XXXVIII. THE USE OF DECINORMAL HYDROCHLORIC ACID FOR STANDARDISING ELECTROMETRIC p_H MEASUREMENTS.

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IN his specifications for the standardisation of p_H measurements, Clark [1928] gives as the ultimate standard the tenth-normal calomel half-cell, to which is assigned the Sørensen [1909] value for the normal hydrogen electrode potential. As a secondary standard any solution of known p_H may be used, the term p_H being defined with reference to the first standard.

The practical application of these specifications is a matter of some difficulty. The tenth-normal calomel cell is not now widely used owing to the amount of labour required for its satisfactory preparation; in addition to the tedious purification of the chemicals it is necessary to make up several cells at a time and take the average potential which must be frequently checked against freshly made cells [Sørensen and Lindestrøm-Lang, 1924]. If the alternative method is used, the materials for the working saturated calomel cell need not be specially purified, but it is difficult to find a satisfactory standard solution.

Of the many buffer solutions whose p_H has been determined, none is suitable even for rough measurements unless the salt is recrystallised several times. The 0.05 *M* potassium hydrogen phthalate recommended by Clark and Lubs [1916] is the simplest to prepare and has undoubtedly been successfully used by many workers, but the presence of impurity is a possible source of danger. Thus it is noted by Clark [1928] that the best commercial phthalic anhydride, although usually satisfactory, sometimes contains impurities which necessitate ten or more recrystallisations of the salt prepared from it; in the absence of an independent standard this precaution would not be taken. The occasional presence of another very troublesome impurity is described in a note at the end of this paper. Most of the other buffer solutions available are even more difficult to prepare and are not often employed for the present purpose.

A solution of the composition 0.01 *N* HCl.0.09 *N* KCl is advocated by Sørensen and Lindestrøm-Lang [1924] and others, but there appears to be some uncertainty both in the p_H and the temperature coefficient [Clark, 1928; Cullen, Keeler and Robinson, 1925]. Decinormal hydrochloric acid has none

of these disadvantages, as the pure acid is readily obtainable and the 0.1 *N* solution easily standardised. It has been used by Cullen [1922] and many others [Cullen, Keeler and Robinson, 1925; Hastings and Sendroy, 1924; Hastings, Baird, Sendroy, Julius and Van Slyke, 1928] who accept the value of 1.08 for the p_H at all temperatures. Since this value is based on the hydrogen ion activity calculated from the E.M.F. measurements of Noyes and Ellis [1917], it gives to the procedure a theoretical basis, the advantage of which has been pointed out by Cullen, Keeler and Robinson. There remains, however, the problem of the potential at the liquid junction

which is certainly much greater than that produced between saturated KCl and any of the other proposed standard solutions. It is, of course, usual to neglect the value of this potential, but it is still necessary that the junction should be formed in a reproducible manner. It has been shown by Clark and Lubs [1916] that the drift of potential which occurs at such junctions as this is considerable, and interferes with the accuracy of the measurement, and Clark [1928] considers that while each worker will be able to reproduce his own results, there is a serious danger of discrepancy between the results of different workers if this solution is used as a standard. The present paper is chiefly concerned with a practical study of the liquid junction in question from the standpoint of Clark's criticism.

EXPERIMENTAL.

The potential difference of the cell

was measured, junction *A* being made by a variety of methods. No importance is to be attached to the absolute value of the voltages recorded, as the chemicals were not specially purified, but the results show that the potentials at the electrodes remained unchanged during each series. The calomel vessels used were similar to those described by Kerridge [1926], and were kept at 25° by means of a simplified air-bath [Clark, 1928]. The temperature of the air in the bath varied by about 0.1° every half-minute, but this fluctuation produced no measurable effect on the readings obtained. Junctions *A* and *B* were made with vertical glass tubes dipping into the saturated KCl which was contained in a small intermediate vessel. Evaporation was prevented by a layer of liquid paraffin.

