The Committee agrees unanimously with Aston's opinion and sees no reason for proposing a change in the present standard of atomic weights, O = 16.0000.

LIQUID JUNCTION POTENTIALS. I. REPRODUCIBLE STATIC LIQUID JUNCTIONS CONSTANT IN POTENTIAL OVER LONG PERIODS OF TIME[1]

BY ALFRED L. FERGUSON, KENNETH VAN LENTE AND RICHARD HITCHENS

Static liquid junctions have caused endless difficulties since measurements of single electrode and concentration cell potentials were first attempted.[2]   To get results at all reproducible, investigators have adopted numerous arbitrary methods for overcoming these difficulties, but none are accepted as satisfactory.   Such procedures, of course, have rendered the data empirical.[3]   An extensive study of the most promising devices was made by Lamb and Larson.[4]   They concluded that results with static junctions, made in various ways, are unsatisfactory, and, therefore, proceeded to develop the flowing junction.

There are many instances, however, where it is not possible or convenient to use flowing junctions and yet it is highly important that constant and reproducible values be obtained; for instance, in the comparison of the standard hydrogen with a calomel or any other electrode, liquid junction potential is included in the measurement and becomes a part of the value given to the calomel or other electrode.   All such values are as uncertain as the boundary potential, and whenever the calomel electrode is used as a standard the assumption must be made that the solution potential, which is a part of its value, always remains the same. When a saturated calomel electrode or a bridge of saturated potassium chloride is used, the common assumption is that no boundary potential exists under these conditions.   It is well known, however, that neither of these assumptions is justified.   The present work is an attempt to construct static boundaries of this nature in such a manner as to give potentials more constant and reproducible than have previously been done.   The

[1] The material in this article is from a portion of the thesis submitted to the Graduate School of the University of Michigan by Kenneth Van Lente in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] The present authors do not include a bibliography because several are now in print; see, for instance, Guggenheim, THIS JOURNAL, 52, 1315 (1930).

[3] These remarks do not apply to junctions which consist of two different concentrations of the same electrolyte.   Such boundaries, according to both theory and practice, give but little trouble.

[4] Lamb and Larson, THIS JOURNAL, 42, 229 (1920).

systems used were selected because of their importance in connection with the determination of the relative values of calomel electrodes and because saturated calomel electrodes, or other calomel electrodes in conjunction with a saturated potassium chloride bridge, are so extensively used in P_H measurements.

Most valuable contributions, both theoretical and experimental, to this field have been made recently by Maclagan, Bjerrum, Guggenheim and their co-workers.[5,2]   Some of the systems used by these investigators are similar to those herein described.   Unmack and Guggenheim, in their last article on this topic, introduced several improvements upon their earlier works, but still they state the tenth normal calomel electrodes have a probable error of ±0.15 mv. and the 3.5 normal are "less stable and slightly less reproducible."   Concerning the boundary potentials it is stated, "We reduced the erratic fluctuations of the free diffusion measurements from about ±0.25 mv. to ±0.1 mv."   The saturated calomel electrodes used in the present work showed a maximum variation of 0.05 mv. and remained constant to 0.02 mv. for several months.   One of the major factors in this reproducibility and constancy is the maintenance of a constant temperature throughout the whole period.   Freshly prepared electrodes required several days in the constant temperature bath before their potentials became stable; and when electrodes were left out of the bath while cells were being reassembled, it required several hours to regain their former value.

Apparatus and Materials

Electrodes.—Several saturated calomel electrodes were used as references.   The type was a slight modification of that used by G. N. Lewis.[6]   Much care was exercised in their preparation.   The silver chloride electrodes were made by a method closely similar to that recommended by Carmody.[7]   Such electrodes were fairly reproducible and remained constant to within 0.02 mv. for periods of time longer than the cells were measured.

The liquid junction vessels were 9-mm. three-way stopcocks.   The stopcocks were placed in such a position that the junctions were horizontal in vertical tubes (see E, Fig. 2).   A special stopcock grease, made by heating at 110° a mixture of equal weights of crepe rubber and white vaseline until it became uniform in body, was found necessary to prevent oil from leaking in and liquid from seeping around the stopcock.

