THE HYDROGEN-ION RESPONSE OF THE GLASS ELECTRODE IN AQUEOUS AND PARTIALLY-AQUEOUS SOLUTIONS

Alan E Bottom MSc CChem FRSC

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ABSTRACT

The existence of small errors, previously reported for hydrogen-ion responsive glass electrodes in standard and other buffer solutions of intermediate pH are confirmed. Such errors, apparent for all types of glass electrode tested above pH 2.5, are independent of the pH and total ionic strength of the solution, but are a function of the buffer composition and its molality. They increase with decreasing buffer concentration and are independent of the nature of added salt. For a particular glass electrode, the magnitude of the error is determined by the glass composition and its past use.

Reports that improved time responses and smaller or insignificant errors are obtainable in partially and non-aqueous solutions for glass electrodes soaked in the test solution solvent medium, and preferably, with internal fillings of either a solution in the same solvent or mercury, were not substantiated. Results of a survey, in aqueous, methanol-water and *N,N*-dimethylformamide-water mixture solutions, for glass electrodes with alternative fillings and conditioning, show responses are modified for some solvent mixtures. More detailed study is necessary before the observations can be properly explained.

Studies of the hydrogen-ion functions and durabilities for soda-lime and lithia-lime glasses reveal a meaningful correlation between pH response properties and the ratio of alkali:lime leached extracts. Compositions with good pH response functions have similar oxide ratios for the glass and the extract.

CONTENTS

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CHAPTER ONE

THE ERRORS OF THE pH GLASS ELECTRODE

1.1 INTRODUCTION

This study of certain aspects of the response characteristics of glass electrodes complements and extends a re-examination at Newcastle of long-accepted, though contentious, views of their performance which are discussed elsewhere in this chapter.

This re-examination has taken, as a basis for glass electrode behaviour assessment, the hypothesis of Beck and Wynne-Jones[1] that two potentials of the glass electrode are to be recognised, namely that instantaneously established in a solution which varies correctly with the hydrogen-ion activity of the solution and the asymmetry potential, which may vary with time as the result of the exchange of ions or water with the solution.

Covington and Prue[2] demonstrated the application of the hypothesis by the precise measurement of activity coefficients for dilute hydrochloric acid solutions by transferring low resistance glass electrodes between solutions. They measured the potential-time variation of the glass electrode and were able to extrapolate to the moment of transfer at which time, if the hypothesis is correct, the asymmetry potential of the electrode is the same in both solutions, and the change of electrode potential is due solely to an ideal response for the change of the hydrogen-ion activity. Their results supported the hypothesis.

For his re-examination of glass electrode behaviour in Newcastle, Caudle[3] developed a similar procedure by which glass electrodes were transferred between solutions containing hydrogen electrodes. If the hydrogen-ion function of a glass electrode is ideal, the cell emf would of course be invariant, regardless of the nature of the solution. If the cell emf varies with time, this is ascribed solely to a time variation of the asymmetry potential of the glass electrode. Extrapolation to the moment of transfer should, for an electrode with correct response, correspond exactly with the final emf in the previous solution, if not, the resulting difference is a measure of the hydrogen-ion error, assuming that there is no error in the previous solution.

Using this procedure with commercial soda and lithia-based glass electrodes, the reponse characteristics for acid solutions were classified by Caudle *et al.*[3,4] and for alkaline solutions by Buck[5]. In the course of these studies, small errors were noted for glass electrodes in buffer solutions of intermediate pH.

The presumption for these studies has been that the potential of a glass electrode in a solution is a function solely of potential determining reactions at the glass-solution interface. Reports, however, by, e.g. Badoz-Lambling *et al.*[6], have suggested that in partially and non-aqueous solvent solutions, the response characteristics are modified by the nature of the internal filling. Such behaviour is at variance with the contention of Dole[7], that the potentials at the inner and outer surfaces of the glass electrode are developed independently, which is assumed in all theories of the reponse of the glass electrode.

1.2 THE ALKALINE ERROR

The alkaline, or positive error, for which the pH indicated is lower than the true pH, was first recognised by Hughes[8] who compared soda-lime glass electrodes directly with hydrogen electrodes. He concluded that 'the glass surface potential is not a linear function of the logarithm of the hydrogen-ion concentration except when the hydrogen-ion concentration is greater than 10^{-11}. Even then this relationship is only approximate'.

Glass electrodes prepared from boroaluminosilicate glasses were found by Horowitz[9] and Schiller[10] to function as hydrogen electrodes only in acid solutions. At higher pH they exhibited a marked sodium-ion response and rather poorer potassium and zinc-ion functions.

Studies of other glass compositions and their pH function by Hughes[11] and by Lengyel and Blum[12] clearly indicated that for glasses containing boron or aluminium oxides, the pH function ceases above pH 4-5 and the electrodes exhibit a sodium-ion function.

Coincident with the introduction of the vacuum-tube electrometer, the systematic study of glass compositions and their pH response by MacInnes and Dole[13] led to the introduction of their preferred soda-lime composition for the first commerical pH glass electrodes, introduced by Corning Glassworks as glass 015. Electrodes of this composition were shown by Dole[7] to exhibit errors above about pH 8.5. The errors increased with increasing pH and increasing cation concentration in the order $Ba^{++} < K^{+} < Li^{+} < Na^{+}$. Later work by Dole and his co-workers[14,15] confirmed the relative order of the error response, however, the lithium and sodium errors observed were less than those obtained in his original work. He explained these discrepancies to the earlier work being performed with a poor sample of glass. They also found the error to increase with increasing temperature[14].

Hill[16] tested soda-glass electrodes up to pH 11.4 in ammonia buffers and reported them to be error free, and Hubbard *et al.*[17] detected no alkaline error in ammonia solutions. Error-free response had previously been noted by MacInnes and Dole[13] in 0.1 M solutions of tetramethyl ammonium hydroxide.

The development of lithia-based glass electrodes by Sokolov and Passynsky[18], Cary and Baxter[19] and Perley[20] resulted in the rather slow supersedence of soda-glass electrodes by the wider pH range, but higher electrical resistance lithia-based glass electrodes which are substantially error-free to about pH 13.

Radiotracer experiments by Izmailov and Vasilev[21] with soda-based and Schwabe and Dahms[22] with both soda and lithia-based glass electrodes established a distinct correlation between the alkaline error of a glass electrode and the absorption of alkali cations. For their test solutions glass electrodes were error-free up to pH 8.5 for soda-based electrodes and to about pH 12 for lithia-based electrodes, and little cation absorption was noted. Above these pH values, errors were exhibited and cations were absorbed, the amount increasing with pH, cation concentration and the immersion time in solution. Using radioactive-isotope tagged cation solutions, the relative order of cation absorption, $Na^{+} > K^{+} > Cs^{+}$ was found to be identical to the relative magnitudes of the alkaline errors for both types of electrode in solutions containing these ions.

Generally, there was little conflict with the characterization or the nature of the alkaline error. The magnitude was shown to be a function of the composition of the glass, the nature of the metal cation and its concentration, the pH of the solution and temperature. These early studies laid the foundation for the subsequent development of glass compositions for the determination of cations other than the hydrogen-ion[23].

1.3 THE ACID ERROR

As Bates[24] has succinctly stated 'from the earliest days, characterization of the acid error has been plagued by conflicting observations'.

The acid, or negative error, of the glass electrode results in a higher indicated pH than the true pH, and was first identified by MacInnes and Belcher[25] using soda-glass electrodes for mineral acid solutions at concentrations greater than 1 M. They found errors to decrease in the relative order $H_3PO_4 > H_2SO_4 > HCl$ and concluded anions were the cause of the deviations.

Dole[26] found the errors for hydrochloric and sulphuric acid solutions to be similar, and that addition of neutral salt with the same anion had marginal effect, concluding that the negative deviation could not be ascribed simply to anions. He also reported that negative errors were exhibited for solutions up to pH 8 on the addition of moderate concentrations of neutral salts, and further, that similar errors were displayed in ethanolic media. On the basis of these results he concluded the source of the negative error was to be found in the lowered activity of water in the solution, and since the activity of water in the solution was less than unity, the error could be expressed by the term $(RT/F)\ln a_{H_2O}$.

Amis and Gabbard[27] reported for Corning 015 electrodes, errors for solutions of up to 2 M magnesium sulphate at pH 3-8 in good agreement with Dole's equation. Buck[5], however, using both lithia and soda glass electrodes, found no errors for these magnesium sulphate solutions.

Using Corning 015 electrodes, Hubbard *et al.*[17] found no error for solutions of sulphuric acid up to 5 M. Likewise, Sinclair and Martel[28] observed no error for 5M sulphuric acid solutions with Corning 015 and other glass electrodes. They noted, for dilute hydrochloric acid solutions up to 1 M, potentials were steady and reproducible, although small errors were exhibited for the 1 M solution. For more concentrated solutions of hydrochloric acid, potentials were non-reproducible and time dependent, drifting to more negative values. The magnitude of the time-dependent error was related to the glass composition. For the 1 M and 5 M solutions, the time dependent errors were greater than those calculated from Dole's water-activity relationship.

The results of Glockner[29], and Schwabe and Glockner[30] for Corning 015 electrodes in phosphoric, sulphuric and hydrochloric acid solutions were in agreement with those of Sinclair and Martel[28] for sulphuric and hydrochloric acid solutions and they found errors for phosphoric acid solutions to be lower than those exhibited in sulphuric acid solutions. They suggested the errors arose by the absorption of excess hydrogen-ions and probably the presence of undissociated acid.

Radiotracer studies by Schwabe *et al.*[31] with Corning 015 electrodes in 4 M solutions of hydrochloric, hydrobromic and hydriodic acids and 10 M solutions of sulphuric and phosphoric acids showed absorption of the halogen acid anions to correspond with the magnitude and time dependence of the errors exhibited. Although errors were apparent in the sulphuric and phosphoric acid solutions, there was no indication of acid or anion absorption. For these solutions they attributed the errors to the reduced water activities and found them to be in satisfactory agreement with error values calculated using Dole's equation.

Beck and Wynne-Jones[1] transferred Corning 015 glass electrodes between dilute aqueous hydrochloric acid and dilute hydrochloric acid solutions in pure ethanol and various ethanol-water mixtures. Potentials of the glass electrodes were measured with hydrogen-gas electrodes and the time variation followed. They were able to extrapolate the time-variant potentials to the moment of transfer between the two solutions and concluded that at the instant of transfer, the hydrogen-ion function of the glass electrode was correct and that the apparent time-dependent error was due to a changing asymmetry potential. They suggested that as there was no water-activity error, the apparent errors in strong mineral acid and non-aqueous solutions could be ascribed to changing asymmetry potentials.

Nikolsky and Iovshits[32] reported similar results for the transfer of Corning 015 electrodes between aqueous and ethanolic acid and buffer solutions. The changing asymmetry potentials were ascribed to the absorption of the non-aqueous solvent into the gel-layer. They termed the final potential, established after many hours immersion in the non-aqueous solutions, the 'inert' potential. Analogous behaviour, the 'specific' effect, was reported for both lithia and soda-based electrodes on transfer between aqueous solutions and solutions in the lower alcohols[33], formic[34] and acetic acids[34,35] and DMF[35] by Shul'ts, Ivanovskaya and Gessen. The specific effects for lithia-based glasses were less than those observed for soda-based glasses.

A detailed study of the potential-time response of soda and lithia glass electrodes for transfer between mineral acid solutions by Caudle *et al.*[3,4] applying the instantaneous potential hypothesis generally confirmed Sinclair and Martel's[28] results. The results revealed transient potential-time variations which were dependent on the glass composition and the nature and concentration of the acid. For each acid, below some critical concentration, errors were zero or very small, in agreement with the hypothesis, but above this concentration, response transients were complex and on extrapolation to the instant of transfer, errors were apparent and found to be concentration dependent.

1.4 AIMS OF THE PRESENT WORK

1. To make a detailed investigation, at high discrimination, of the response characteristics of a representative selection of commercial glass electrodes in buffer solutions of pH 1-9.2 by direct comparison with hydrogen glass electrodes.

   The small errors of 0.005 - 0.20 in pH, noted by Caudle[3,4] and Buck[5], for commercial glass electrodes in buffer solutions of intermediate pH, are of significance for the calibration of pH cells. They are of paramount importance for pH measurements where high precision is essential, e.g., the routine measurement of the pH of body fluids in clinical laboratories and the determination of the dissociation constants of acids and bases in research and development departments.