Saturation of the KCl was ensured by using a solution saturated at 37°, which was allowed to come to 25° and then well stirred. Junction *B* was always made at the end of a tube of 3 mm. internal diameter; its contribution to the P.D. of the cell was probably negligible. Junction *A* was formed both inside and at the end of tubes of different diameters. In the former case it was made by pinching the rubber tube, which held the glass tube in which the junction was to be established, in order to expel two or three drops of

HCl into a waste vessel when the glass tube was dipped into the KCl and the pressure released; a sharp junction was thus drawn into the tube about 1 cm. from the end (see Fig. 3). With wide tubes (7 mm.) it was found necessary to use a Y-piece and rubber teat. In practice, instead of the cell being lowered, the KCl was raised and a support finally pushed underneath. It was necessary to dislodge the drop of liquid paraffin which sometimes adhered to the end of the tube before drawing the junction inside. The following table shows typical results obtained with one pair of half-cells.

Table I.

(a) Junction at end of tube of 7 mm. internal diameter							
Reading (mv.)	84.8	84.6	84.4	84.2	84.0	83.8	83.7
Time (min.)	1	3	6	11	19	35	54
(b) Junction at end of 3 mm. tube							
Reading (mv.)	84.5	83.9	83.65	83.35	83.2	83.1	
Time (min.)	1	6	12	42	76	138	
(c) Junction inside 7 mm. tube							
Reading (mv.)	84.9	84.75	84.75				
Time (min.)	1	10	60				
(d) Junction inside 3 mm. tube							
Reading (mv.)	84.9	84.75	84.75				
Time (min.)	1	10	60				
(e) Junction inside 1 mm. tube							
Reading (mv.)	85.1	84.9	84.8				
Time (min.)	1	10	60				

It will be noticed that there is a surprising difference between junctions formed inside the tube and those formed at the end. The former are much to be preferred for the following reasons.

(a) They are more reproducible.

(b) The time change is only about one-tenth as great and occurs almost wholly within the first ten minutes.

(c) The diameter of the tube is unimportant if 3 mm. or over.

The final readings (10 minutes or longer) in Table I (c) and (d) were the most reproducible. The order of accuracy obtainable is shown by the following series of consecutive readings (obtained with another pair of cells) for junctions inside 3 mm. tubing. Each reading represents a different junction 10 minutes or longer after forming.

84.84, 85.00, 84.85, 84.95, 84.93, 84.94, 84.97, 84.90, 85.00, 84.90, 84.85, 84.90, 84.95 mv.
Av. deviation = 0.04 mv.; max. deviation = 0.08 mv.; mean: 84.92 mv.

None of the other readings was reproducible to less than about ± 0.2 mv. This type of junction was compared with a flowing junction by means of the apparatus sketched in Fig. 1.

The lighter HCl enters through tube *C* and meets an upward stream of the heavier KCl in the broad tube *D*. The mixed stream overflows at *E*. The junction can be made or broken as often as desired by raising or lowering tube *C* which fits the cork somewhat loosely. *C* and *D* are connected with reservoirs of HCl and KCl with rubber tubing, the rate of flow being regulated with screw clips. A T-piece is included on each side for connecting with the

two calomel cells. A convenient rate of flow is about 20 drops per minute from *E*, and the P.D. then reaches almost immediately a constant value which is unaffected by large increases in the rate of flow of either solution, or by the alteration of the diameter of tube *C* from 3 mm. to 1 mm. The exact degree of reproducibility is uncertain as the galvanometer was only sensitive to 0.05 mv. with the greater resistance introduced. No variation could be detected over periods of a quarter of an hour. Static junctions were made inside tube *C* in the usual way.

Fig. 1.

Fig. 2.

This form of flowing junction appears to possess certain advantages over the possibly more reproducible types of Lamb and Larson [1920] and McInnes and Yeh [1921], since contact can be made or broken as often as desired and the rate of flow of each solution can be varied independently. It was designed to imitate the first flowing junction described by Lamb and Larson, where the lighter solution runs slowly into a large volume of the heavier. Another pair of cells was used which, with the flowing junction at *A*, gave a potential difference of 88.9 mv. at the beginning and at the end of the experiment. This value fell to about 87.6 mv. when the flow of HCl was stopped, and rose to about 90.4 mv. when the flow of KCl was stopped. The average final reading of five static junctions made inside tube *C* was 88.89 mv. Taking into account the sensitivity of the galvanometer, it is evident that the two methods agree to within 0.05 mv.

The junction between saturated KCl and some other solutions was studied at room temperature with the arrangement shown in Fig. 2, using the system

Junction y was first made inside the tube with the aid of a rubber teat and after 10 minutes junction x was made at the end of the tube. The pair of cells used for these experiments gave a P.D. of < 0.05 mv. before and after the series. The following results are typical of those obtained.

