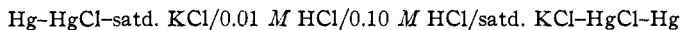


2. Static junctions of the type 0.1 *M* HCl/satd. KCl or 0.01 *M* HCl/satd. KCl must be made very definitely in order to be reproducible or constant, and when so made are constant for days to  $\pm 0.04$  mv. average deviation, and reproducible to less than 0.1 mv.

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



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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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN]

## LIQUID JUNCTION POTENTIALS. II. A DIRECT COMPARISON OF STATIC AND FLOWING JUNCTIONS<sup>1</sup>

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

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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,<sup>2</sup> 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,<sup>3</sup> 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<sup>4</sup> modified the apparatus used by MacInnes and Yeh in order to obtain an equal rate of

<sup>1</sup> The material presented 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 fulfillment of the requirements for the degree of Doctor of Philosophy.

<sup>2</sup> Lamb and Larson, *THIS JOURNAL*, **42**, 229 (1920).

<sup>3</sup> MacInnes and Yeh, *ibid.*, **43**, 2563 (1921).

<sup>4</sup> Scatchard, *ibid.*, **47**, 696 (1925).

flow of the solutions. He also lengthened the horizontal part of the outlet tube to lessen the effects of mixing. His results with solutions of hydrochloric acid and saturated potassium chloride were reproducible and constant to a few hundredths mv. even with molal hydrochloric acid. He found that the potentials always rose when the flow was stopped, the maximum rise being 3.5 mv.

Other types of flowing junctions have been used by Aten and Van Dalfsen,<sup>5</sup> by Roberts and Fenwick,<sup>6</sup> and by Maclagan.<sup>7</sup>

It is evident from the literature that for a given piece of apparatus the flowing junction gives reproducible potentials at constant rates of flow but the values differ for different pieces of apparatus, and with the rate of flow, and do not agree with the values for static junctions.

The authors, in an earlier article, have described a method for obtaining highly reproducible and constant potentials for static junctions between saturated potassium chloride and different concentrations of hydrochloric acid. In the present work the apparatus was modified somewhat to make it possible to compare directly the potentials of static and flowing junctions.

### Apparatus

**Stopcock.**—The stopcock which permitted the direct comparison of static and flowing junctions is shown in Fig. 1. A horizontal static junction may be made at the

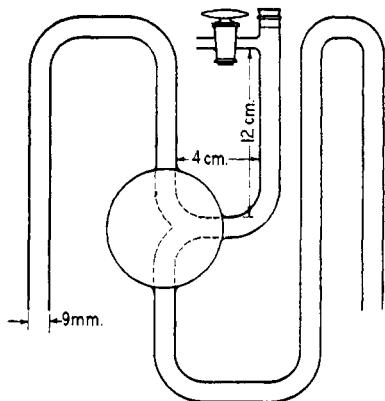


Fig. 1.—A diagram of a 9-mm. three-way stopcock which permitted the direct comparison of static and flowing junctions.

lower edge as described in the previous article. For the best results it is essential that the bore of the stopcock be exactly the same as that of the tubes leading to it. It was found necessary to have these made to order. The rate of flow was controlled by a stopcock in the exit tube. The small projection within the stopcock and opposite the outlet tube prevents the solutions from mixing when the junction is flowing. Preliminary experiments with sodium hydroxide solution on one side and water containing phenolphthalein on the other showed a very thin red ribbon-like layer which extended from the tip of the projection completely throughout the exit tube. This layer indicated that the junction was very thin at medium rates, somewhat mixed at high rates and diffuse at low rates of flow.

The measuring apparatus is the same as described in the previous article, except that the small dropping funnels were replaced with those of 250-cc. capacity in order to supply sufficient solutions for the flowing junctions, thus making readjustment of the levels of the solutions infrequent.

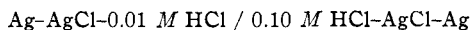
<sup>5</sup> Aten and Van Dalfsen, *Rec. trav. chim.*, **45**, 177 (1926).

<sup>6</sup> Roberts and Fenwick, *THIS JOURNAL*, **49**, 2787 (1927).

<sup>7</sup> Maclagan, *Biochem. J.*, **23**, 309 (1929).

### Experimental

The first cell studied was the concentration cell



It consisted of two silver chloride electrode vessels with side arms dipping into beakers of the respective acid solutions. These two beakers were joined by one of the large stopcocks shown in Fig. 1, in which the liquid junction was made. The potentials of the static junctions were measured over periods of about twenty-five hours; then the static junctions were changed to flowing. The rate of flow was not changed in any case until the potential had become constant to 0.01 mv. for at least fifteen minutes.