2. To make a detailed investigation, using commercial electrode blanks, of the effects of varying the nature of the internal construction and conditioning of, otherwise nominally similar, glass electrodes in aqueous, aqueous-methanol and aqueous-dimethylformamide acid and buffer solutions.

   Improved performance, in partially and non-aqueous solvent solutions, has been reported by Badoz-Lambling *et al.*[6] for glass electrodes with internal fillings of, and conditioned in, the same solvent media in which they are used. Such behaviour is at variance with the long-held acceptance of the hypothesis of Dole[7] that the potentials at the inner and outer surfaces of a glass electrode are developed independently. The hypothesis is the basis for all theories of the glass electrode.

3. To ascertain if simple durability measurements can be used as a means of screening glasses for potential pH glass compositions, a series of soda-lime and lithia-lime glasses has been prepared and their durabilities and hydrogen-ion functions determined.

CHAPTER TWO

THEORIES FOR THE RESPONSE OF THE GLASS ELECTRODE

2.1 INTRODUCTION

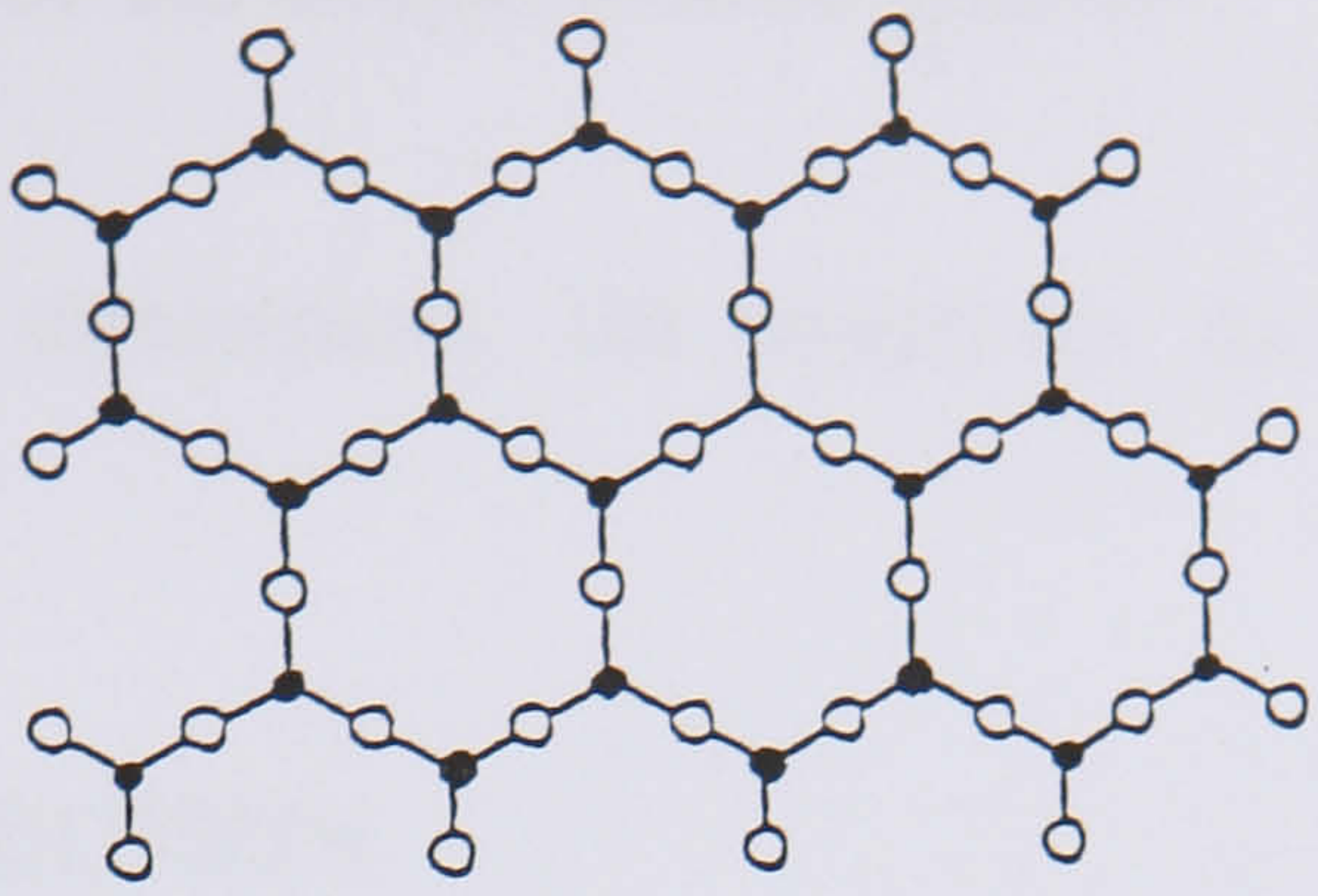
All current theories for the response of the glass electrode have as their basis the three-layer model of the conditioned glass membrane proposed by Haugaard[36,37] and confirmed by, for example, Lengyel and Dobos[38] (see Fig. 2.2A below). Before these are presented, the nature of the silicate glass membrane and its conditioned surface is considered.

2.2 THE STRUCTURE OF GLASS

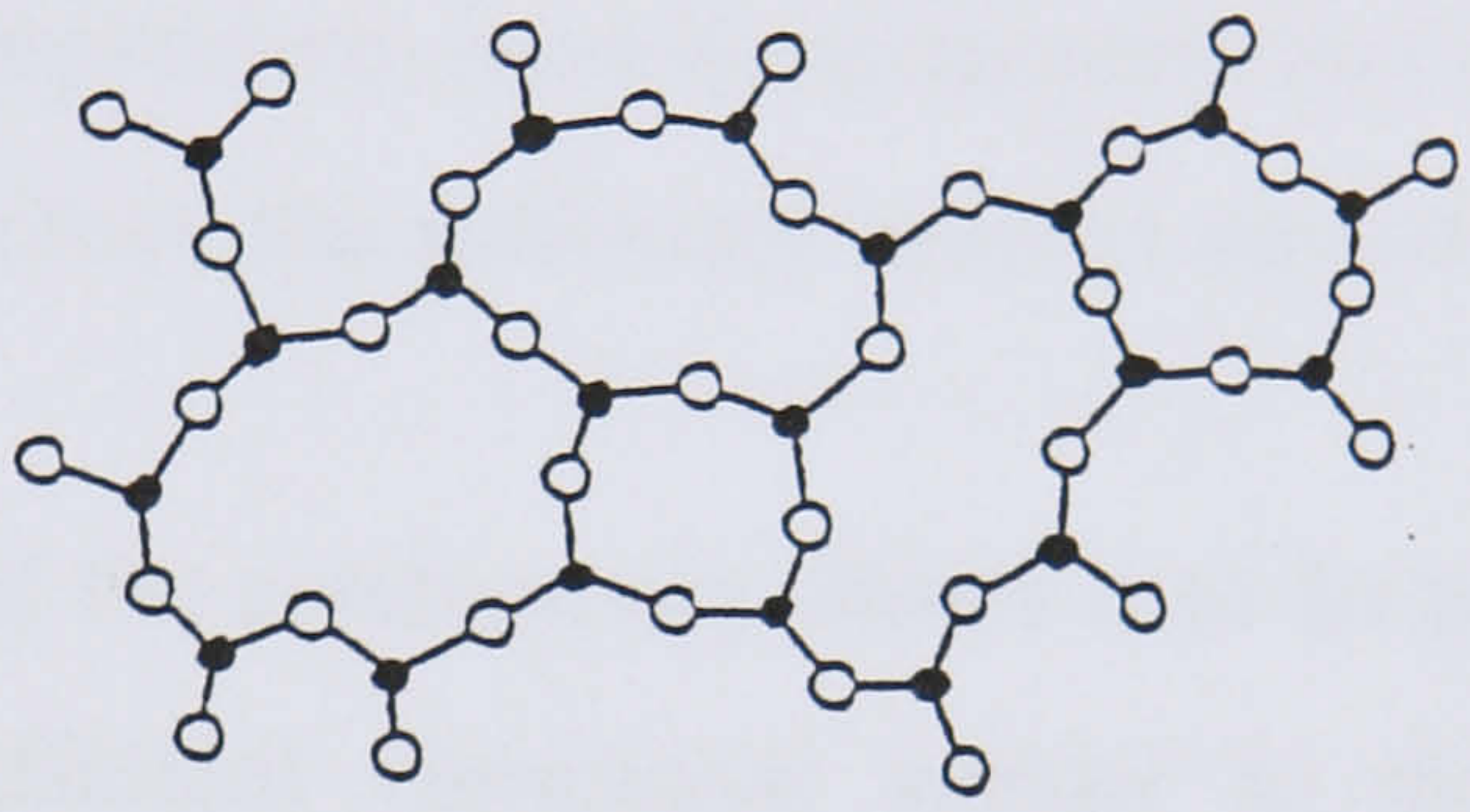
The structure of silicate glasses is similar to that for water near its freezing-point, possessing short-range order, but beyond a few atomic dimensions lacking any long-range order. The random-network structure proposed by Zachariasen[39] and endorsed by Warren's[40] X-ray diffraction studies is generally accepted.

For fused quartz, each silicon atom is coordinated in tetrahedral conformation with four oxygen atoms, and each tetrahedron is joined at its corners to four other tetrahedra to create a three-dimensional random network, for which, unlike the crystalline form, there is no long-range order. Silica is classed as a 'network former': the oxygen atoms, each co-ordinated to two silicon atoms are 'bridging oxygens'. For an alkali silicate glass, each alkali cation introduced results in the formation of a 'non-bridging oxygen' ion coordinated to one silicon atom linked to three tetrahedra. Similarly, the addition of an alkaline earth cation results in the creation of two non-bridging oxygen ions. The cations fit into the interstices of the network, bonded to adjacent network oxygen anions. Alkali and alkaline-earth oxides are designated 'network modifiers'. If the average number of non-bridging oxygens per tetrahedron exceeds two, the continuous network disintegrates and the glass will devitrify.

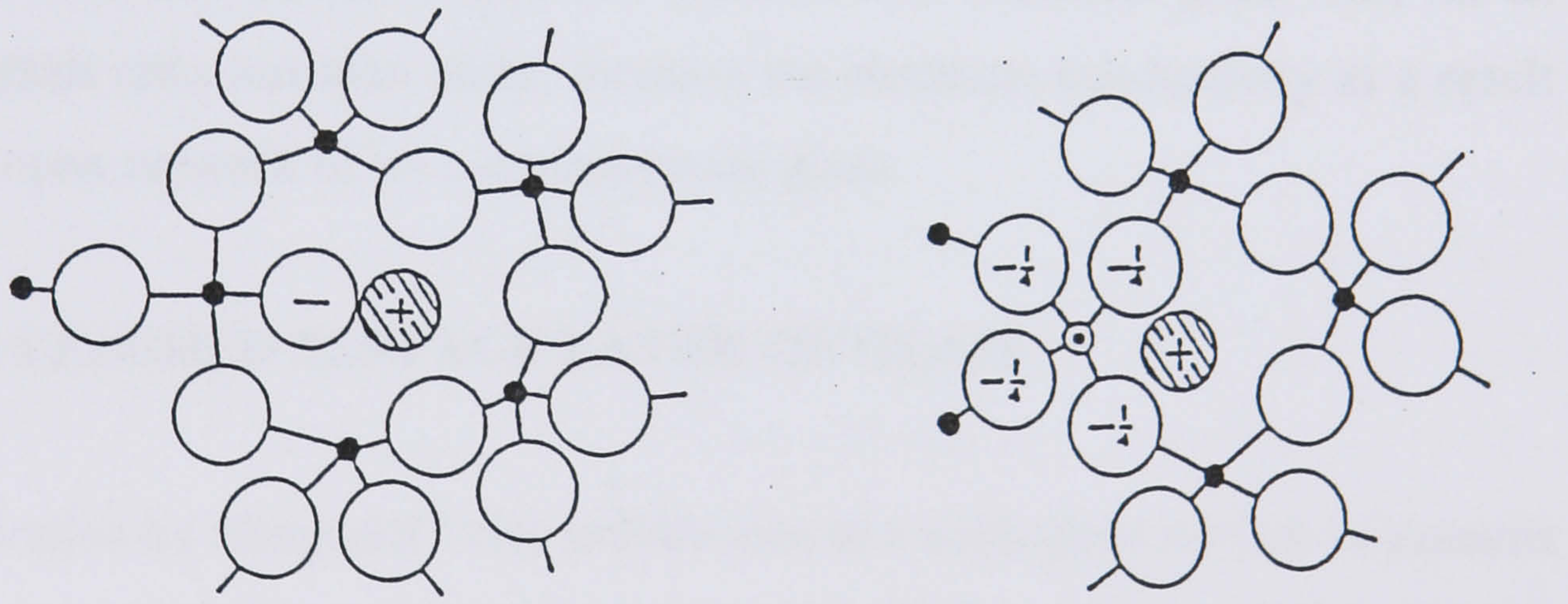
Oxides of trivalent and other tetravalent oxides may be incorporated into the glass network. In alumino-silicate glasses, aluminium enters the network as AlO_4^- tetrahedra replacing SiO_4 tetrahedra if, for each aluminium ion, an alkali cation enters the structure to balance the negative charge. For such glasses, the alkali cations are



A, Quartz.