Measuring Apparatus.—The potentials were measured on a Leeds and Northrup Type K potentiometer equipped with a Leeds and Northrup 2285-c High Sensitivity galvanometer.   The Weston saturated standard cell was calibrated by the Bureau of Standards.   Measurements were checked frequently on another potentiometer set-up in the same room and always found to agree within 0.01 mv.   The temperature was maintained constant at 25.00° by an electrically controlled oil-bath.

[5] Maclagan, Biochem. J., 23, 309 (1929); Unmack and Guggenheim, Kgl. Danske Videnskab. Selskab., Math.-fys. Medd., 10, No. 8 (1930).

[6] Lewis, Brighton and Sebastian, THIS JOURNAL, 39, 2245 (1917).

[7] Carmody, ibid., 51, 2901 (1929).

Solutions.—Extensive precautions were taken to make certain that the potassium chloride solutions were at all times saturated.   This is an important factor.   The hydrochloric acid solutions were made from redistilled Baker and Adamson c. p. hydrochloric acid.   They were analyzed by three gravimetric determinations and the results showed that they were exact for this work.

Experimental

Boundaries were made first in the customary manner by dipping the side arms of two saturated calomel electrodes into a beaker of 0.10 M
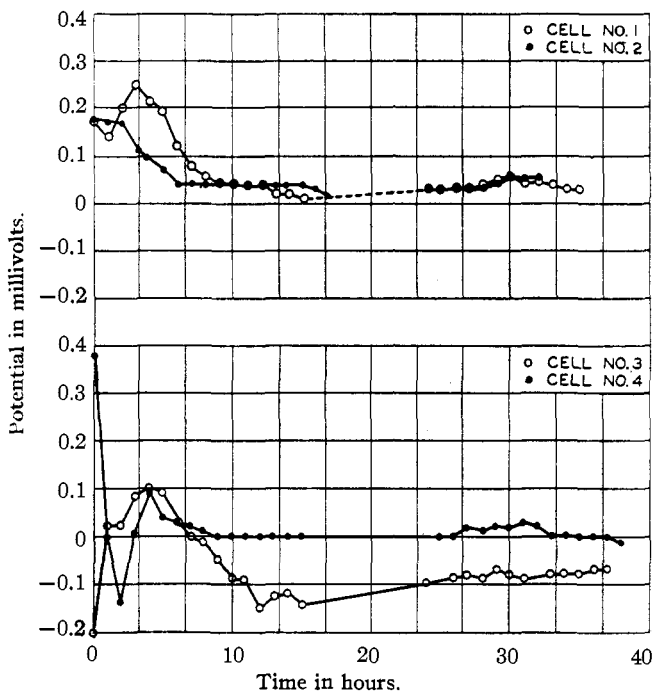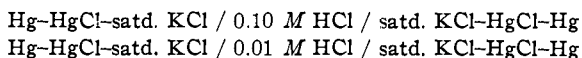

Fig. 1.—Curves showing how the potentials of the cells Hg–HgCl–satd. KCl/0.10 M HCl/satd. KCl–HgCl–Hg; Hg–HgCl–satd. KCl/0.01 M HCl/satd. KCl–HgCl–Hg varied with time when the junctions were made horizontally in 9-mm. stopcocks.
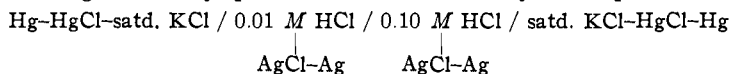
hydrochloric acid.   The potentials were neither zero, reproducible nor constant.   The nature of the junction was varied in several ways.   The electrode side arms with and without constricted tips in some cases were dipped straight down into the acid solution; in others the tips were turned up, and in still others the vertical parts of the tubes were filled with various mixtures of the two solutions so as to produce a more "continuous mixture" boundary.   The results showed clearly that cells which contain liquid junctions between saturated potassium chloride and 0.10 M hydrochloric acid solutions made by any of these methods are indefinite to the extent of 0.2 mv. or more.

In earlier work in this Laboratory the major boundary under investigation has been made in three-way stopcocks with considerable success. In the present work this system was applied also to the supporting boundaries which are usually made in an indefinite manner. The two following types of cells were used

$$\text{Hg–HgCl–satd. KCl / 0.10 } M \text{ HCl / satd. KCl–HgCl–Hg}$$
$$\text{Hg–HgCl–satd. KCl / 0.01 } M \text{ HCl / satd. KCl–HgCl–Hg}$$

Typical results are represented in Fig. 1. The potentials, of course, should be zero, but, especially at first, this is not the case. The results show, however, that in time the potentials approach zero and remain so for many hours. They are more constant and reproducible than any previously reported.