In order to determine how much of the flowing junction was actually effective, the solutions in the outlet tube were stirred with a piece of fine rubber tubing. This stirring was started at the top of the vertical tube and continued until the solutions in the stopcock itself were mixed. The corresponding changes in potential were noted.

A summary of the results obtained with this concentration cell is given in Table I.

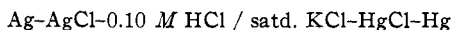
TABLE I  
A COMPARISON OF THE VALUES OBTAINED WITH A CONCENTRATION CELL USING VARIOUS TYPES OF LIQUID JUNCTIONS

Cell no.	Static pot., mv.	Flowing pot.			Stopped flow pot., mv.	Stirred junct. pot., mv.
		Low 0.3 cc. per min.	Med. 1.0 cc. per min.	High 2.0 cc. per min.		
1	92.27	92.32	92.32	92.30	92.30	92.30
2	...	92.33	92.33	92.30	...	...
3	92.27	92.32	92.30	92.30	92.30	92.30
4	...	92.32	92.30	92.31	92.30	92.30

It may be seen from Table I that the type of junction in a concentration cell makes practically no difference in the potential. These results confirm those obtained by Scatchard and Buehrer<sup>8</sup> with somewhat similar systems.

In these experiments the electrodes remained constant in potential to 0.02 mv. for periods longer than the cells were studied.

The next junction studied was that contained in the cell



It was made in a manner similar to the one just described. In this case it was necessary, however, to adjust the solutions to the same hydrostatic pressure. Leaks in these cells were found especially troublesome when the junctions were flowed and all places had to be absolutely air-tight. The importance of keeping the potassium chloride solution saturated, as pointed out by Scatchard,<sup>4</sup> was observed here and to ensure this, crystals of potassium chloride were kept in the lower tube leading to the stopcock. Three

<sup>8</sup> Scatchard and Buehrer, THIS JOURNAL, 53, 574 (1931).

cells were measured first with static and then with flowing junctions. The average potentials of the three static junctions were 44.76, 44.76 and 44.75 mv., respectively, with a mean average deviation over forty-eight hours of  $\pm 0.02$  mv. The results obtained with the flowing junction are represented graphically in Fig. 2.

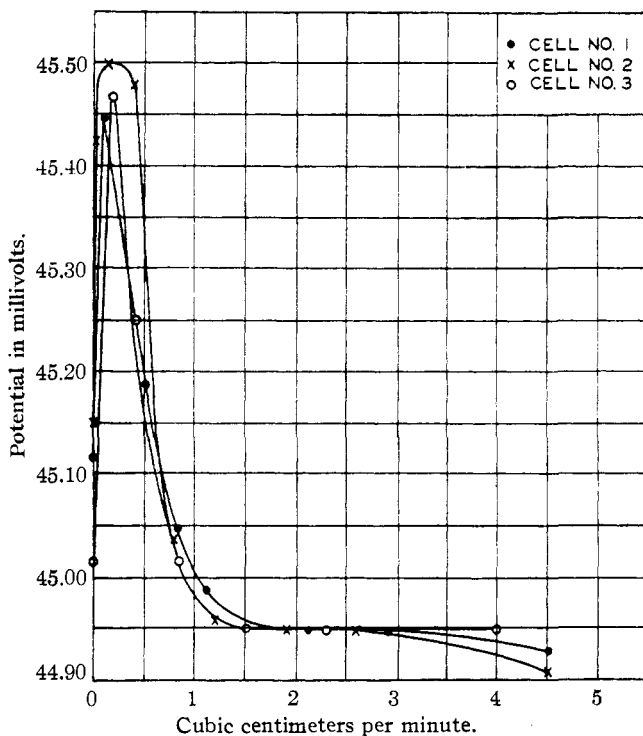


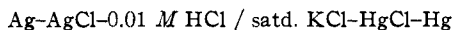
Fig. 2.—Curves showing the variations with the rate of flow of the potentials of the cells Ag-AgCl-0.10 *M* HCl/satd. KCl-HgCl-Hg.

It is evident, immediately, that the potentials vary greatly with the rate of flow and rise to a maximum at low rates. This maximum could be reproduced to 0.05 mv. and could be approached equally well from either direction. The potentials always decreased from the maximum when the flow was stopped, to values which might differ in separate experiments by 0.1 mv. and which were, on an average, about 0.1 mv. higher than the constant value at moderate rates. With rates of flow from 1.5 to 3.5 cc./min. the potentials were constant and reproducible in the different cells to 0.01 mv. For rates of flow greater than 3.5 cc./min. there was a slight decrease in potential. The constant potential obtained at medium rates of flow was about 0.2 mv. higher than the equally constant and reproducible value for the static junction obtained with identically the

same system before the flow was started. The shape of the curves was the same whether the rate of flow was varied from low to high or from high to low rates of flow.