B, Fused Silica



C, Soda Glass

D, Soda Aluminosilicate Glass

Fig. 2.1 Two-Dimensional Illustration of Atomic Structures.

associated with the negatively charged tetrahedra rather than with the more negatively charged, non-bridging oxygens of the simple silicate glasses.

Figure 2.1 illustrates, in two dimensions, the structures for silica, silicate and aluminosilicate glasses.

2.3 ELECTRICAL CONDUCTION

For alkali-lime silicate glasses, electrical conduction is ionic. Electrolysis experiments by Burt[41] in molten salts at elevated temperatures, and Haugaard[36] in aqueous solution at ambient temperature, have demonstrated that the current is carried exclusively by alkali cations across the stationary anionic network.

The temperature dependence of the conductivity shows it to be an activated process, an alkali cation requiring sufficient vibrational energy to move to an adjacent interstitial site.

Isard[42] has shown that the introduction of alumina into a silicate glass will, for an aluminium:alkali ratio less than unity, increase the electrical conductivity as a result of the more open network of an aluminosilicate glass.

2.4 THE LEACHED SURFACE LAYER OF GLASS

The demonstration by Haugaard[36] that sodium ions at a soda-glass surface in aqueous solution are exchanged for hydrogen-ions from the solution supported Horowitz's[43] theory that ion-exchange ability is the source of the response of the glass electrode. Further studies[37] showed that water is absorbed at the glass surface and led to his three-layer model for the glass membrane, illustrated in Figure 2.2, where the surface or gel-layers are formed by the uptake of water facilitating ion exchange at the silicaceous network surface.

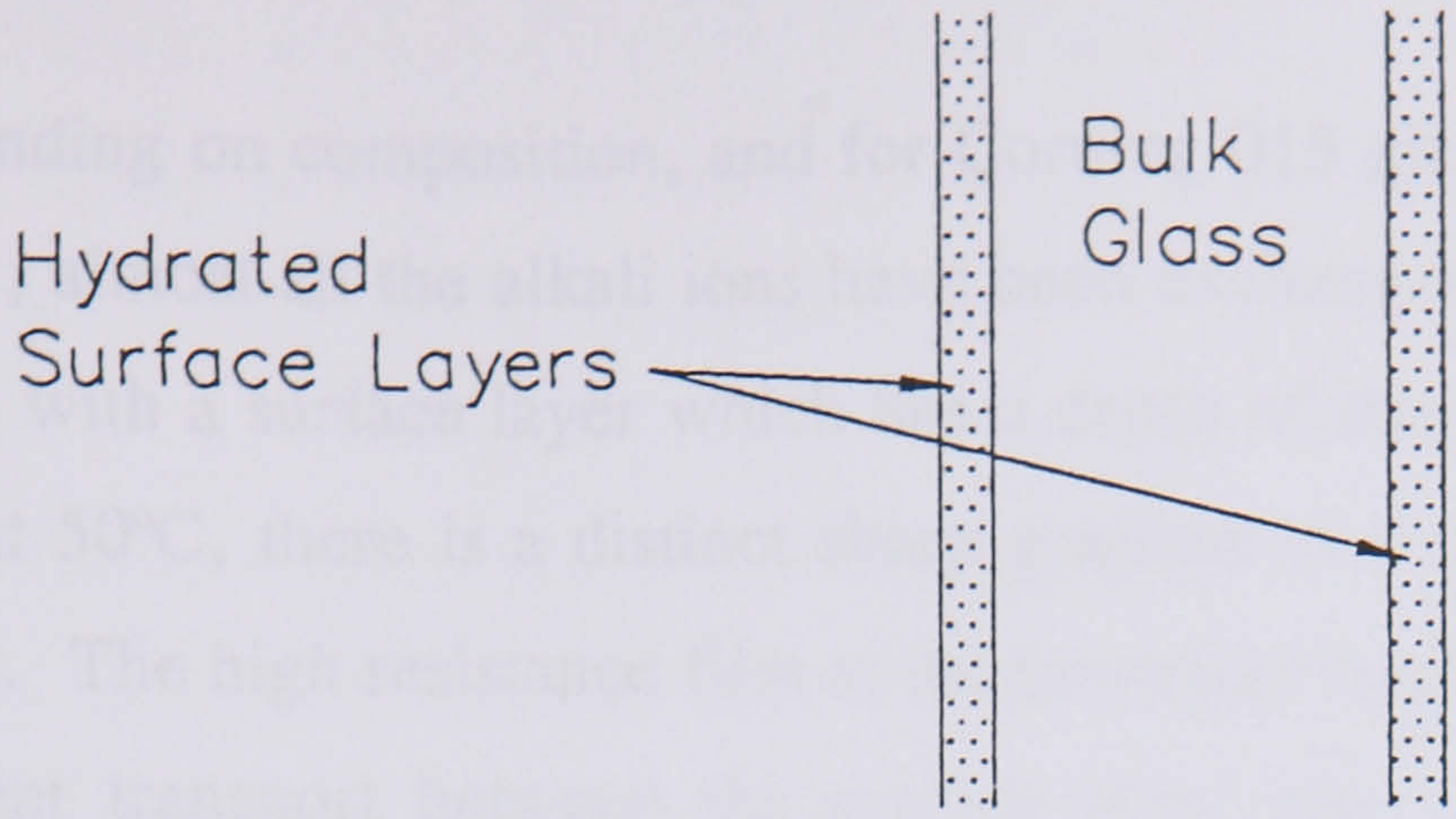
The model was supported by the observations of Hubbard *et al.*[17] who found, using an interferometric technique, that the surface of an optically flat plate of Corning 015 glass was attacked on immersion in solutions above 8.5 pH. In buffer solutions, below about pH 7, a slight swelling of the surface was apparent. For acid solutions below about pH 2 and in strong salt solutions the rate of swelling was repressed. In 10 M sulphuric acid solution, no swelling was observed. They concluded that a glass will display a uniform durability for the range of correct pH response.

Studies of the durability of glasses by Rana and Douglas[44] have confirmed that a 'leached gel-layer' is developed between the bulk glass and the solution in which alkali ions are exchanged for hydrogen-ions and pass into solution. As a result of the uptake of water into the glass surface, a relatively open gel-layer structure was proposed by Lengyel and Dobos[38].

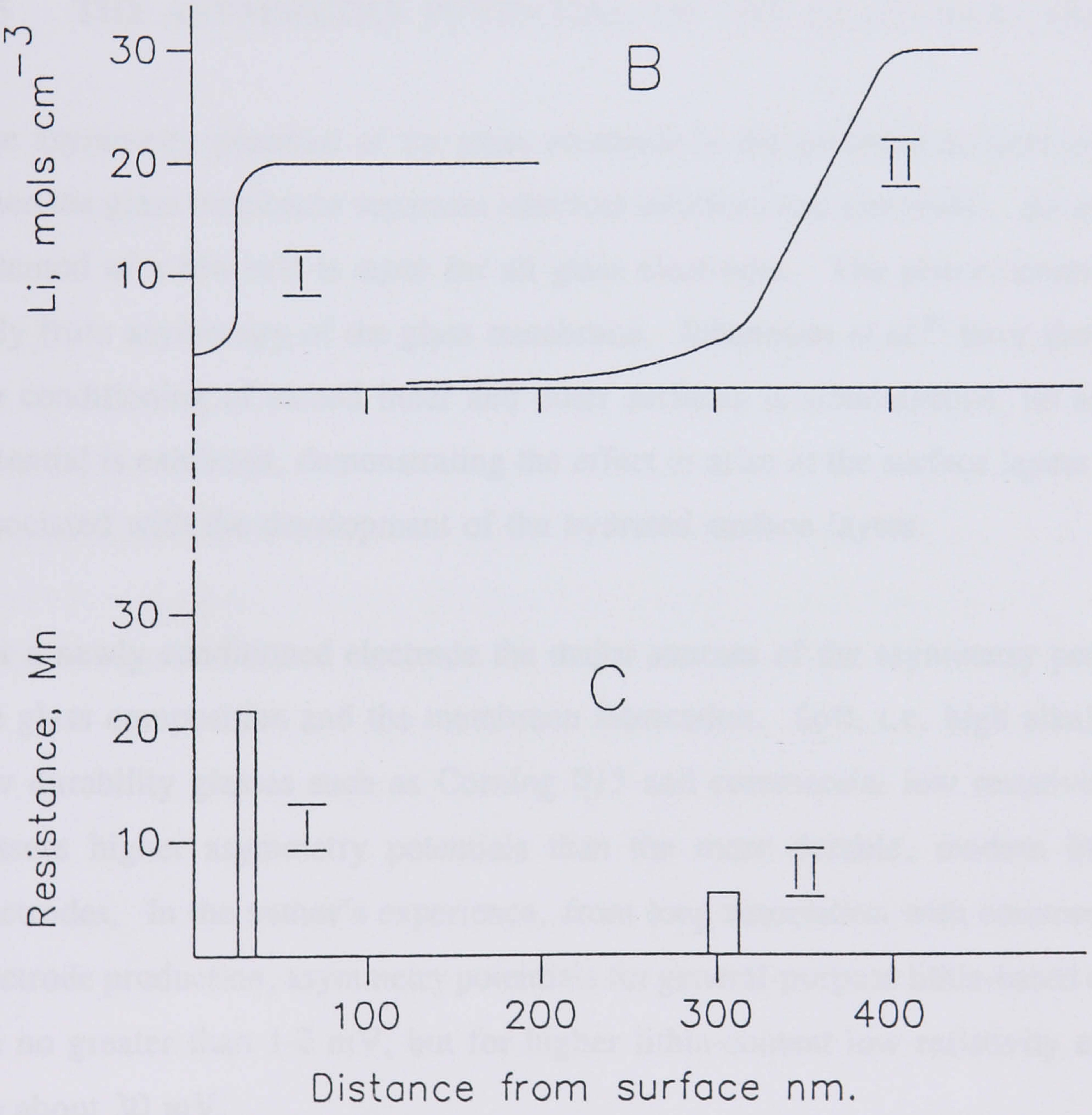
Electrical studies by, e.g. Buck[45], identified the existence of a high resistance in the surface gel-layer. Using a constant-current pulse technique, Wikby and Johannson[46] showed that the total resistance of the glass electrode consisted of separate contributions for the bulk glass and the surface gel-layers. Time constants for the two contributions were distinctly different, milliseconds for the bulk compared with seconds to hours for the surface. The resistance associated with the slow time constants could be eliminated by etching the glass surface[47].

Profile examination by chemically etching away the gel-layers of soda and lithia-based electrodes and analyzing the products for alkali, together with resistance measurements, revealed the alkali concentration to rise sharply at the bulk glass-gel-layer interface from a much lower concentration within the surface gel-layer[48]. The high resistance is located at the boundary layer in a film of less than 10 nm and has a conductivity about a thousand times less than that of the bulk glass. The more sensitive technique of 'Ion Bombardment for Spectrochemical Analysis' (IBSCA) was used by Bach and Baucke[49]. This technique has a depth resolution of 3 - 5 nm and the lithium concentration profiles for the surface layers agree with those determined by Wikby[48].

The spectroscopic profile studies have shown the surface gel-layer to be almost devoid of alkali ion, and a thickness, for lithia glass electrodes, of about 10-200 nm,



A, Three-layer Model of Hydrated Glass Membrane (after Haugaard, ref. 37)



B, Lithium-ion Concentration and
C, Electrical Resistance in Surface
Layers of General Purpose (I) and
Low Resistivity (II) pH glass Compositions.
(after Wikby, ref 48).

