



## SATURATED CALOMEL ELECTRODES — ABNORMAL POTENTIALS

The cell which is the basis of pH measurements and of the calibration of glass electrode + pH meter systems:

Pt, H <sub>2</sub> or glass el.	buffer solution	bridge solution	reference electrode I
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involves a choice of reference electrode and bridge solution, usually between the Ag | AgCl electrode or the calomel electrode and 3.5M or saturated KCl. Attention has been drawn [2, 3] to the occurrence of erroneous emf values of cell I, when the buffer solution is «Tris» (Tris hydroxymethyl aminomethane) and its hydrochloride. The blame for this error was put on a reaction between the buffer

solution and the «linen-fibre» used to establish the liquid junction [2].

During work [4] with cells II, at 25°C, we came across an unexpected situation of different explanation

Pt, H <sub>2</sub> or glass el.	buffer solution + BCl NaClO <sub>4</sub> (X)	KCl sat	calomel II
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where  $X = 0,10^{-2}, 10^{-1}, 1\text{mol l}^{-1}$  and B is one of the compounds mentioned in table 1 partially neutralized with constant boiling HCl.

Saturated calomel electrodes from Radiometer and Electronic Instruments Ltd. (EIL) with a piece of porous stone as means of establishing the liquid junction, were used.

Our two different saturated calomel electrodes did not yield identical emf values owing to their individual characteristics. KATER, LEONARD and MATSUYAMA [5], have published a detailed study of the «repeatability» of the liquid junction potential aspect and concluded this was probably  $\pm 1\text{mV}$ . However the magnitude of the difference between our electrodes varied in unpredictable ways as it is shown in table 2 referring to one particular experimental run.

The traces of emf versus time followed on a recorder, particularly for 1M Na<sup>+</sup> solutions, showed interesting features as illustrated in figure 1. For sodium free systems, electromotive forces followed

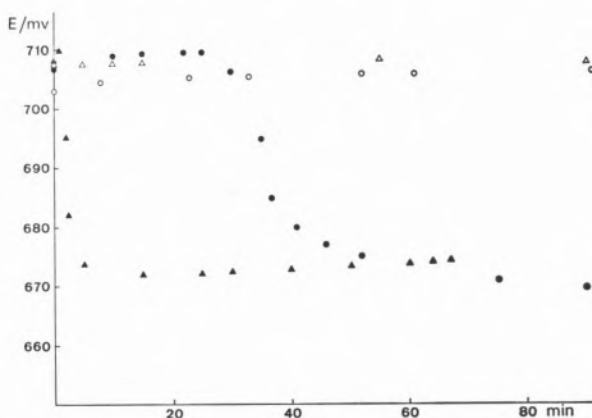


Fig. 1

Pt, H<sub>2</sub> | Tris buffer, Na<sup>+</sup> | calomel el.  
calomel EIL (Δ-0M Na<sup>+</sup>; ▲-10<sup>-1</sup>M Na<sup>+</sup>;  
calomel Radiometer (○-0M Na<sup>+</sup>; ●-10<sup>-1</sup>M Na<sup>+</sup>)

Table 1

Substance	Formula	Supplier (brand)
2,2-Bis (hydroxymethyl) — 2,2',2''-Nitrilotriethanol «Bis-Tris»	$(\text{CH}_2\text{CH}_2\text{OH})_2 - \text{NC} - (\text{CH}_2\text{OH})_3$	Aldrich — U.S.A.
Tris (hydroxymethyl) aminomethane «Tris»	$(\text{CH}_2\text{OH})_3 - \text{C} - \text{NH}_2$	Koch-Light (Puriss — A.R.)
Ethanolamine	$\text{CH}_2(\text{OH}) - \text{CH}_2 - \text{NH}_2$	BDH
Piperidine	$\begin{array}{c} \text{CH}_2 - (\text{CH}_2)_3 - \text{CH}_2 \\   \qquad \qquad   \\ \text{---} \text{N} \text{---} \\   \\ \text{H} \end{array}$	BDH

