8 | 469.4 |
| 60 | 478.1 | 486.9 | 495.8 | 504.8 | 513.9 | 523.1 | 532.4 | 541.8 | 551.3 | 561.0 |
| 70 | 570.8 | .. | .. | .. | .. | .. | .. | .. | .. | .. |

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# REPRODUCIBLE LIQUID JUNCTION POTENTIALS: THE FLOWING JUNCTION.[1]

By Arthur B. Lamb and Alfred T. Larson.

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The potentials of liquid junctions in voltaic cells are sources of perplexity in measurements of the electromotive force of cells and of the single potentials of electrodes, not only because they evade direct observation, complete elimination, or a rigorous calculation, but because they are also a frequent source of considerable experimental uncertainty. It has been particularly difficult to secure reproducible liquid junction potentials when the ions on the two sides of the junction have marked differences in mobility. Uncertainties in such junctions frequently amount to several millivolts.[2]

We have recently been engaged upon a study of the Thomson effect in electrolytes, which involved the precise measurement of the electromotive force of cells containing 2 or more liquid junctions. This has led us to a study of the reproducibility of such junction potentials and ultimately to the development of a type of junction, which, even under unfavorable conditions, that is, with ions of marked differences in mobility, gives electromotive forces reproducible to 0.01 of a millivolt.

In this study we followed 2 procedures: first, we constructed cells similar to those of Chanoz[3] containing 2 identical but oppositely directed liquid junctions, and 2 identical electrodes, for example:

$$\text{Ag AgCl.0.1 } N \text{ HCl} \mid 0.1 \, N \text{ KCl} \mid 0.1 \, N \text{ HCl.AgCl Ag} \qquad (1)$$
$$\qquad\qquad (1) \qquad\qquad (2)$$
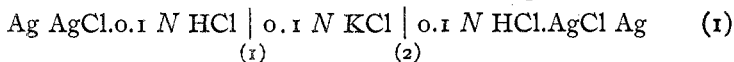
Such a cell should give a constant zero potential. If it does not, and the

[1] This investigation was completed in December, 1915; an account of it was presented before the Harvard-Technology Physical-Chemical Club in February, 1916.

[2] Chanoz, Ann. Univ. Lyon, Nouv. Ser., 1, 1906, 18; Cumming, Trans. Faraday Soc., 9, 174 (1913); Lewis, Brighton and Sebastian, THIS JOURNAL, 39, 2253 (1917).

[3] Loc. cit.

electrodes are known to be identical and constant, the observed effect must be due to differences and inconstancies in the liquid junctions.

Second, we constructed cells containing constant and reproducible electrodes of the second type, connected by a single liquid junction, as follows:

$$\text{Ag AgCl.} N \text{ KCl} \mid N \text{ HCl.AgCl Ag} \qquad (2)$$
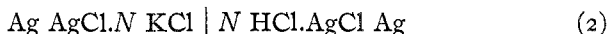
Such a cell should have a definite and constant electromotive force, whose magnitude will depend, first, on differences in the single potentials of the electrodes in the different solutions, and, secondly, on the potential of the liquid junction itself.

The first method is, perhaps, more convenient than the second, in that identical electrodes are used which can be readily checked against each other; on the other hand, it is inferior to the second in the important respect that with *two* junctions the possibility still remains that each junction may be changing at the same rate but in opposite directions, and thus give an apparent but not a real constancy at each junction. For that reason our final experiments have all been carried out by the second method.

The electromotive force measurements were made with a potentiometer reading to one or two millionths of a volt. Elaborate precautions were taken in the matter of screening, and the cells were kept in an oil thermostat at $25° \pm 0.01°$.

Since the reproducibility of the electrodes was a matter of primary importance in this investigation, electrodes of several different kinds were prepared and studied. The hydrogen electrode was found to be almost ideally reproducible and very convenient, but the slight fluctuations of the electrolyte, caused by the bubbling of the hydrogen gas, produced serious disturbing effects on the liquid junctions.