Stirring the solutions in the outlet tube had no effect upon the potential until a point within 3 cm. of the stopcock itself was reached. From this point on the effect became greater until a maximum drop of 1.5 mv. was observed, when the solutions in the stopcock itself were completely mixed. This shows that the effective part of the junction is about the first 3 cm. of the horizontal tube.

The third junction studied was that in the cell



which is identical with the previous cell except for the concentration of the acid solution. Three cells of this type were run with static and flowing junctions. The averages of the three cells with static junctions were 99.04, 99.14 and 99.16 mv., respectively, with a mean average deviation of  $\pm 0.03$  mv. for forty-eight hours. The potentials of the cells with flowing junctions are represented graphically in Fig. 3.

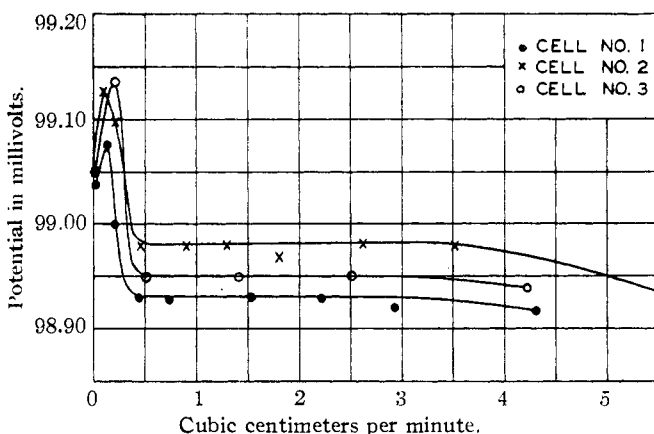


Fig. 3.—Curves showing the variations with the rate of flow of the potentials of the cells Ag-AgCl-0.01 *M* HCl/satd. KCl-HgCl-Hg.

In many respects the behavior of this junction is similar to the previous one, but in some respects it is distinctly different. There is an increase in potential at low rates and a slight decrease at high rates of flow. The values at medium rates are just as constant but less reproducible than those obtained with 0.10 *M* acid. There is also a decrease from the maximum when the flow is stopped, to a value about 0.1 mv. higher than that at medium rates of flow. When stirred, however, the junction with 0.01 *M* solution increased in potential 0.3 mv., while the 0.1 *M* decreased 1.5 mv.; also, with the 0.01 *M* solution the value at medium rates of flow

was 0.15 mv. lower than the average potential of the static junctions, while with the 0.10 *M* solution it was 0.2 mv. higher. These results indicate that saturated potassium chloride does not eliminate the boundary potential against hydrochloric acid solutions, that the remaining potential is different for different concentrations, and that it cannot be assumed that boundaries of different concentrations will respond in the same manner to disturbing influences.

### Summary

1. An apparatus has been developed for the direct comparison of static, flowing, "stopped flowing," and stirred junctions.

2. For concentration cells of 0.10 *M* and 0.01 *M* hydrochloric acid the potential is practically the same for all these types of junction.

3. For the junctions 0.10 *M* HCl / satd. KCl and 0.01 *M* HCl / satd. KCl the potential in each case depends upon the type of junction and the rate of flow, but these two junctions respond in opposite ways to certain treatments.

4. The effective part of this type of flowing junction is that contained in the first three cm. of the horizontal outlet tube.

5. For the systems involving saturated potassium chloride, the potentials with static junction are less empirical than those with flowing, because the variations of the potentials of the former with time are less than the variations of the latter with rate of flow.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF SYRACUSE UNIVERSITY]

## THE FREE ENERGY OF FORMATION OF ETHYL ACETATE. EQUILIBRIUM IN THE GASEOUS STATE<sup>1</sup>

BY HARRY ESSEX AND JOSEPH D. CLARK

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### Introduction

In this investigation the standard free energy change of the reaction

$$\text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH} = \text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O}$$

has been calculated at several temperatures from values of the equilibrium constant of the reaction in the gaseous state, which, together with data already available in the literature, leads to an evaluation of the standard free energy of formation of ethyl acetate.

Sabatier and Mailhe<sup>2</sup>, working with metal oxides, reported that titanium oxide catalyzed only the esterification reaction in a gaseous mixture

<sup>1</sup> Submitted to the Faculty of Syracuse University by Joseph D. Clark in partial fulfillment of the requirements for the Degree of Doctor of Philosophy, January, 1931.

<sup>2</sup> Sabatier and Mailhe, *Compt. rend.*, **152**, 669, 1044 (1911); **150**, 823 (1910); *Ann. chim. phys.*, **20**, 289, 351 (1910).