Boundaries made in this manner were then incorporated into a typical cell involving boundary potential. The cell may be represented as

$$\text{Hg–HgCl–satd. KCl / 0.01 } M \text{ HCl / 0.10 } M \text{ HCl / satd. KCl–HgCl–Hg}$$
$$\text{AgCl–Ag} \qquad \text{AgCl–Ag}$$

A diagram of the set-up is shown in Fig. 2.
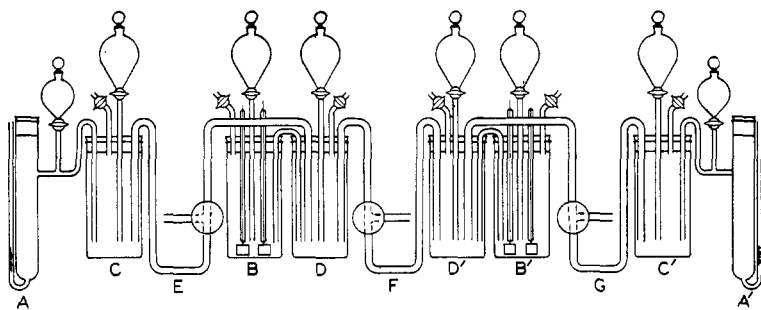
Fig. 2.—A diagram of the apparatus in which were made the cells
Hg–HgCl–satd. KCl/0.01M HCl/0.10 M HCl/satd. KCl–HgCl–Hg.
AgCl–Ag   AgCl–Ag

With this arrangement the combined potential of all three boundaries could be determined, and also any variations in individual boundaries.

A typical set of data is given in Table I. The letters above each column correspond to those used to designate the parts of the cell system represented at the head of the table and in Fig. 2, and indicate over what portion of the whole cell system the values in the respective columns apply. The last three columns give data regarding the constancy of the three individual boundaries, G, F, and E, respectively. It is obvious that the individual boundaries are extremely constant in potential. The potential between the two concentrations of hydrochloric acid is as constant as the silver chloride electrodes themselves, which is in complete agreement with past experimental work by many investigators.

TABLE I

A TYPICAL EXAMPLE OF THE RESULTS OBTAINED WITH A CELL OF THE TYPE

Hg–HgCl–satd. KCl / 0.01 M HCl / 0.10 M HCl / satd. KCl–HgCl–Hg

		AgCl–Ag	AgCl–Ag	
A	B		B'	A'
Time, hours	Pot. A-A', mv.	Pot. B'-A', mv.	Pot. B-B', mv.	Pot. A-B, mv.
0	37.99	44.81	92.37	99.19
1	37.97	44.79	92.37	99.19
2	37.95	44.76	92.37	99.18
3	37.95	44.75	92.38	99.18
4	37.93	44.73	92.38	99.18
5	37.92	44.73	92.38	99.19
6	37.93	44.75	92.38	99.20
7	37.92	44.76	92.37	99.21
8	37.93	44.77	92.37	99.21
9	37.93	44.78	92.37	99.22
10	37.92	44.77	92.38	99.22
11	37.93	44.77	92.37	99.21
12	37.94	44.77	92.37	99.20
13	37.94	44.77	92.37	99.20
14	37.94	44.77	92.38	99.20
15	37.98	44.77	92.37	99.17
24	38.07	44.76	92.36	99.06
25	38.09	44.76	92.37	99.06
26	38.09	44.76	92.36	99.05
27	38.07	44.76	92.37	99.06
28	38.07	44.76	92.37	99.07
29	38.00	44.76	92.37	99.14
30	37.96	44.76	92.37	99.17
31	37.93	44.76	92.37	99.21
32	37.93	44.76	92.38	99.21
33	37.97	44.76	92.37	99.17
34	37.98	44.76	92.37	99.16
35	37.99	44.76	92.38	99.15
36	37.98	44.76	92.37	99.15
37	37.99	44.77	92.37	99.15
38	37.99	44.77	92.38	99.15
48	37.99	44.77	92.38	99.15
Av.	37.98	44.76	92.37	99.16
Av. dev.	±0.04	±0.01	±0.00	±0.04

It should be mentioned that the technique involved in making the assembly is an important factor. After all parts were rigidly located through the use of suitable supports and clamps and the vessels filled with their respective solutions, the boundaries were formed within the large three-way stopcocks. To do this the lower part was filled by suction with the more dense solution, the stopcock was then turned through 180°, the remaining solution drawn out, the stopcock washed several times with

the less dense solution, and finally filled by suction with the less dense solution. It was closed by turning through an angle of 45°. In adjusting the liquid levels, account had to be taken, of course, of the difference in densities of the solutions on opposite sides of the boundary.