The calomel electrode was also studied, but after repeated trials was discarded as less permanently reliable than a silver chloride electrode prepared essentially according to the method described by Lewis[1] and by Jones and Hartman,[2] but with the difference that we deposited the silver chloride in the sunlight and kept the supply solution of hydrochloric acid and potassium chloride, containing silver chloride in suspension, also in the sunlight. This exposure of all the silver chloride to sunlight seemed to bring it into a final condition of equilibrium, for electrodes thus prepared were found to adjust themselves almost immediately after immersion to their definitive potentials, and after standing short-circuited overnight were found to be constant and identical to 0.01 of a millivolt.

**Junctions between Ground Glass Surfaces.**—In view of the favorable

[1] Lewis, THIS JOURNAL, **28,** 166 (1906).
[2] Jones and Hartman, *Ibid.*, **37,** 356 (1915).

results obtained by Jones and Hartman[1] we first studied the behavior of liquid junctions formed between the bearing surfaces of ground glass stoppers. For this purpose the above-mentioned cell (No. 1) was assembled as in Fig. 1. Each end of the siphon tube containing the potassium chloride solution was provided with a coarsely ground glass stopper. The
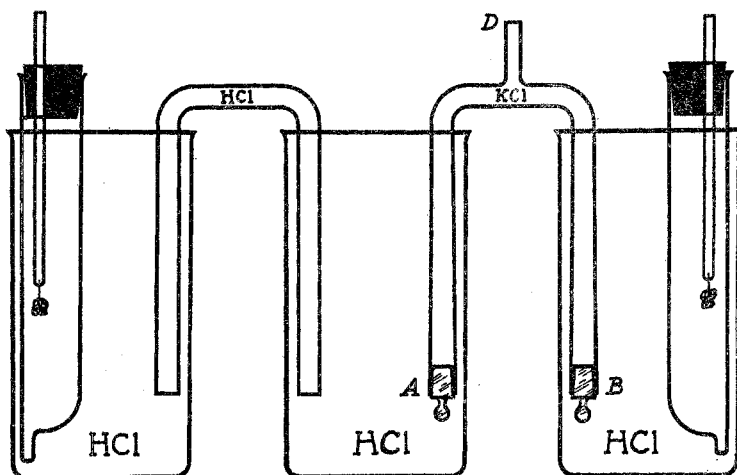


Fig. 1.

solution was poured in and allowed to creep well along the bearing surfaces before the siphon was closed at D and placed in position connecting the 2 beakers. The following are typical readings obtained for the potential of the cell which, since the electrodes have been shown to be identical, should be zero.

TABLE I.

Junctions between Ground Glass Surfaces.

| Time. | Millivolt. |
| --- | --- |
| 11:50 A.M. | +0.09 |
| 12:15 P.M. | —0.28 |
| 2:30 P.M. | —0.22 |

In general, the e. m. f. varied ±0.25 millivolt. While such a junction might be suitable in cases where the abutting ions differ but slightly in mobility, it was by no means satisfactory for our purposes.

Diaphragm Junctions.—The glass stoppers were removed from the above siphon and pieces of cotton gauze were stretched tightly over each open end. These ends were then dipped in hot gelatin, which on cooling gave a thin but mechanically strong diaphragm. Using the same potassium chloride solution in the siphon, the following typical results were obtained; they were even less satisfactory than the preceding ones.

[1] *Loc. cit.*

TABLE II.

Gelatin Diaphragm Junctions.

| Time. | Millivolt. + |
|---|---|
| 1:00 P.M. | 0.12 |
| 3:00 P.M. | 0.14 |
| 6:00 P.M. | 0.22 |
| 10:00 A.M. | 0.39 |
| 12:00 M. | 0.34 |
| 1:30 P.M. | 0.43 |

Inasmuch as slight differences and irregularities in the permeability of the gelatin might be responsible for the variable e. m. f., the gelatin-cotton diaphragms were replaced by more permeable ones of parchment paper. Provision for a steady flow of electrolyte was also made by attaching a small separatory funnel containing potassium chloride solution to the upper opening of the siphon D and arranging a small propeller-stirrer to operate just underneath each diaphragm. We hoped by this dynamic method to secure constant conditions at the lower surface of the parchment diaphragm. The typical results obtained are given in Table III.

TABLE III.