Table 2

			E (mV)	cal EIL cal Rad. $\Delta E$ (mV)
buffer soln.	(Na <sup>+</sup> ) M	Radiometer cal.	EIL cal.	
Bis-Tris (0.02M) + Bis-Tris HCl(0.02M)	0	626.4	628.7	+ 2.3
	10 <sup>-1</sup>	631.3	632.3	+ 1.2
	1	643.6 (↓603.4)	644.0(↓608.9)	+ 0.4 (+ 5.5)
Tris (0.05M) + Tris HCl (0.1M)	0	706.2	707.9	+ 1.7
	1	709.4 (↓669.1)	709.8 (↓674.3)	+ 0.4 (+ 5.2)
	0	796.2	794.9	— 1.3
Ethanolamine (0.02M) + Ethanolamine HCl (0.03M)	10 <sup>-2</sup>	796.3	795.4	— 0.9
	10 <sup>-1</sup>	798.6	798.5	— 0.1
	1	809.7 (↓773.0)	805.6	— 4.1 (?)
Piperidine (0.075M) + Piperidine HCl (0.03M)	0	910.5	907.5	— 3.0
	10 <sup>-2</sup>	910.5	907.7	— 2.8
	10 <sup>-1</sup>	912.4	909.7	— 2.7
	1	923.6 (↓888.6)	920.5	— 3.1 (?)

with time (up to 2 hours in the case of Tris buffer) attained, after initial transients, steady values. For the 1M Na<sup>+</sup> systems an initial rise in emf, towards the value expected from the knowledge of published pk values [1] was suddenly followed by a steep decrease, whose time of appearance could not be predicted. This was then followed by a more or less steady state characterized by an emf value which could not be accounted for by considerations of effects of salt addition. The magnitude ( $\sim 40\text{mV}$ ) of such variation was remarkably reproducible for the buffer systems studied, whatever the concentration of added Na<sup>+</sup> and which the calomel electrode used as reference. Similar observations were made using hydrogen-ion responsive glass electrodes instead of the hydrogen gas electrode.

Additional tests were done in order to check the stability of the solution. This was done by emf measurements in solutions B and B + Na<sup>+</sup> using the Ag | AgCl electrodes placed directly in the solution, that is without liquid junctions being involved. These measurements were followed by the ones of cell II with the calomel electrodes. Finally repeating the first set of experiments, the Ag | AgCl electrodes reproduced the first emf values, which indicates that unexpected values given by calomel electrodes are not a result of contamination of the cell solution. This leaves the calomel electrode as the only possible source of error.

Ryan, mentioned an error of 36mV with a Beckman reference electrode which is comparable in magnitude with that found in the present work. However the origin cannot be the one mentioned by Ryan, as the calomel electrodes used in our experiments do not have linen-fibre junctions.

Our experimental results imply that misbehaviour comes from the addition of NaClO<sub>4</sub> and not from the buffer substance itself. At the junction KCl<sub>sat.</sub>/NaClO<sub>4</sub>, KClO<sub>4</sub> may have been formed establishing a new potential KCl/KClO<sub>4</sub>.

Due to the wide use of calomel electrodes and the buffer solutions, such as «Tris», as secondary pH standards we think it is advisable to stress the advantages of an improved method of calibrating glass electrodes described elsewhere [6].

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## REFERENCES

- [1] BATES, R. G., «Determination of pH», 3rd Ed., J. WILEY, New York, 1973.
- [2] RYAN, M. F., *Science*, **165**, 851 (1969).
- [3] Sigma Chemical Co., *Tech. Bull.*, 106B, Supplement No. 1 (1970).
- [4] CAMÕES, M. F. G. F. C., «Ph. D. Thesis», University of Newcastle Upon Tyne, 1973.
- [5] KATER, J. A. R., Leonard, J. E. and Matsuyama, G., *Ann. N. Y. Acad. Sci.*, **148**, 54 (1968).
- [6] CAMÕES, M. F. G. F. C. and Covington, A. K., *Anal. Chem.*, **46**, 1547 (1974).

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