Fig 2.2 The Glass Electrode Surface-Layer.

depending on composition, and for Corning 015 glass about1000nm depth[50]. In this layer, almost all the alkali ions have been exchanged for hydrogen ions. For a lithia glass with a surface layer which has a depth of about 10 nm increasing to about 100 nm at 50°C, there is a distinct sharp gradient to the alkali concentration of the bulk glass. The high resistance film at the boundary layer has a high activation energy for current transport between the surface layer and the bulk glass, and consequently provides a barrier to alkali ion transport. The rupturing of siloxane bonds as hydration proceeds moves the surface layer inwards as the bulk glass is attacked. Glass surface profiles are illustrated in Figure 2.2, B,C.

2.5 THE ASYMMETRY POTENTIAL OF THE GLASS ELECTRODE

The asymmetry potential of the glass electrode is the potential difference observed when the glass membrane separates identical solutions and electrodes. An asymmetry potential of a few mV is usual for all glass electrodes. The phenomenon can arise only from asymmetry of the glass membrane. Johannson *et al.*[51] have shown that if the conditioning of etched inner and outer surfaces is simultaneous, no asymmetry potential is exhibited, demonstrating the effect to arise at the surface layers and to be associated with the development of the hydrated surface layers.

For a newly conditioned electrode the major sources of the asymmetry potential are the glass composition and the membrane fabrication. Soft, i.e. high alkali content, low durability glasses such as Corning 015 and commercial low resistivity glasses possess higher asymmetry potentials than the more durable, modern lithia-based electrodes. In the author's experience, from long association with commercial glass electrode production, asymmetry potentials for general-purpose lithia-based electrodes are no greater than 1-2 mV, but for higher lithia-content low resistivity electrodes, are about 30 mV.

Whitfield[52] has argued that during glassblowing, alkali is lost at each surface at different rates, and consequently, the surface compositions of the blown membrane differ, the outer surface being somewhat more alkali-deficient than the inner surface inducing strain. After the membrane is blown, the outer surface cools at a faster rate than the inner surface, and Bach and Baucke[49] have shown that different pretreatments of the dry glass will result in different surface structures.

The inner surface of the glass electrode is, of course, in contact with the same solution during its working life, and the nature of this solution will slowly change with the gradual accumulation of the products of leaching, resulting in a very slow change of the asymmetry potential.

The small asymmetry potential of most modern glass electrodes is not a serious problem, indeed the vast majority of users are unaware of the phenomenon, as its contribution is eliminated in the calibration process. It can, however, for electrodes with large asymmetry potentials, have an indirect, deleterious effect for pH temperature compensation when used with pH meters incorporating a fixed isopotential pH.

The acid or negative time-dependent errors displayed by glass electrodes in strong mineral acid solutions and non-aqueous media, discussed in Chapter 6, are regarded by Beck and Wynne-Jones[1] to be merely changing asymmetry potentials. They proposed that the time-dependent errors are the result of dehydration or penetration by solvent of the surface layer. Radio-tracer studies by Schwabe *et al.*[30,31] supported the dehydration proposal for errors observed in concentrated sulphuric and phosphoric acids, but for the halogen acids they found the errors to be proportional to halide absorption in the surface layer.

2.6 THE THEORY OF THE GLASS ELECTRODE RESPONSE

Of the various theories proposed for the development of the glass electrode potential, the phase-boundary or ion-exchange theory initially proposed by Nicolsky[53] and later extended with his co-workers[54], and also by Eisenman[55] and his colleagues, is generally accepted to account for most of the response phenomena.

2.6.1 The Phase Boundary Potential Theory

The potential at a glass-solution interface was derived by Nicolsky[53] in terms of the ion-exchange reaction,

$$I^+_{glass} + J^+_{soln.} \rightleftharpoons J^+_{glass} + I^+_{soln.} \quad 1$$

for which the equilibrium constant is,

$$K_{ij} = a_i a_{jg}/a_{ig}\, a_j, \quad 2$$

where a are activities for the ions i and j, and g refers to the glass.

At equilibrium, the electrochemical potential of each ion species in the solution and the surface-layer will be idential at both inner and outer glass membrane surfaces, i.e.

$$\mu_i + F\Psi = \mu_{ig} + F\Psi_g \text{ and,} \quad 3$$

$$\mu_j + F\Psi = \mu_{jg} + F\Psi_g \quad 4$$

where μ_x is the chemical potential and Ψ and Ψ_g are the phase potentials. Introducing activities,

$$\mu_x = \mu^o_x + RT\ln a_x \quad 5$$

where μ^o_x is the standard chemical potential for ion x,

giving, $F(\Psi_g - \Psi) = \mu^o_i - \mu^o_{ig} + RT \ln (a_i/a_{ig})$. 6

Within the glass surface layer, ion activities are assumed to be equal to ion concentrations, and the number of ion-exchange sites is considered to be constant, thus

$$a_{ig} = c_{ig} \text{ and } c_{ig} + c_{jg} = c \quad 7$$

giving, $K_{ij} = a_i\, (c - c_{ig})/a_j c_{ig}$ 8

and, $c_{ig} = a_i c/(a_i + K_{ij} a_j)$ 9

then, since $a_i/a_{jg} = a_i/c_{ig} = (a_i + K_{ij} a_j)/c$ 10

and, $\Psi_g - \Psi = \mu^o_i - \mu^o_{ig} + (RT/F) \ln ((a_i + K_{ij} a_j)/c)$ 11

Similar equilibria apply at both inner and outer glass-solution interfaces, however, as conditions are, at constant temperature, held constant at the inner surface, variation of the potential at the outer glass-solution interface only is considered, and the potential of the glass electrode is expressed by,

$$E = E_o + (RT/F) \ln (a_i + K_{ij} a_j) \quad 12$$

where E_o, a constant, includes the potentials at the inner glass surface and the internal reference electrode.

In the error-free response range of the pH glass electrode the only electrochemical process of interest is the exchange of hydrogen-ions (i) between the solution and the glass surface-layer and the response of the electrode is simply,

$E = E_o + (RT/F) \ln a_{H+}$ 13

In the alkaline, or positive, error region of the glass electrode, other cations (j) alter the ion-exchange process and occupy some of the surface sites,

$H^+_{glass} + M^+_{soln.} \rightleftharpoons M^+_{glass} + H^+_{soln.}$ 14

Nicolsky's[53] equation, derived above, although precisely describing the hydrogen-ion (i) and metal-ion (j) functions of the electrode, does not adequately portray the intermediate response region. An identical equation had earlier been developed by Dole[56] from a statistical mechanical approach.

Nicolsky's equation was modified by Eisenman, Rudin and Casby[55] to represent more closely the findings from further experimental data.

$E = E_o + (nRT/F) \ln (a^{1/n}_i + (K_{ij}a_j)^{1/n})$ 15

in which both n and K_{ij} depend on the particular ion pair and the glass composition.

The equation was further refined by Karreman and Eisenman[57] to include diffusion potential contributions within the surface layer.

$E = E_o + (nRT/F) \ln (a^{1/n}_i + K^{pot}_{ij} a_j)^{1/n})$ 16

where, $K^{pot}_{ij} = (u_j/u_i)^n K_{ij}$ 17

and u_i and u_j are the ion mobilities within the surface layer.

Of course, this latter refinement to the theory of the electrode response is inconsistent with the phase boundary potential theory, which strictly assumes the potential to be established at the glass-solution interface.

The equations are applicable to all cation responsive glass electrodes. The extensions to the simple Nicolsky equation[53] were developed to describe more precisely the behaviour of alkali-ion responsive glass electrodes.

The specificity of the exchange-sites at a glass-solution interface, i.e. the reaction constant K_{ij} has been determined by Eisenman[58] to be related to the anionic field strength of the particular glass composition, illustrated in Figure i.e., 2.1. The high anionic field strength silicate glasses are selective to hydrogen-ions up to about pH 11-12, above which alkali metal-ion errors are exhibited, the magnitude of the error decreasing with increasing cation size. As the anionic field strength of the glass structure is decreased with the introduction of, e.g., increasing amounts of aluminium oxide, the error-free range of the pH response is reduced. Glass compositions containing more than about 8% aluminium oxide for lithia-based glasses or about 15% for soda-based glasses, are, above about pH 5 satisfactory compositions for alkali-ion responsive glasses. For these compositions, as the anionic field strength is lowered with increasing aluminium oxide addition, the selectivity of the ion-exchange sites changes smoothly from a preference for small to large cations. Eisenman has demonstrated the selectivity to be dependent on the relative solvation energies for the cations.

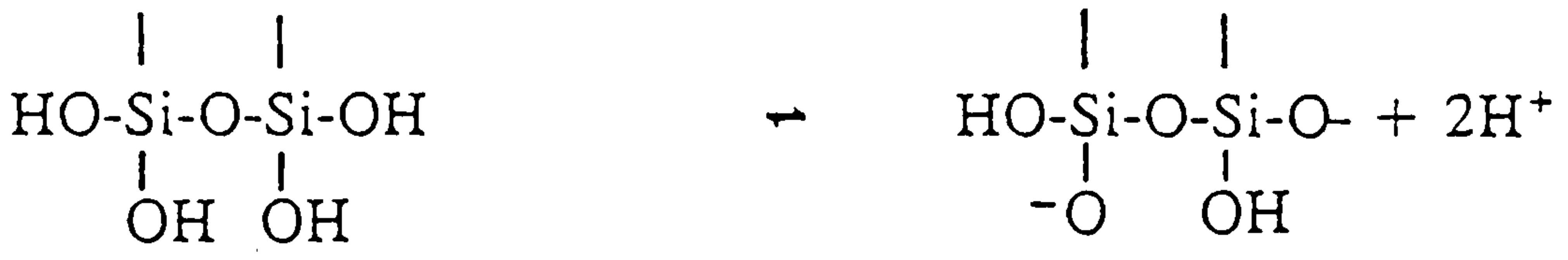
2.6.2 The Dissociation Mechanism

From their study of the durability of alkali-silicate glasses discussed in Chapter 7, Douglas and El-Shamy[59] have shown that the predominant equilibria at the glass-solution interface result in the formation of sites available to cations which may be preferentially occupied by one of the ions in solution,

$\equiv$ Si-O^- $\equiv$ Si-O^- Na^+ or $\equiv$ Si-OH
(empty) (occupied)

Ion-exchange equilibrium is determined by the concentration and solvation energies of ions in solution and in the surface layer. If there is more than one species of ion in solution, ions of the lowest chemical potential occupy the surface sites if their concentration is sufficiently great. Other ions, will commence occupying the sites if their concentration is too low. For alkali-silicate glasses, hydrogen-ions will occupy all the surface sites and the situation becomes that of the equilibrium between surface sites and hydrogen-ions.

For the hydrated surface of silica,



$$HO-\underset{OH}{\overset{|}{Si}}-O-\underset{OH}{\overset{|}{Si}}-OH \rightarrow HO-\underset{^{-}O}{\overset{|}{Si}}-O-\underset{OH}{\overset{|}{Si}}-O^{-} + 2H^{+} \qquad 18$$

Iler[60] considered use of the reaction constant for the first dissociation constant of silicic acid,

$H_4SiO_4 \rightarrow H^+ + H_3SiO_3^-$, $K = 10^{-9.8}$ at 30 °C 19

was appropriate. Douglas and El-Shamy[59] assumed this to apply also to the $\equiv SiOH$ groups at the glass solution interface,

$(\equiv SiO^-)\ (H^+)/(\equiv SiOH) = 10^{-9.8}$ 20

and that the hydrogen-ion site occupancy can be estimated,

$(\equiv SiO^-)\ /\ (\equiv SiOH) = 10^{(-9.8\ +\ pH)}$ 21

where $(\equiv SiO^-)$ and $(\equiv SiOH)$ are concentrations of the sites in g mol dm^{-3} glass, i.e. the activity coefficients are assumed to be unity.