Dynamic Parchment-Diaphragm Junctions.

| Time. | Millivolt. |
|---|---|
| 4:20 P.M. | +0.08 |
| 4:25 P.M. | —0.25 |
| 4:50 P.M. | —0.13 |
| 5:15 P.M. | +0.14 |

The variations here, although somewhat less in extent than before, were very sudden and erratic. It developed that they were largely due to irregularities in stirring. Thus, by stopping one stirrer the potential became 0.08 millivolt more positive; stopping the other propeller produced an equal change in the opposite direction. This indicated that a properly controlled dynamic junction offered decided possibilities. It seemed desirable, however, to attempt to secure a similar result by simpler means.

**Fresh Junctions.**—Influenced by the favorable results obtained by the dynamic compared with the static junction, we studied the effect of forming a fresh junction in an open tube. Following the conclusions of Cumming that reproducible junctions can be secured in this way only in tubes of at least 4 mm. bore, the siphon shown in Fig. 2 (but without the median stopcock) was constructed. C and D were glass tubes of a uniform bore of 5 mm. A fresh junction was established by running out about one cc. of solution from each funnel, whereupon the potential reading was made as rapidly as possible. Typical results secured in this way are given in Table IV.

TABLE IV.

Fresh Junctions.

| Time. | | Millivolt. |
|---|---|---|
| 9:45 | Fresh junction........................ | —0.01 |
| 10:00 | | —0.31 |
| 10:05 | Fresh junction........................ | —0.03 |
| 11:00 | | —0.40 |
| 11:05 | Fresh junction........................ | —0.00 |
| 11:15 | | +0.04 |
| 11:25 | | —0.41 |
| 11:27 | Fresh junction........................ | —0.02 |
| 11:48 | | —0.35 |
| 11:49 | Fresh junction........................ | +0.01 |

In each case the establishment of a fresh junction brought the liquid junction potential down substantially to zero.

It seemed possible that the wide divergence in potential which these junctions developed on standing, that is, the pronounced "ageing" effect, might be caused by the disturbing oscillations of the liquid in the siphon tube. To eliminate this a glass stopcock was inserted in the median connecting arm. This was kept always closed, but as it was not lubricated, the film of electrolyte between the ground glass surfaces furnished sufficient conductance for our measurements. This arrangement gave very satisfactory results, as shown in Table V. In these experiments, even in the absence of liquid junctions, the e. m. f. would not be zero, as one electrode was, for reasons, connected with our study of Thomson effects, maintained at zero instead of 25°. The extra middle beaker shown in Fig. 1 was necessary under these conditions. The hydrochloric acid solution was 0.09 N, the potassium chloride 0.1 N.
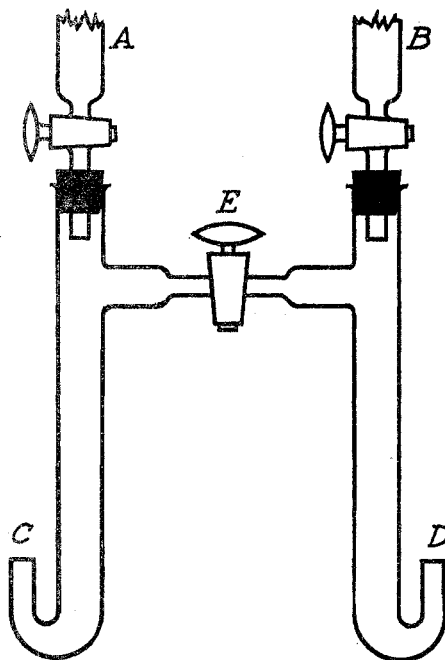


Fig. 2.

These results confirm the great reproducibility of fresh junctions, and also show that where oscillations are prevented very slight ageing effects occur.

TABLE V.
Fresh Junctions. Closed Tube 0.1 $N$ Solutions.

| Time. | | Millivolts. + |
|---|---|---|
| 2:28 | Fresh junction............................. | 8.31 |
| 2:49 | | 8.36 |
| 2:50 | Fresh junction............................. | 8.32 |
| 3:45 | | 8.30 |
| 6:30 | Fresh junction............................. | 8.32 |

This reproducibility, however, quite vanishes when instead of 0.1 $N$, normal solutions are employed. Thus, with all the other arrangements as before, but using $N$ instead of 0.1 $N$ solutions, the following typical results were obtained:

TABLE VI.
Fresh Junctions. Closed Tube, $N$ Solutions.

| Time. | | Millivolts. + |
|---|---|---|
| 3:37 | Fresh junction............................. | 7.37 |
| 3:39 | Fresh junction............................. | 7.62 |
| 3:40 | Fresh junction............................. | 7.45 |

Here rapid variations of ±0.3 millivolt were constantly occurring.