Table II.

0.1 <i>N</i> HCl					
Reading (mv.)	+0.6	+0.7	+0.85	+0.98	+1.10
Time (min.)	1	3	6	13	19
0.01 <i>N</i> HCl. 0.09 <i>N</i> KCl					
Reading (mv.)	+0.17	+0.26	+0.28		
Time (min.)	0.5	5	10		
Potassium hydrogen phthalate 0.05 <i>N</i>					
Reading (mv.)	-0.06	+0.06	+0.07		
Time (min.)	1	7	10		
Phosphate solution p_H 7.4					
Reading (mv.)	+0.05	+0.10	+0.14	+0.16	
Time (min.)	1	4	7	19	

The difference between the two types of junction is not very serious except in the case of 0.1 *N* HCl.

The above system was also used to test the reproducibility of saturated KCl agar bridges and of the ground glass junctions used by Kerridge [1926] with the glass electrode; these were substituted for the tube shown at junction x . The agar bridges were prepared as directed by Michaelis and Fujita [1923] in tubing of 1 mm. internal diameter. The two cells used here had a P.D. of $+ 0.5$ mv. before and after the experiment.

Table III.

Agar bridge with 0.1 <i>N</i> HCl ¹						
Reading (mv.)	+1.0	+1.5	+1.7	+2.0	+2.5	} (±0.5 mv.)
Time (min.)	1	3	9	20	60	
Agar bridge with phosphate solution						
Reading (mv.)	+0.5	+0.8	+0.9	}	(±0.5 mv.)	
Time (min.)	1	5	15			
Glass caps with HCl						
Reading (mv.)	-20	-10	-4	-6	-1	-1.5
Time (min.)	1	3	10	1	3	15
Glass caps with phosphate solution						
Reading (mv.)	-1.5	0	+1	}	(±0.5 mv.)	
Time (min.)	1	5	20			

It will be seen that with the phosphate buffer both methods gave results corresponding roughly with the junction inside the tube, the order of accuracy being about ± 0.5 mv. The same is true of agar bridges with 0.1 *N* HCl, but the glass caps are unsuitable for making contact with this solution. In using the ground glass caps it was essential to exclude air bubbles, which may cause large errors. This is best accomplished by running some KCl solution into the cap as it is placed in position; the outside can then be rinsed and dried with filter paper as usual.

¹ The correct reading here is about 1.5 mv., since junction y was formed with 3.5 *N* in place of saturated KCl (see Table IV).

DISCUSSION.

In the case of static junctions it has always been the practice to take the initial readings, largely on the recommendation of Cumming and Gilchrist [1913]. The junctions have sometimes been at the ends of tubes [Fales and Vosburgh, 1918; Sørensen and Lindestrøm-Lang, 1924; Harned, 1926] and sometimes inside tubes [Clark, 1915; Stern, 1925], but even in the latter case the results have not been satisfactory for HCl solutions. For example, Clark and Lubs [1916], using 0.01–0.05 *N* HCl/sat. KCl, report a maximum deviation from the mean of 0.22 mv., and an average deviation of 0.14 mv. These results presumably correspond to the initial readings in Table I (c) and (d), which showed about the same variation. McInnes and Yeh [1921] also note that the initial reading differs from that given by their flowing junction in the case of 0.1 *N* HCl/0.1 *N* KCl. It is significant that Cumming and Gilchrist favoured initial readings chiefly on the evidence afforded by junctions made at the end of the tube; actually they record a negligible time change in the case of junctions inside a 1 cm. tube.

Since the absolute value of the potential at the liquid junction is unknown, all that is required is a reproducible result. It is therefore suggested that for the present purpose it is better to take the final reading (10 minutes or longer) with a junction made inside a tube of 3 mm. or over by the technique described above. Even with 0.1 *N* HCl, the degree of reproducibility is satisfactory for most purposes, ± 0.05 mv. or $\pm 0.001 p_H$, and the value obtained in this case is very close to that given by the flowing junction, and probably within 0.3 mv. of the value given by initial readings with the Clark hydrogen electrode. Final readings could no doubt be taken with this electrode, and should be identical with those obtained by the above method. The modification of Bunker's [1920] electrode as sketched in Fig. 3 is simpler and was found to be quite suitable for checking buffer solutions. It saturates quickly and, if provided with taps, the current of hydrogen may be turned off for at least half an hour without affecting the potential, which shows that the protection from the air is adequate. With this electrode there is no difficulty in duplicating results on 0.1 *N* HCl to within 0.1 mv.