Baucke[61] has proposed that the non-ideal response of the pH glass electrode in solutions of moderate pH, for which there is no acid or alkaline error, can be explained in terms of the dissociation mechanism. For the cell,

$Pt, H_2 \mid$ solution X $\mid$ glass electrode 22

the reaction at the hydrated glass surface is,

$\equiv SiOH_s + H_2O \rightarrow \equiv SiO_s^- + H_3O^+$ 23

At equilibrium, the electrochemical free energy change μ is zero,

$$\mu = \mu'_{SiO-} + \mu_{H_3O+} - \mu'_{SiOH} - \mu_{H_2O} - FE_m = 0 \qquad 24$$

the superscript slash represents glass surface identity. Introducing the chemical standard free energy for the reaction, and activities,

$$\Delta G = \Delta G^\circ + RT\ln (a'_{SiO-}a_{H_3O+})/(a'_{SiOH}a_{H_2O}) - FE_m = 0 \qquad 25$$

and, rearranging,

$$E_m = - k \log K_D + k \log (a'_{SiO-})/(a'_{SiOH}.a_{H_2O}) - kpH \qquad 26$$

where the theoretical slope, $k = RT/F \ln 10$, and K_D is the thermodynamic dissociation constant for reaction 23 for the glass. The dissociation equilibrium is strictly defined by equations 25 and 26. A decrease of pH will result in an increase of silanol activity, a'_{SiOH}, and a decrease of siloxy activity, a'_{SiO-} as $\Delta c'_{SiOH} = - \Delta c'_{SiO-}$, where c_x' is the concentration of surface sites. The siloxy concentration, and activity is much smaller than the silanol concentration and its change, due to pH variation, even less,

$$|\Delta c'_{SiO-}| < c'_{SiO-} << c'_{SiOH} \approx c'_{total} \qquad 27$$

As a first approximation, $a'_{SiO-}/(a'_{SiOH}.a_{H_2O})$ is assumed constant, and consequently the first and second terms of the right side of equation 26 are combined to furnish the standard potential, E°_m of the glass membrane,

$$E^\circ_m = - k \log K_D + k \log (a'_{SiO-}/(a'_{SiOH}.a_{H_2O}) \qquad 28$$

and substituting into equation 26,

$$E_m = E_m^\circ + kpH \qquad 29$$

which expresses the linear variation of the glass electrode potential with pH. If the response of the glass electrode is ideal,

$$dE_m/dpH = - k \qquad 30$$

and deviations are expressed by introducing the practical slope, k_{gl}, to modify equations 29 and 30,

$E_{m1} = E_{m1}^{\circ} - k_{g1}pH = E^{\circ}_{m1} - \alpha kpH$ 31

and,

$dE_{m1}/dpH = -k_{g1} = -\alpha k = -k + nk$ 32

where, α is the electromotive efficiency, and n, the electromotive loss factor.

He suggests that the activity changes in the second term of the right side of equation 26, caused by pH variation are not sufficiently small to permit the approximation used to derive equations 28-30. The equation for the potential difference for a pH change includes the ratio of the activities,

$E_{m1} - E_{m2} = k\log(a'_{SiO-.1}.a'_{SiOH.2}.a_{H_2O.2})/(a'_{SiO-.2}.a'_{SiOH.1}.a_{H_2O.1}) - k\,(pH_1 - pH_2)$ 33

The ratio of the siloxy activities is larger than the ratios of the silanol activities and of water, which is almost unity in dilute solutions, i.e.,

$|a'_{SiO-.1}/a'_{SiO-.2}| > |a'_{SiOH.2}.a_{H_2O.2}/a'_{SiOH.1}.a_{H_2O.1}|$ 34

The change of pH is associated with an activity term, which, if large enough, will make a measureable contribution to the potential difference. The contribution will reduce the Nernstian slope of equation as pH and siloxy activity changes have the same sign.

Differentiation of equation 26 with respect to pH provides the thermodynamically correct slope for the glass membrane,

$dE_{m1}/dpH = kd(\log(a'_{SiOH}/a'_{SiOH}.a_{H_2O}))/dpH - k$ 35

which differs from the Nernstian response, equation 30 by,

$dE'_{m1}/dpH - dE_{m1}/dpH = -kd(\log(a'_{SiO-}/a'_{SiOH}.a_{H_2O})/dpH$ 36

and from equations 30 and 32,

$n = d(\log(a'_{SiO-}/a'_{SiOH}.a_{H_2O})/dpH$ 37

The dissociation mechanistic treatment illustrates the thermodynamically correct hydrogen-ion response of the glass electrode is sub-Nernstian.

2.7 THE TIME DEPENDENCE OF THE GLASS ELECTRODE POTENTIAL

Various attempts have been made to describe the time-dependence of the potential of the glass electrode as a function of time. If the hypothesis of Beck and Wynne-Jones[1] is correct, then for solutions for which the pH glass electrode is responsive to the hydrogen-ion only, there will be no error at time t=zero, and any time dependent variation of potential can be ascribed to a changing asymmetry potential as the result of ion and water exchange at the glass-solution interface.

Distèche and Dubuisson[62] subjected Corning 015 glass electrodes to rapid, small changes of pH for acetate and phosphate buffer solutions using a solution displacement technique. They adopted an equivalent electrical circuit treatment for the observed exponential response and determined a time constant of about 30 ms. An empirical equation was derived by Schwabe and Glöckner[30] to express the time response they observed in mineral acid solutions,

$$-\Delta E_t = A + B \log (C + t) \qquad 38$$

where, t is the time following change of solution,
ΔE_t, the error at time t, and
A, B and C are empirical constants.

They regarded the error to be zero at time t=zero and assigned B the value of 59.16 mV, simplifying the relationship to,

$$q = \text{antilog} (-\Delta E_t/59.16) = 1 + t/C \qquad 39$$

Values of q were plotted against t for results obtained in HCl, H_2SO_4 and H_3PO_4 solutions, at various concentrations, for periods of time up to 30h. If the relationship is correct, the plots would be linear with intercepts of unity. Dependent on the nature of the acid and its concentration, plots were either in reasonable agreement with the equation or the error tended towards a constant value with increasing time. With the exception of 4 M and 5M hydrochloric acid solutions, errors were zero at time = zero.

Schwabe and Glöckner regarded their equation to be in accord with the phase boundary potential theory, ascribing errors in concentrated acid solutions to be the result of acid absorption or surface layer dehydration.

Their equation is not applicable to many of the results of this present work, those which display a decreasing error with time that cannot be extrapolated to zero error at time t=zero, or those that exhibit turning points, examples are shown in Figures 7.5 -7.12.

An exponential equation, incorporating a specific response constant γ, has been proposed by Rechnitz and Hameka[63] from a dynamic treatment of the electrode potential as a function of time,

$$E = E_\infty (1 - e^{-\gamma t}) \qquad 40$$

where E_∞ is the equilibrium potential for the electrode, and γ the specific response constant.

A plot of log $((E_\infty - E_t)/E_\infty)$ against time should be linear and provide a value for γ.

The equation was successfully applied by them to results reported for potassium-ion responsive glass electrodes by Savage and Isard[64], however, Buck[5] regards the sluggish response reported for these electrodes to be indicative of a mixed-ion response, and agreement with the equation is quite fortuitous.

Rechnitz and Hameka[63] proposed that γ, the specific response constant, is a function of the glass composition and the potential-determining ion, providing a criterion for the ion-selectivity of the glass.

The development of the theory was criticized, for the fundamental errors in the derivation of the equation 40 by Johannson and Norberg[65], who proposed that the plot of a similar relationship, log $(E_t - E_\infty)$ against time t, should be linear. They developed their equation by ascribing the time-dependent electrode potential to be the result of the time taken to charge the double-layer at the interface, an assumption questioned by Covington[66].

It is difficult to envisage a simple relationship for the time-dependent variation of the glass electrode that will encompass the variety of response phenomena encountered, at least for the physical transfer of an electrode between solutions as described by Chapters 5 to 7 of this work.

CHAPTER THREE

EQUIPMENT AND MATERIALS

3.1 GLASS ELECTRODES

A variety of electrodes was used, commercial screened electrodes from various manufacturers and both screened and unscreened fabricated from electrode blanks, i.e. stem plus membrane bulb, of commercial types and others of 'home-made' membrane glasses prepared for this work. This section discusses their assembly; details such as manufacturers' specifications, membrane compositions and internal filling solutions are given in Chapters 5, 6 and 7.

3.1.1 Commercial Glass Electrodes

With the exception of electrode 24, Jena type 9000, which was prepared for use in the same manner as the 'home-made' electrodes, commercial electrodes were screened and had a stem length of 105-120 mm and diameter of about 12 mm. Electrodes were mounted in polythene stoppers machined to fit into B45 sockets as illustrated in Figure 3.1a. The hole into which an electrode fitted was filled with polythene turnings and glass wool to centralize and provide support.

To suppress electrical leakage, electrode stems and the stopper bases were coated, to just above the membrane-steam seal, with acid-free paraffin wax[2] (Shell Stanlow, fully refined, 125° - 130°F, EMP). Before each set of electrode transfer experiments electrode assemblies were rewaxed.

Where necessary, electrode lead terminations were replaced with polythene-insulated Belling-Lee TV coaxial connectors, care being taken to remove the antimicrophonic layer, if present, from the dielectric.

All electrodes were conditioned and stored in deionized water.

3.1.2 Glass Electrode Blanks

Commercial electrode blanks were kindly donated by W.G. Pye & Co.

Limited, Cambridge and Corning Glass Works, Medfield, U.S.A. The former were combination electrode blanks and accordingly incorporated an inner tube sealed into the outer stem some 5 mm above the membrane seal. A porous ceramic rod, sealed into the outer stem above the annular tube seal as a liquid junction, was removed and the hole fusion-sealed. The Corning electrode blanks were simply stem tubing plus membrane bulbs.

(a) Pye Electrode Blanks

The assembly of these electrodes is illustrated in Figure 3.1b. A selected electrolyte solution was introduced into the inner tube, filling the membrane bulb and extending about 30 mm up the tube. Details of the various fillings used for these electrodes are presented in Chapter 6, Table 6.2.

An electrolytic silver, silver chloride wire electrode was inserted into the solution and supported at the top of the tube within a sealing rubber bung. The space between the tubes was filled with mercury to within 3 - 4 mm of the top and a length of approximately 0.25 mm diameter tinned-copper wire inserted as an electrical contact. The space above the mercury was filled and sealed with paraffin wax.

The screened electrode assembly was inserted into a machined B24 polythene stopper and firmly supported in a mixture of glass wool and paraffin wax. The two wires were sleeved with woven silica-fibre sleeving and the inner wire soldered to the central conductor of a polythene insulated Belling-Lee coaxial panel-mounting socket which was then inserted into the top of the stopper. The mercury-screen connection wire was wrapped around one of the two socket retaining screws.

(b) Corning Electrode Blanks

Assembly of the electrodes detailed in Figure 3.1c.

Into the base of a double-walled lead glass tube with outer diameter 7 mm, an annular spacing of 1-5 mm and an inner tube internal diameter of 2.5 mm, 15 mm of 0.25 mm diameter platinum wire was sealed with about 10 mm protruding, to form the base of the inner electrode. Connection to the platinum was made with a few drops of mercury into which a tinned-copper wire connector supported in a top-sealing bung was inserted. This platinum electrode formed the base for the internal electrolytic silver, silver chloride electrode prepared as described in Section 3.3a. The annular gap was filled with mercury to within about 6 mm of the top, a thin tinned-copper connection wire inserted, and the gap filled and sealed with paraffin wax.

Glass electrode blanks were filled with the appropriate electrolyte to about 5 mm above the membrane-stem seal. Strips of 5 mm width 'Parafilm', a paraffin-wax based insulating tape, were wrapped around the glass stem of the internal electrode which was inserted into the body of the glass electrode blank. Gentle heating 'melted' the tight 'Parafilm' inserts on to the glass tubes. The gap between the two tubes was filled at the top with paraffin wax. The final assembly into a B24 polythene stopper was identical to that described in (a).

The details of the various internal filling solutions used, and the different conditioning and storage of these glass electrodes are collated in Chapter 6, Tables 6.2, 6.3 and 6.4.

(c) 'Home-made' Electrodes

The assembly of these unscreened electrodes is shown in Figure 3.1d.

All were simple electrodes of the type attributed to Haber[67] comprising lead glass stem tubes of about 6 mm diameter on to which were blown either soda-lime or lithia-lime glass membrane bulbs of 8-10 mm diameter. Because of the high electrical resistance of pH membrane glasses it was essential to use lead glass as the stem material. It was fortunate that the thermal coefficients of expansion for the membrane glasses were apparently compatible with that for the lead glass[68], *viz.* approximately 8 - 10 x 10^{-6} deg^{-1}. Lead glass tubing was supplied by A.W. Dixon and Co., London.