**Flowing Junctions.**—We now tried feeding the electrolyte slowly but continuously from the separatory funnels into the two arms of the siphon, the stopcock, as before, remaining closed. The results, using $N$ solutions, were as follows:

TABLE VII.
Flowing Junctions.

| Time. | | Millivolt. + |
|---|---|---|
| 4:05 | Flowing................................... | 7.85 |
| 4:20 | Flowing................................... | 7.85 |
| 4:40 | Flowing................................... | 7.83 |
| 7:13 | Flowing................................... | 7.81 |

These results show that even with $N$ solutions containing ions as different in mobility as those of potassium and hydrogen, very closely reproducible potentials can be secured by the simple device of a flowing junction.

To confirm this and, if possible, to understand the phenomenon better, we now applied the same technique to the second type of cell described above (2). This was accomplished by placing 2 silver chloride electrodes of the form shown in Fig. 1, one immersed in $N$ hydrochloric acid, the other in $N$ potassium chloride, in a large beaker containing $N$ potassium chloride. The electrode vessel containing the hydrochloric acid was provided with a separatory funnel to allow a slow flow of electrolyte from the electrode vessel into the beaker. With such a cell containing but a single liquid junction, any change which might have cancelled out with the 2 symmetrical junctions of the first type of cell would be here dis-

closed. Typical results obtained with this arrangement are given in Table VIII.

### TABLE VIII.
#### Flowing Single Junctions.

| Time. | | Millivolts. + |
|---|---|---|
| 1:25 | Flowing................................ | 32.75 |
| 3:00 | | 34.27 |
| 3:03 | Flowing................................ | 32.77 |
| 3:49 | | 34.13 |
| 3:52 | Continuously flowing................... | 32.76 |
| 3:57 | | 32.75 |
| 4:00 | | 33.13 |
| 4:11 | | 33.67 |
| 4:22 | | 33.73 |
| 4:27 | | 33.89 |
| 4:29 | Flowing................................ | 32.75 |

These results confirm the constancy and reproducibility of the flowing junction. They also disclose the marked ageing effect which occurs with these solutions.

**Effect of Stirring.**—Cumming[1] states that he was able to secure reproducible results by establishing a fresh boundary and then stirring it. We attempted to test this point, and to compare the potential thus secured with that given by a flowing junction, by alternately establishing a flowing junction, then interrupting the flow and stirring the electrolyte in the mouth of the exit tube with a small glass rod. The following results were obtained (Table IX):

### TABLE IX.
#### Comparison of Stirred and Flowing Junctions.

| Junction. | Millivolts. + |
|---|---|
| Flowing........................................ | 30.29 |
| Stirred........................................ | 30.54 |
| Flowing........................................ | 30.30 |
| Stirred........................................ | 30.56 |
| Flowing........................................ | 30.30 |
| Stirred........................................ | 30.52 |
| Flowing........................................ | 30.30 |

The potential of the stirred junctions was fairly constant but quite different from the very constant value for the flowing junction.

Again, the effects of stirring and of forming the flowing junction in quite a different way were studied with the same electrode and solution as used above, but so arranged that the liquid junction was formed at the meeting point of *two* streams, one of hydrochloric acid and the other of potassium chloride solution in a glass tube. The arrangement of tubes and funnels for this purpose is shown in Fig. 3. The denser liquid (potassium