It is claimed that this treatment of the liquid junction will remove any danger in the use of 0.1 *N* HCl for the standardisation of p_H measurements, and that this is, therefore, the safest solution available for this purpose. At the same time, the justice of Clark's criticism, referred to above, is clearly shown by the results obtained. Thus for the solutions 0.1 *N* HCl/sat. KCl the initial readings for junctions at the end of the tube may differ from those obtained with the above method by 0.3 mv., and probably from those usually obtained with the Clark electrode by 0.6 mv.; in addition to this they are less reproducible on account of the greater time change, a delay of even one or two minutes in taking the reading being serious. Agar bridges or capillary tubing may give rise to errors of one or two millivolts, and ground glass junctions are not recommended.

The "elimination" of the liquid junction potential.

There are two empirical methods which aim at the elimination of the liquid junction potential; the Bjerrum [1911] extrapolation method, and that of Michaelis and Fujita [1923]. The latter consists in interposing a solution of 0.1 *N* HCl saturated with KCl thus:

The two half-cells used in the first experiment (84.92 mv.) were compared by both these methods with the following results, which apply to final readings inside 3 mm. tubes.

Michaelis and Fujita	...	...	90.4 mv.
3.5 <i>N</i> KCl	83.8	} Bjerrum's point	87.7 mv.
1.75 <i>N</i> KCl	79.9

Fig. 3.

The two results differ widely and, therefore, do not support the validity of either method for this junction. Somewhat better agreement is obtained by following the practice of Walpole [1914] and Clark and Lubs [1916], who apply the Bjerrum extrapolation, determined substantially as above, to the voltage developed when saturated (4.1 *N*) KCl is used as a bridge. This gives 88.8 mv. for Bjerrum's point. It was noted in using the method of Michaelis and Fujita that the time change was in the opposite direction to that observed in all the other cases. This time change was almost entirely due to

junction *A*, since remaking junction *B*, when *A* had attained equilibrium, produced a negligible (< 0.05 mv.) change in the voltage. This observation suggested that some intermediate strength of HCl would eliminate the time change, and the following results (Table IV) show that the required strength is about 0.0185 *N*. The values obtained for Nos. 4 and 5 were very close, and as they were not reproducible to less than ± 0.1 mv. they overlapped. The average has, therefore, been taken as representing the mixture sat. KCl- 0.0185 *N* HCl with a very small time change of variable sign. This difficulty was probably due to slight initial diffusion which has a relatively great effect on these junctions.

Table IV.

The P.D. of the cell

+ Hg/HgCl. 0.1 <i>N</i> HCl/solution <i>x</i> / 3.5 <i>N</i> KCl.HgCl/Hg -		Final reading, inside junction mv.	Average time change mv.
No.	Solution <i>x</i>		
1	1.75 <i>N</i> KCl	79.9	-0.5
2	3.5 <i>N</i> KCl	83.8	-0.3
3	Sat. (4.1 <i>N</i>) KCl	84.9	-0.2
4	Sat. KCl. 0.0185 <i>N</i> HCl	86.15 av.	-0.1*
5	Sat. KCl. 0.0185 <i>N</i> HCl		+0.1*
6	Sat. KCl. 0.085 <i>N</i> HCl†	90.4	+1.0
7	Sat. KCl. 1.0 <i>N</i> HCl	119.0	+1.2

* These figures refer to junctions at the end of the tube; the time change for inside junctions was negligible in these cases.

† This mixture is 0.1 *N* HCl shaken with solid KCl to saturation, as directed by Michaelis and Fujita [1923].