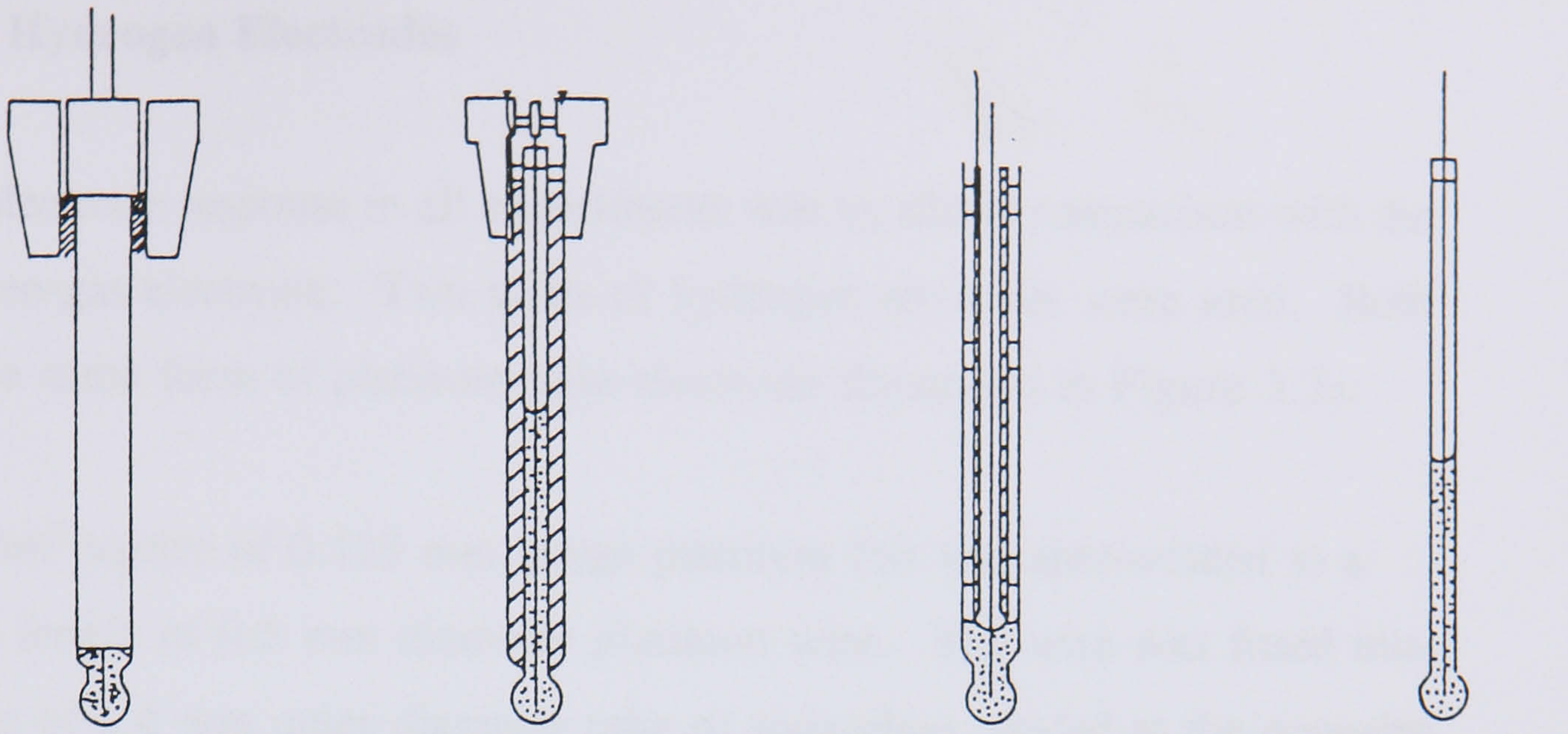
0.1m hydrochloric acid was used as the internal electrolyte for all these electrodes with electrolytic silver, silver chloride wire electrodes supported in top-sealing rubber bungs.

In use, the electrodes were mounted in split no. 21 rubber bungs supported in machined B45 polythene stoppers and the stems waxed.

Compositions of the membrane glasses are presented in Chapter 7, tables 7.1 and 7.2.

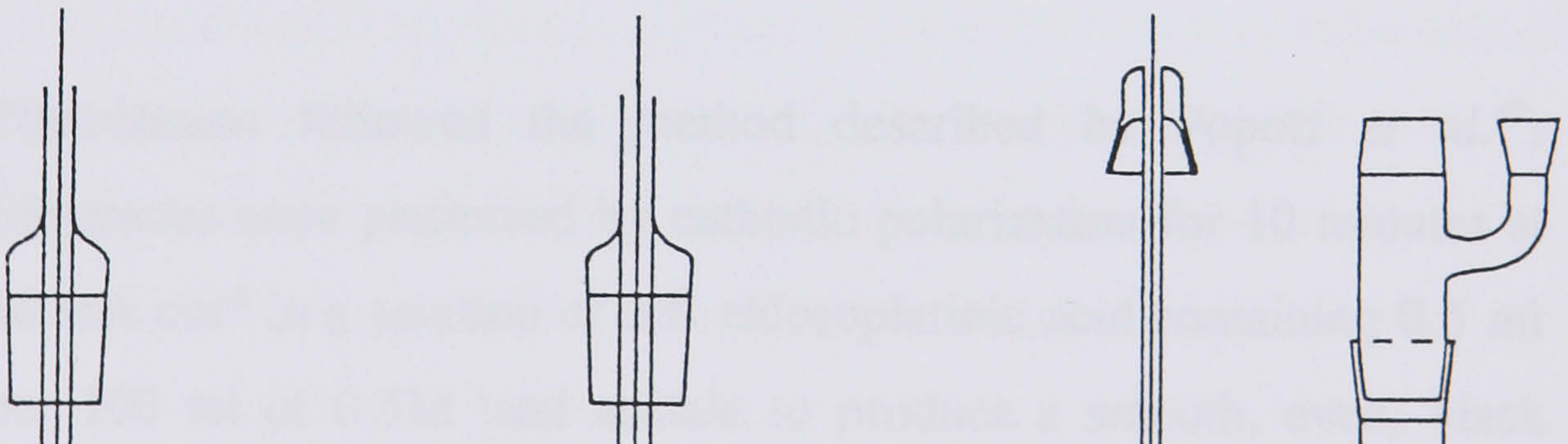
(d) Jena 9000 Electrode

Although this is a commercial electrode, it was of the same form as the 'home-made' electrodes described in (c) above, but with a 30 mm diameter membrane bulb. It had been previously used within the Department. The internal filling was replaced with 0.1m hydrochloric acid and a new electrolytic silver, silver chloride electrode inserted. Because of the large bulb diameter, the electrode had been previously mounted on a no. 43 rubber bung from which a protective glass cirumferential ring about the bulb was suspended.



A. Commercial B. Pye Blank C. Corning Blank D. Home-made

Fig. 3.1 Glass Electrodes



A. Hydrogen B. Silver, Silver Chloride C. Mercury, Mercury(I) Sulphate

Fig. 3.2 Reference Electrode Bases

3.2 REFERENCE ELECTRODES

3.2.1 Hydrogen Electrodes

Glass electrode response in all experiments was by direct comparison with the hydrogen-gas electrode. Two types of hydrogen electrode were used. Both used the same form of platinum base electrode illustrated in Figure 3.2a.

A 10 mm^2 square of 0.125 mm gauge platinum foil was spot-welded to a 15 mm length of 0.5 mm diameter platinum wire. The wire was fused into the base of a 4 mm outer diameter tube of soda-glass, sealed at the opposite open end into a B19 soda-glass cone. Electrical contact was made with tinned-copper wire dipping into a small pool of mercury above the glass-metal seal. The electrode bases were prepared for platinization or palladization by a modification of the procedure of Popoff *et al*[69] omitting the gold flash. Bases were cleaned by immersion in concentrated nitric acid at about 60°C for 5 minutes and after washing with water, anodically polarized against a platinum cathode for 5 minutes at a current density of 10 mA cm^{-2} in concentrated hydrochloric acid and washed with water.

(a) Platinized-platinum Electrodes

Platinization followed the method described by Popoff *et al.*[69]. Electrodes were platinized by cathodic polarization for 10 minutes at 10 mA cm^{-2} in a solution of 3% chloroplatinic acid containing 0.5 ml per 100 ml of 0.5M lead acetate to produce a smooth, even, black deposit. Platinization was followed by anodic polarization in 0.1m sodium hydroxide for 15s and after washing, by cathodic polarization in 0.1m sulphuric acid for 30s. Between each step, electrodes were rinsed with water. A platinum electrode was used as the counter electrode. Electrolysis was conducted at a current density of 10 mA cm^{-2} using a 6 V battery.

Bias potentials were regularly checked in various test solutions and if greater than 30 mV electrodes were replatinized after removing the old deposit by dissolution in aqua regia followed by washing and heating carefully to dull-redness for a few seconds in a Bunsen-burner flame.

(b) Palladized-platinum Electrodes

The use of platinized-platinum electrodes in potassium hydrogen phthalate solutions was precluded because of their high catalytic activity that causes phthalate reduction and consequent drifting potentials. In these solutions the less catalytically active palladized-platinum electrode has been reported to be satisfactory[70]. The electrode bases were coated with a finely-divided, light-grey deposit by cathodic polarization in a solution of 2% palladium chloride in 1m hydrochloric acid, at a current density of 10 mA cm^{-2} using a platinum anode. Electrodes were washed and stored in deionized water without further treatment.

(c) Hydrogen

As the hydrogen-gas electrode is sensitive to oxygen[71], traces were removed by passing the gas through a silica tube packed with copper-turnings in a tube furnace of 500°C. Deoxygenated gas was passed through a column of potassium hydroxide pellets to remove any carbon dioxide[72] and via a manifold-feed to the transfer cells.

3.2.2 Silver, Silver Chloride Electrodes

Electrolytic and thermal-electrolytic types of this electrode were used. The former were used as internal reference electrodes in the self-assembled glass electrodes described in Section 3.1.; the latter in the transfer cells to determine cell emfs and as a check on the condition of the hydrogen-gas electrodes.

(a) Electrolytic Electrodes

These electrodes were used as the internal electrodes for self-assembled glass electrodes. Some were simply wire electrodes, others described in Section 3.1 were of wires fused into glass stems. Regardless of form, all were similarly prepared using the procedure described by Janz and Taniguchi[73].

Platinum wire base electrodes were cleaned in concentrated nitric acid at about 60°C for a few minutes and washed with water. Silver was deposited electrolytically from a solution of 3% potassium silver cyanide at a current density of about 1 mA cm^{-2} for 6 hours in an H-cell using a silver anode. A cotton-wool plug was loosely inserted into the interconnecting tube between the two limbs of the cell, separating the cathode electrodes from the anodic reaction products[74]. Electrodes were subsequently washed in water, immersed in 0.88 ammonia solution for 30 minutes and soaked overnight in water. The silver electrodes were chloridized by anodic polarization with a silver cathode in 0.1m hydrochloric acid at a current density of 1 mA cm^{-2} for 40 minutes, resulting in conversion of some 10-15% of the silver to an off-white-pink adherent deposit of silver chloride. Prior to anodizing the electrode bases, 'sacrificial' silver anodes were chloridized, conditioning the electrolyte.

After ageing of the electrodes for two days by storage in 0.1m hydrochloric acid, bias potentials were measured and generally found to be wihin 0.2 mV.

(b) Thermal-electrolytic Electrodes

Electrodes of this type, illustrated in Figure 3.2b, were prepared using substantially the method suggested by Bates[75].

The electrode base was formed from a 20 mm length of 0.5 mm diameter platinum wire wound into a tight coil of about 2 mm diameter fused into the base of a 4 mm outer diameter soda-glass tube sealed into a soda-glass B19 cone, and similar to the platinum electrodes detailed in Section 3.2. The base was cleaned in hot concentrated nitric acid.

Silver oxide was prepared by dropwise addition of 2m sodium hydroxide into a well-stirred slight excess of 2m silver nitrate. The black precipitate was filtered-off, washed forty times with, and stored under deionized water.