The apparatus was left in the thermostat overnight. The next morning the small stopcock in each beaker was opened to ensure atmospheric pressure. The boundaries were then formed by turning the large stopcocks through 45°, and were left undisturbed throughout the experiment. These are true "free diffusion boundaries."

In order to test the reproducibility and constancy over long periods of time of the potentials of this cell system and to establish an accurate value for the so-called boundary potential between 0.1 and 0.01 N hydrochloric acid, fifteen cells were measured which were the same as those described above. The results are recorded in Table II. The first column

TABLE II

A SUMMARY OF THE RESULTS OBTAINED WITH FOURTEEN CELLS OF THE TYPE

Hg–HgCl–satd. KCl/0.01 M HCl/0.10 M HCl/satd. KCl–HgCl–Hg

Time, hours	Av. pot., mv.	Av. dev., mv.
26	38.08	±0.03
48	38.09	± .05
29	38.03	± .03
43	38.10	± .04
51	38.06	± .06
48	38.03	± .07
13	38.08	± .03
42	38.04	± .05
14	38.00	± .04
12	37.97	± .03
11	37.97	± .02
32	38.12	± .01
49	37.99	± .07
48	37.98	± .04
	Av. 38.04	

gives the number of hours during which readings were made on the respective cells; the second, the average potentials in mv. over the time interval indicated; the third, the averages of the deviations of the single readings from the average of each cell. The average potential of all the averages is 38.04 mv. The maximum deviation of this average potential from that for any one cell is 0.08 mv. and the mean of the average deviations is ±0.04 mv.

Summary

1. An improved method for making a "free diffusion" type of static junction is described.

2. Static junctions of the type 0.1 M HCl/satd. KCl or 0.01 M HCl/ satd. KCl must be made very definitely in order to be reproducible or constant, and when so made are constant for days to ± 0.04 mv. average deviation, and reproducible to less than 0.1 mv.

3. The junction between 0.1 and 0.01 M hydrochloric acid is constant and reproducible within the limits of dependability of the silver chloride electrodes used, or within 0.02 mv.

4. The potential of the cell system

Hg–HgCl–satd. KCl/0.01 M HCl/0.10 M HCl/satd. KCl–HgCl–Hg
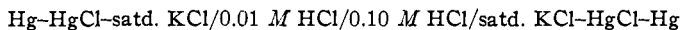
commonly called the boundary potential between 0.01 and 0.10 M hydrochloric acid has been determined to be 38.04 $\pm$ 0.04 mv. average deviation.

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LIQUID JUNCTION POTENTIALS. II. A DIRECT COMPARISON OF STATIC AND FLOWING JUNCTIONS[1]

BY ALFRED L. FERGUSON, KENNETH VAN LENTE AND RICHARD HITCHENS

Many careful and extensive investigations during the last quarter century developed the general feeling that static liquid junctions are neither reproducible nor constant.   This situation led to the development of the flowing junction.

Lamb and Larson,[2] who were the first to work extensively with the flowing junction, formed their junctions by allowing the more dense solution to flow up a vertical tube and meet the less dense solution flowing down, both then flowed out a common horizontal exit.   This junction gave results constant and reproducible to one or two hundredths of a millivolt but the values were different from those which they obtained with static junctions. They also differed as much as 2.46 mv. from results obtained with another type of flowing junction apparatus which they used.

MacInnes and Yeh,[3] with a modified form of the Lamb and Larson apparatus, showed that the potentials of cells containing solutions of the same concentration of a common ion varied with the rate of flow. They showed, also, that the potentials increase appreciably at low rates and decrease slightly at high rates of flow.   Scatchard[4] modified the apparatus used by MacInnes and Yeh in order to obtain an equal rate of

[2] Lamb and Larson, THIS JOURNAL, **42**, 229 (1920).

[3] MacInnes and Yeh, *ibid.*, **43**, 2563 (1921).

[4] Scatchard, *ibid.*, **47**, 696 (1925).