The significance of this nul point is doubtful, but a consideration of Table IV suggests the possibility that the liquid junction potential has been eliminated in this case. In the first place it is probable on theoretical grounds that the liquid junction potential at *A* in No. 3 is small. The reading which corresponds to elimination of this potential is then not more than a few millivolts positive to 84.9. Thus, possibly in No. 6 and certainly in No. 7, the potential has been reversed. It is quite probably reversed in No. 6 since Harned [1916] has shown that the hydrogen ion activity of 0.1 *N* HCl is doubled by the presence of 3 *M* KCl. Now the amount of time change is frequently considered to be an index of the liquid junction potential. In Nos. 1, 2, 3 and 7, it is undoubtedly an index both of the sign and magnitude of the potential; if the same be true of Nos. 4, 5 and 6, it follows that the potential at *A* is zero in Nos. 4 and 5. This argument ignores the effect of junction *B* which, however, showed no appreciable time change even in the case of No. 7. In order to obtain some estimate of the potential at this junction, which cannot be zero, the Bjerrum extrapolation was used thus:

$$+ \text{Hg/HgCl. } 0.1 \text{ } N \text{ HCl} / \begin{matrix} 0.0185 \text{ } N \text{ HCl} \\ \text{sat. KCl} \end{matrix} / \begin{matrix} \text{sat. KCl (86.20)} \\ 3.5 \text{ } N \text{ KCl (86.15)} \\ 1.75 \text{ } N \text{ KCl (85.95)} \end{matrix} / 3.5 \text{ } N \text{ KCl.HgCl/Hg -}$$

A' *B'*

This gives the P.D. at B' (with 3.5 N KCl) as -0.2 mv. No accuracy can be claimed for this value, but it is probably of the right order of magnitude. On these assumptions the potential at the flowing junction

is 1.45 mv. Two recently calculated values are 1.58 mv. [Harned, 1926] and 4.7 mv. [Scatchard, 1925]. It is doubtful, however, whether the P.D. at A' can really be zero, as the hydrogen ion activity is different on the two sides of the junction. The p_H of the solution 0.0185 N .HCl sat. KCl was measured with the hydrogen electrode; assuming 1.08 for the p_H of 0.1 N HCl and neglecting liquid junction potentials the p_H of the mixture was found to be 1.32.

A NOTE ON THE USE OF POTASSIUM HYDROGEN PHTHALATE.

A commercial sample of "pure" potassium hydrogen phthalate contained less than 0.1 % water and required the theoretical volume of 0.1 N NaOH for neutralisation when titrated as directed by Dodge [1915]. Yet the p_H of the 0.05 N solution was 3.92 instead of 3.97. This was found to be due to the presence of a trace of impurity, presumably the acid salt mentioned by Dodge [1920]. This impurity was sparingly soluble in cold water, more soluble in hot, so that after four recrystallisations, carried out above 20° , the resulting product would not dissolve completely in water at ordinary dilution.

50 g. of the original material were shaken with 100 cc. water and allowed to stand, when the clear solution was decanted. This process was repeated until an apparently insoluble residue was obtained. 0.5016 g. of this residue was dissolved in hot water and required 26.60 cc. 0.1 N NaOH for neutralisation instead of the theoretical 24.54 cc.

The impurity might be introduced during the preparation either by an error of neutralisation or by recrystallisation below 20° [see Dodge, 1920], and, as it cannot be removed by recrystallisation and may not be obvious at a dilution of 0.05 N , it represents a danger which should not be overlooked. In view of this, and of Clark's note on phthalic anhydride mentioned above, it is suggested that if potassium hydrogen phthalate is to be used as a standard the only safe course is to recrystallise until the p_H of the 0.05 N solution is unaffected by further recrystallisation (above 20°). This can be done without using an independent standard and is not very laborious if the original material is pure; samples such as that described above are of course quite unsuitable, but at least the presence of the impurity is revealed by this treatment.

SUMMARY.

1. The advantages of using decinormal hydrochloric acid for standardising p_H measurements are pointed out. The liquid junction requires special treatment.

2. Some of the factors influencing the P.D. at the liquid junction 0.1 N HCl/sat. KCl have been investigated and a simple method of forming

the junction is described, which is reproducible to ± 0.05 mv. or $\pm 0.001 p_H$. This method is also recommended for general use in accurate p_H determinations.

3. A new type of flowing junction is described which gives for these solutions results almost identical with those obtained by the above method.

4. The degree of reproducibility of junctions formed with agar bridges and with ground glass surfaces is considered.

5. Some observations on the time change at the junction $0.1 N$ HCl/sat. KCl. xN HCl are presented and the possibility of eliminating the potential at this junction is discussed.

6. The occurrence of an impurity in a certain sample of potassium hydrogen phthalate is described. This affected the p_H of the $0.05 N$ solution but could not be removed by recrystallisation.

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