A thick paste of silver oxide was prepared, spread on to the platinum coil and dried at 120°C. Reduction to silver was effected by heating in a small tube furnace at 500°C for 15 minutes. This sequence was repeated three of four times to provide a roughly spherical, spongy silver electrode of about 5 mm diameter, comprising about 300 - 500 mg silver.

The electrode was anodized in 1m hydrochoric acid at a current density of 10 mA cm^{-2} using an annular platinum gauze cathode converting about 15% of the silver to silver chloride.

Electrodes were washed with and stored in 0.1m hydrocholoric acid for two days to age, prior to measuring bias potentials. Those with bias potentials greater than 0.1 mV were discarded. Generally, bias potentials ranged between 30 and 50 μV, and were regularly checked in use.

Prior to use, electrodes were immersed overnight in the test solutions in which they were to be used. When not in use, they were stored in 0.1m hydrochloric acid.

3.2.3 Mercury, Mercury(I) Sulphate Electrodes

Schematically illustrated in Figure 3.2c, these electrodes were similar to those described by Beck, Dobson and Wynne-Jones[76].

Mercury(I) sulphate was prepared by Hulett's flowing anode method[77]. Doubly-distilled mercury flowed from a separating funnel through a 1 mm capillary tube into 1m sulphuric acid contained in a second separating funnel. Platinum wire electrodes in the mercury reservoir and the acid were connected across a 2 V accumulator. The light-grey coloured product, an intimate mixture of mercury(I) sulphate and mercury, was separated from excess mercury, washed with 0.1m sulphuric acid by decantation and stored under this solution.

The electrode base shown in Figure 3.2c comprised a borosilicate-glass tube fused to the lower end of a B19 conical joint, to the upper end of which a B10 socket was fused for introduction of a platinum electrode. A filling side-arm with a B10 socket was incorporated into the tube wall. Doubly-distilled mercury was introduced to a depth of about 10 mm. Electrical connection was made by a 4 x 4 mm^2 platinum foil electrode sealed into soda-glass tubing introduced through the upper socket. A layer of about 1 mm of mercury(I) sulphate was washed onto the mercury surface with 0.1m sulphuric acid, excess acid being expelled through a small hole above the mercury(I) sulphate. The electrode was stoppered and stored in 0.1m sulphuric acid.

Bias potentials were checked, and as these were no greater than 30 μV all electrodes were retained for use.

3.3 TRANSFER CELLS

A series of transfer cells of the type illustrated in Figure 3.3 were used in each experimental run. The cell design was that devised by Caudle[3] to meet the requirements of the transfer technique described by Covington and Prue[2], ensuring constancy of the hydrogen-gas electrode potential during transfer of a glass electrode and also maintaining test solution saturation with silver chloride in the vicinity of the silver, silver chloride reference electrode used for the majority of the experimental runs.

The linear cell of borosilicate glass contained three compartments separated by 4mm taps. The central compartment, incorporated a B45 socket to accommodate a glass electrode supported in a polythene mount. The other compartments incorporated B19 sockets, one for a hydrogen electrode, the other for an appropriate anion reference electrode. The hydrogen electrode chamber contained a gas outlet below the joint, and at the base, a 1 mm gas jet, terminated externally with a B7 socket. Concentration changes in the cell were avoided by bubbling gas from the purification train through a sintered-glass disc in a gas wash bottle containing the test solution. Some cells incorporating two hydrogen electrode chambers were made for checking bias potentials of the hydrogen electrodes. Cell taps were lightly greased with 'Apiezon L' around the top and bottom allowing electrolyte, about the central section, to provide electrical continuity in the closed position. All joints were lightly greased with 'Apiezon L' and the connection between the cell and the presaturator secured with rubber bands around hooks. Between experimental runs, cells were thoroughly cleansed.

3.4 THERMOSTAT

All transfer experiments were carried out at 25° ± 0.05°C in an air-thermostated chamber. This was a bench-mounted wooden cabinet approximately 1 m high x 1 m wide x 0.8 m deep with 50 mm cork insulation. The internal wall was lined with earthed aluminium sheet to provide electrical screening. Air was circulated by an electrically driven fan mounted within the rear wall. The air temperature, checked by thermometers in air and water, was maintained by electric heaters controlled by a mercury-toluene thermostat positioned on the rear wall. Access to the body of the chamber for arranging the cells before an experimental run was by a hinged door, insulated and screened, which had a doubled-glazed window above two arm holes, through which electrode transfers could be made without significantly affecting the

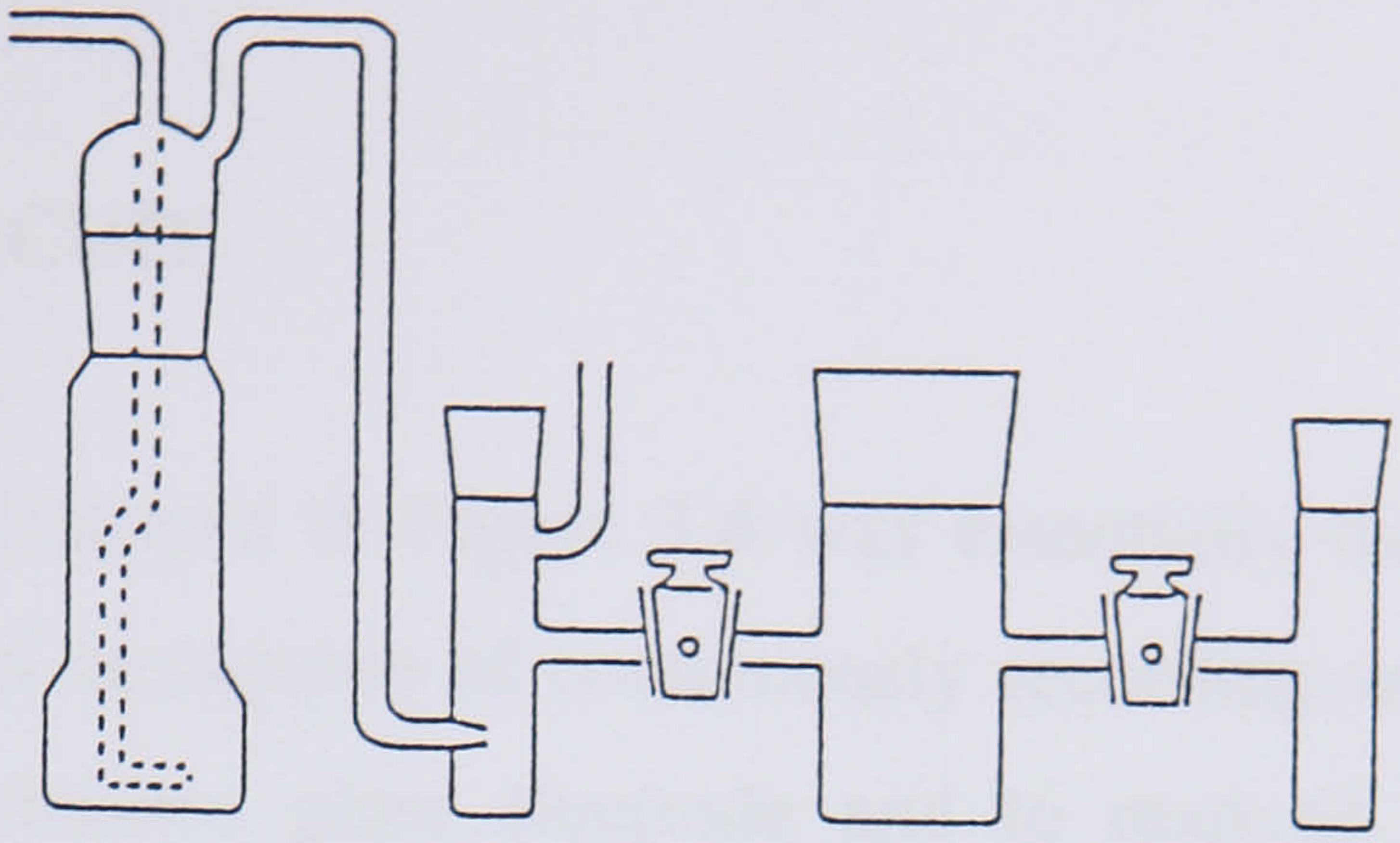


Fig. 3.3 Transfer Cell.

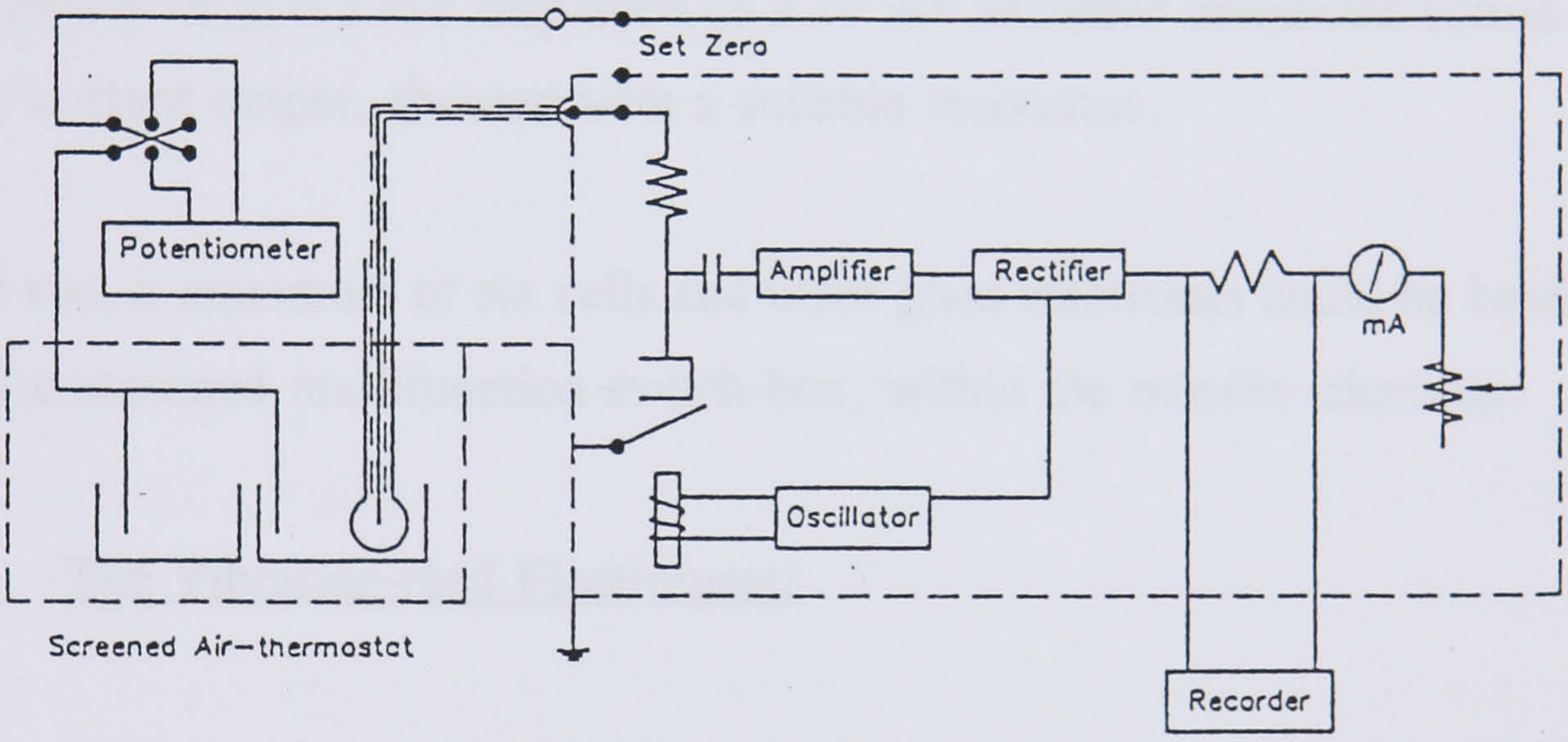


Fig. 3.4 Experimental Arrangement.

