XVII. A BUFFER MIXTURE FOR THE ALKALINE RANGE OF HYDROGEN ION CONCENTRATION DETERMINATIONS.

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THE preparation of carbonate-free sodium hydroxide, as required for the Sørensen and Clark and Lubs buffer mixtures is undoubtedly troublesome, and neglect of the proper precautions gives rise to appreciable errors in the resulting buffer solutions. In the course of a biological research it was necessary to leave an alkaline solution, the alkalinity being due to sodium hydroxide, exposed to the air, with the natural result that carbon dioxide was absorbed and the alkalinity reduced. It was thought possible that were sodium carbonate used, instead of sodium hydroxide, the preparation of fresh solutions would be facilitated and the error due to absorption lessened. Were such a carbonate mixture however to be used much below p_H 8 it would tend to become more, and not less, alkaline, this being due to the solution giving off more carbon dioxide than it absorbs, the partial pressure of this constituent having risen.

Another point had to be considered, namely, whether the sweeping out of carbon dioxide during the bubbling of hydrogen through the Clark [1922] electrode vessel used in standardisation might not be a source of error. Owing, however, to the fact that the carbonate solution used was concentrated enough to be highly buffered no difficulty was experienced on this score.

The following solutions are accordingly recommended for use from p_H 7·8–10·8, though they cover a slightly more extended range:—(a) 0·2 *M* boric acid made 0·2 *M* with respect to potassium chloride also, as recommended by Clark [1922]. One litre should contain 12·4048 g. boric acid (taking the atomic weight of boron as 11·0, not 10·9 the more recent value) and 14·912 g. potassium chloride. (b) 0·2 *M* sodium carbonate 21·2000 g. per litre, prepared anhydrous from the bicarbonate as is usual in alkalimetry. To make up the mixtures for use the quantities of (a) and (b) shown in the table are mixed and diluted with 100 cc. water.

The first three columns of the table record the p_H values found for various mixtures of the two solutions in multiples of 5 cc. The last three columns show the volumes of the two solutions to be mixed to give p_H values differing

by 0.2; the volumes were read off from a graph, which has been omitted to economise space. These buffer solutions keep well if stored in waxed bottles tightly stoppered.

Water 100 cc. and			Water 100 cc. and		
Boric solution	Carbonate solution	p_H at 16°	Boric solution	Carbonate solution	p_H at 16°
cc.	cc.		cc.	cc.	
95	5	7.44	93.8	6.2	7.6
90	10	7.93	91.7	8.3	7.8
80	20	8.43	88.8	11.2	8.0
70	30	8.78	85.0	15.0	8.2
60	40	9.09	80.7	19.3	8.4
50	50	9.39	75.7	24.3	8.6
45	55	9.53	69.5	30.5	8.8
40	60	9.69	63.0	37.0	9.0
30	70	9.98	56.4	43.6	9.2
20	80	10.25	49.7	50.3	9.4
10	90	10.59	42.9	57.1	9.6
5	95	10.85	36.0	64.0	9.8
—	—	—	29.1	70.9	10.0
—	—	—	22.1	77.9	10.2
—	—	—	15.4	84.6	10.4
—	—	—	9.8	90.2	10.6
—	—	—	5.7	94.3	10.8
—	—	—	3.5	96.5	11.0

When working at p_H values above 9.6 difficulties are experienced in the choice of indicators; below that, thymol blue and xylene blue are both satisfactory and stable, but the only sulphonaphthalein recorded by Clark as covering a markedly higher range is nitrothymolsulphonaphthalein, which changes from violet to yellow between p_H 9.2–11.5; it, however, does not appear to be obtainable at present. Phenolphthalein may, however, be used up to p_H 10.5, and we have found the indicator now sold by the British Drug Houses, Ltd., as alizarin yellow G useful beyond this, the range being given as from p_H 10.1–12.1. According to Clark's list of synonyms this is identical with Michaelis' alizarin yellow GG, which is *m*-nitrobenzene-azo-salicylic acid, and changes from almost colourless to yellow. The alizarin G supplied to us, however, changes from pale yellow to orange and is Sørensen's alizarin yellow R, which is the corresponding *para* compound. In future it will be described as the latter. Thymolphthalein, which gives very beautiful blue shades between p_H 9.3–10.5, unfortunately fades rapidly.

EXPERIMENTAL.

The determinations were made with a Clark electrode vessel and shaking apparatus and a Leeds and Northrup potentiometer. The hydrogen used was generated electrolytically and traces of oxygen removed by passing over platinised asbestos in a hot tube. The two electrodes and connections were protected from air currents by a wooden box, but the temperature taken was that of the liquid in the hydrogen electrode vessel; the mean temperature of the twelve readings was 15.6°, but each reading was corrected to 16°, assuming that the coefficient is such that a rise of 6° results in reducing the

p_H value by 0.10, as for pure water; the assumption is certainly not accurate but appears to be sufficiently near for the purpose required and the results were found to lie well upon a curve.

The values given are for one atmosphere pressure of pure hydrogen at 0°; they have been corrected for the pressure of water vapour and for temperature. The potassium chloride used was of analytical reagent quality once recrystallised from glass-distilled water.

The standard cell was taken to give 1.0185 volts at 16° and the potentiometer was set accordingly. The value taken for the *N*/10 calomel electrode was 0.3381 volt at 16°, obtained by extrapolation from Clark's value 0.3380 at 18°. In making up the electrode re-distilled mercury and specially prepared calomel, from the Cambridge Instrument Co., Ltd., were used.

In order to test the accuracy of the working, *M*/20 acid potassium phthalate was prepared by resubliming phthalic anhydride and half neutralising. This was twice recrystallised and dried at 110°. By extrapolation from 18°, Clark's values for this solution were 0.5663 volt at 16.5° and 0.5657 volt at 15.4°, whereas those found by us were 0.5655 and 0.5664 respectively, differences of -0.0008 and $+0.0007$. Closer agreement is desirable, and the differences are probably due to inadequate temperature control, as the calomel electrode was not necessarily at the same temperature as the hydrogen electrode. The 0.8 millivolt difference however corresponds in this region to only p_H 0.013 and the value for *M*/20 acid potassium phthalate at 15.4° is p_H 3.996. In the region of p_H 10 a difference of 0.8 mv. corresponds to slightly under p_H 0.01. Since the differences between our values and Clark's for the 0.05 *M* acid potassium phthalate solution almost vanish when the two results are averaged, it is clear that no systematic error impairs the accuracy of these results.

It may be added that the inclusion of a variable resistance rheostat of 225 ohms, in addition to the fixed resistance supplied in the circuit of the rocking apparatus, was found to be essential.

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REFERENCE.

Clark (1922). *Determination of Hydrogen Ions*, 2nd edition.