[1] *Loc. cit.*

chloride) was fed upward from the bottom and the mixed liquids passed out the horizontal exit tube B. It will be noted that the tube was constricted at the point A, where the 2 streams met. This was designed to eliminate any dead space and to produce a rapid flow at this point. The constant level attachment at B was found to be quite essential; if
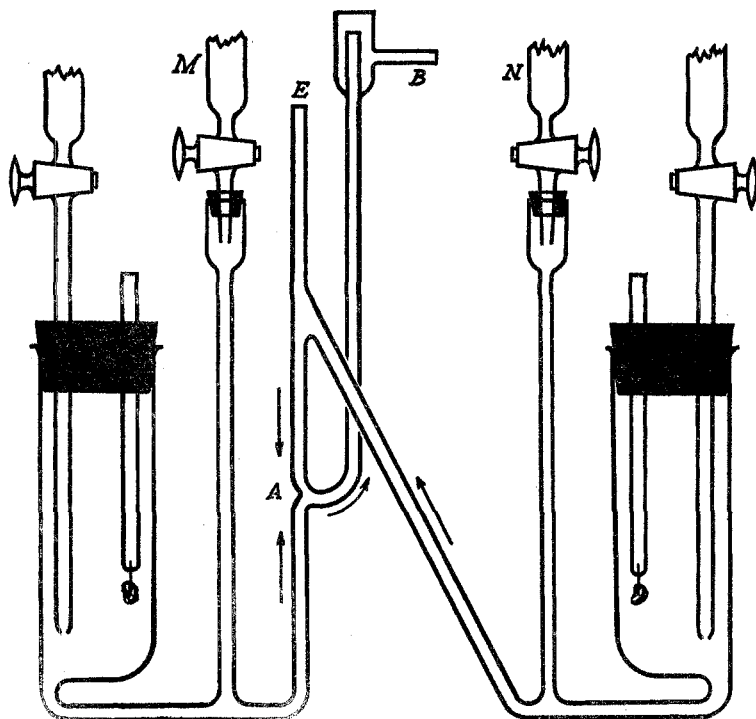


Fig. 3.

it were omitted, and the mixed liquid siphoned off, the slight pumping action which resulted was sufficient to disturb the boundary. A long glass rod was also fitted into the tube E by means of rubber tubing, so that by pushing it down and up the junction of A could be stirred. Some typical results obtained with this arrangement are given in Table X.

TABLE X.

Comparison of Stirred and Two-way Flowing Junctions.

| Date. | Junction. | Millivolts. + |
|---|---|---|
| Mar. 3..................... | Flowing | 30.30 |
| Mar. 4..................... | Flowing | 30.28 |
| Mar. 4..................... | Stirred | 30.04 |
| Mar. 4..................... | Flowing | 30.30 |
| Mar. 6..................... | Flowing | 30.29 |
| Mar. 6..................... | Stirred | 30.20 |
| Mar. 6..................... | Flowing | 30.30 |

These results show that the liquid junction formed by the confluence of the 2 streams gives exactly the same and just as constant a potential as does the one-way flow of a single electrolyte. However, the stirred junctions formed here were not constant and in general gave lower potentials than the flowing junctions, whereas in the previous arrangement higher results were obtained.

## Summary.

The above experiments have shown:

1. That liquid junctions formed between the bearing surfaces of ground glass stoppers, in gelatin diaphragms and in parchment paper diaphragms, with 0.1 $N$ hydrogen chloride and potassium chloride solutions are not constant and reproducible to closer than 0.2 or 0.4 of a millivolt.

2. That parchment diaphragms with stirring give somewhat more constant results.

3. That fresh junctions in tubes of 5 mm. bore give potentials reproducible in 0.1 $N$ solutions to about $\pm 0.03$–$0.06$ millivolt when oscillations of the electrolyte are prevented, but that with $N$ solutions variations of $\pm 0.3$ millivolt occur.

4. That stirred junctions sometimes give very constant potentials, but these are quite different from that produced by a "flowing" junction and, moreover, they differ, depending on the mode of stirring, etc.

5. That a "flowing" junction, obtained simply by having an upward current of the heavier electrolyte meet a downward current of the lighter electrolyte in a vertical tube at its point of union with a horizontal outflow tube, or by allowing the lighter electrolyte to flow constantly into a large volume of the heavier electrolyte, even with $N$ solutions, gives potentials constant and reproducible to $\pm 0.01$ of a millivolt.

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# THE REACTION BETWEEN HYDROCHLORIC ACID AND POTASSIUM PERMANGANATE.

BY F. P. VENABLE AND D. H. JACKSON.

On account of its convenience and ease of regulation, the reaction between hydrochloric acid and potassium permanganate has become the usual one for the preparation of chlorine for laboratory purposes. On looking over the text-books one finds some confusion of thought, some misstatements, and a certain amount of evasion of the facts involved. The equation given for this reaction in most of the text-books is

$$2KMnO_4 + 16HCl \longrightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2.$$