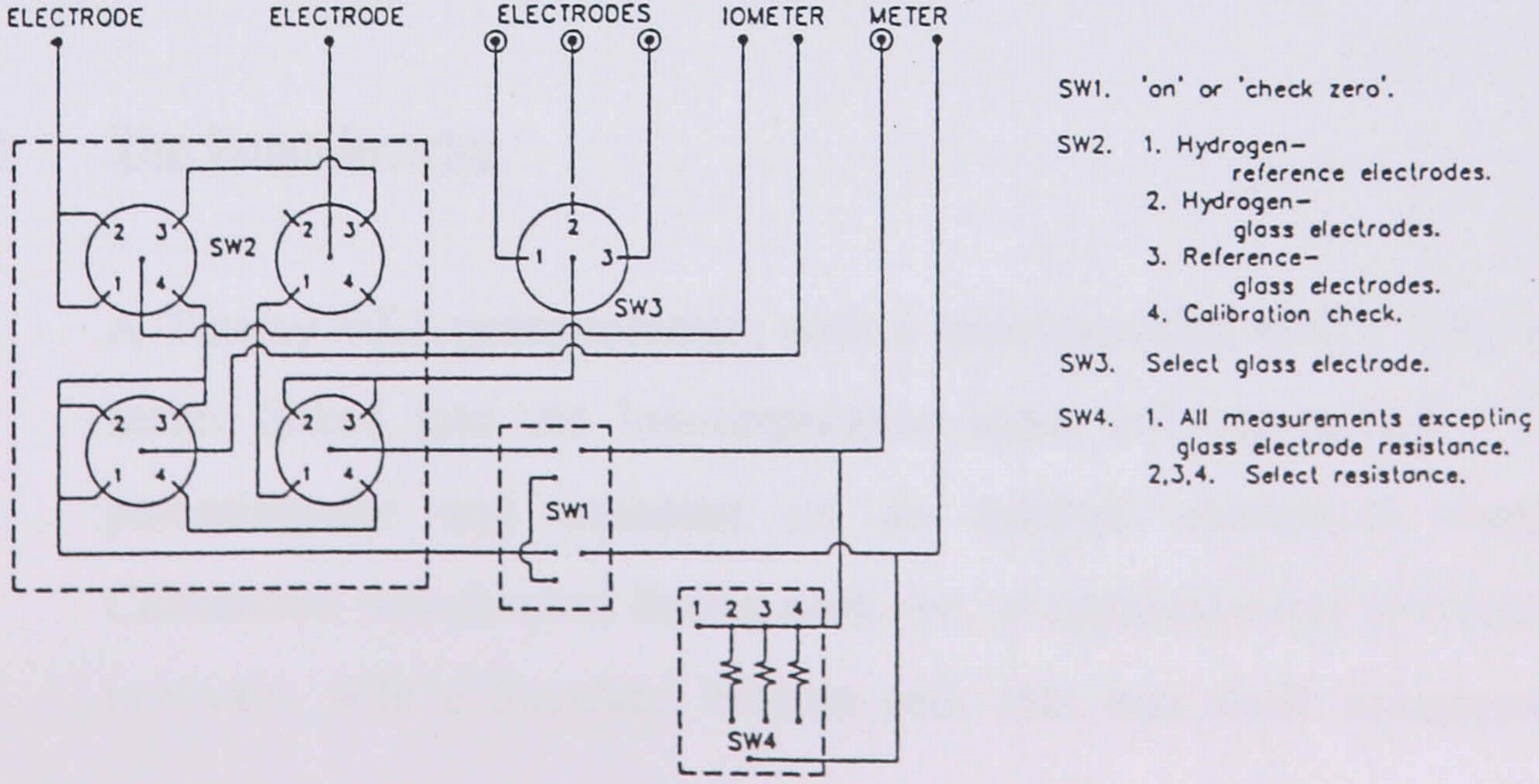


Fig.3.5 Schematic of Switch Connector Box.

air temperature within the cabinet. When not in use, the arm-holes were closed with swinging covers.

3.5 MEASURING CIRCUIT

The measurement circuit illustrated in Figure 3.4 was essentially that described by Caudle[3]. It was designed to be capable of continuously recording small changes of the potential of a high resistance glass electrode and to respond rapidly on the formation of a high resistance cell.

A high-impedance, vibrating-reed electrometer (see below) was used in conjunction with a series-connected potentiometer to measure on the 10 mV scale, the emf of a cell to an accuracy of ± 0.1 mV displayed on a 10 mV recorder connected across the electrometer current output, shunted with a suitable resistance.

In a transfer run, a maximum of six cells and three glass electrodes could be handled by means of a screened multifunction switch-box, within the transfer chamber.

(a) The Vibrating-reed Electrometer

Two instruments of similar performance were used. An EIL-Harwell 1086A instrument was used initially, but as it required a considerable degree of maintenance was replaced by an EIL62A electrometer that was used for all subsequent work. During each run the electrometer zero was checked at approximately two hourly intervals.

(b) The Potentiometer

A Tinsley 4025 potentiometer, with a discrimination of 0.1 mV, was series linked into the low-impedance input cell connection. The potentiometer was mounted on an earthed aluminium sheet[78]. Calibration was checked during each run, at approximately two-hourly intervals, with a Standard Weston cell, that was itself occasionally checked against a NPL certified cell held within the Department. After calibration the Cambridge null-type spot-galvanometer terminals were shorted to prevent damage during experimental measurements.

(c) The Recorder

A Honeywell-Brown 10 mV recorder, type 153 x 117 VH.II.III-30-C2-DR, was connected across a suitable resistance to the current output of the electrometer. Although the recorder incorporated self-standardization, the calibration was checked with the potentiometer during the frequent circuit checks.

(d) The Multifunction Switching Box

The circuit of the switching unit is schematically shown in Figure 3.5

A 'double-pole-double-throw', ceramic switch, SW1, either closed the cell for measurement or short-circuited the electrometer and opened the circuit for instrument calibration or glass electrode transfer between solutions. Cell-type selection was effected by a 4-ganged rotary PTFE wafer switch SW2. Switch SW3, a rotary 'make-before-break' PTFE wafer switch, connected to Belling-Lee panel-mounted, polythene insulated coaxial sockets, selected glass electrodes. A similar 2-ganged switch S4, selected either simple cell measurement or precision, glass-encapsulated, high megohm 'Victoreen' resistors for glass electrode resistance - measurement cells.

Switches and sockets were mounted in an earthed metal box that incorporated a silica-gel drier capsule which was frequently heat-regenerated. Connection of self-assembled glass electrodes and the electrometer was made with 'Telcon' anti-microphonic 0.25 in diameter coaxial cable, type PT1 GM (MOD).

3.6 REAGENTS AND SOLUTIONS

Analytical grade reagents, where available, were used without further preparation.

Disodium hydrogen phosphate, potassium dihydrogen phosphate, potassium hydrogen tartrate and potassium hydrogen phthalate were dried at 110°C for two hours prior to use, as recommended by Bates[79].

Calcium hydroxide was prepared by heating calcium carbonate at 1000°C for an hour. After cooling, the oxide was added, with stirring, to water. The suspension was heated to boiling and after cooling, calcium hydroxide was filtered-off, dried in a desiccator and crushed to a powder.

TRIS, i.e. tris(hydroxymethyl)aminomethane, supplied by Sigma Chemicals as Technical Grade material, was purified by recrystallization from hot 60 volume % methanol, filtered and dried in a desiccator[80].

Acetic acid was crystallized by freezing the glacial acid.

Hydrochloric acid solutions were made from constant-boiling acid using the pressure-composition data of Foulk and Hollingsworth[81]. Any traces of bromide and iodide were removed by chlorination and the acid boiled to remove chlorine prior to distillation. Solutions of the acid were used to standardize sodium hydroxide solutions employed to titrate sulphuric and acetic acid solutions.

Sodium hydroxide solutions were prepared by dilution of 'Convol' solutions supplied by BDH in sealed polythene phials.

Methanol was dried over Union Carbide Limited 'Molecular Sieve 4A' supplied by BDH and distilled.

N.N.dimethylformamide was fractionated under reduced pressure after drying over 'Molecular Sieve 4A'.

Deuterium oxide was supplied by Norsk-Hydro Limited.

Deionized water was prepared by passing distilled water through a mixed resin column of Permutit Limited ‘Zeo-Karb 225’ and ‘De-Acidite FF’.

Deionized water had a specific conductivity no greater than 0.2 μS cm^{-1} at 25°C and was monitored with a conductivity cell at the column outlet. All solutions were prepared by weight on the molal scale. Buoyancy corrections were made. Solutions were stored in 2 dm^3 flasks fitted with lightly greased ground reverse stoppers.

CHAPTER FOUR

EXPERIMENTAL PROCEDURE

4.1 GLASS ELECTRODE TRANSFER TECHNIQUE

The method adopted for all glass electrode transfers was that developed by Caudle[3] to monitor continuously the time-potential response, to a precision of 0.1 mV, of high resistance glass electrodes on transfer between solutions. This was an adaptation of the procedure devised by Covington and Prue[2] to test, with very low resistance glass electrodes to a precision of 0.01 mV, the 'instantaneous' potential hypothesis of Beck and Wynne-Jones[1], that at the moment of transfer, the hydrogen-ion function of the glass electrode is correct and any subsequent variation of cell emf is ascribable to a changing asymmetry potential of the glass electrode.

Caudle's[3] procedure compares directly the potential of the glass electrode with that of the hydrogen electrode, the only manner by which the hydrogen-ion function of the glass electrode can be examined without assuming either activity coefficient values or liquid-junction potential constancy.

If the hydrogen-ion function of a glass electrode were ideal, the emf of the cell,

$$\text{Pt, H}_2 \mid \text{Solution X} \mid \text{glass electrode} \qquad 1$$

would be invariant, regardless of the nature and composition of the solution, assuming, of course, that the function of the hydrogen-gas electrode is correct. For the procedure, glass electrodes are transferred between cells of type 1 containing different solutions, and any variation of emf observed is attributed solely to a change of the glass electrode potential.

To check the correct functioning of the hydrogen electrode and the constancy of the solution, if appropriate, a third electrode, reversible to the anion of the solution is introduced, e.g. for chloride ion containing solutions, a silver, silver chloride electrode, and measurement of the cell,

$$\text{Pt, H}_2 \mid \text{Solution X, Cl}^- \mid \text{AgCl, Ag} \qquad 2$$

will both check the constancy of the cell and provide the acidity function $pa_H\gamma_{Cl}$, discussed in the following section.

The precautions necessary to ensure a rapid transfer between solutions, avoiding extraneous electrical and chemical effects that may affect the response and satisfactory extrapolation of the glass electrode potential to the instant of transfer, were rigorously examined by Caudle[3].

Spurious electrical effects affecting the response characteristics were suppressed, e.g., by attention to meticulous electrical screening, mounting glass electrodes in substantial polythene stoppers and coating electrode stems with paraffin wax[2].

Chemical effects are associated with the manner of electrode treatment on transfer from one solution to another. Best results were obtained by rinsing the stem and bulb from a wash bottle with a portion of the solution to which it was to be transferred in 10-20s. Washing for longer times magnified the transient. Rinsing, by dipping into a beaker of solution and swirling, also increased the transient, as did wiping the electrode dry with filter paper as recommended by Mattock[82].

4.2 GLASS ELECTRODE TRANSFER PROCEDURE

Up to six transfer cells, of the type described in Chapter 3, were used for an experimental run.

Hydrogen-gas electrodes were connected by a common lead to the circuit switch-box. Hydrogen was supplied from a manifold through plasticized PVC tubing to the cell jet-inlets, and the flow of each cell adjusted, with screw-clamps, at a rate of about four bubbles per second. Gas exited the cells and chamber via an outlet tube to atmosphere.

A reference electrode, reversible to the test solution anion, provided the means of regularly checking each cell for most experiments. Reference electrodes were stored overnight in a portion of the solution in which they were to be used the following day.

Glass electrodes to be tested, immersed in their particular conditioning media, wash-bottles containing test solutions, and cells were allowed to attain thermal equilibrium.

The potentiometer was calibrated against a Weston Standard cell, and the electrometer and recorder zeroes and spans were checked. During an experimental run the measuring circuit calibration was verified, before the hydrogen-gas electrode-reference electrode emf of each cell was measured, at approximately two hourly intervals. Emf measurements were made to a precision of ±0.1 mV and corrected to a dry hydrogen pressure of 1013.25 Pa. Corrected values were constant to ±0.1 mV for up to ten hours for the aqueous solutions. Perhaps unnecessarily, partially aqueous test solutions were renewed after about five hours use.

When transferring a glass electrode between cells, Switch SW1 of the switch-box described in Chapter 3, was put to 'SET ZERO', both shorting the electrometer and opening the cell circuit. The electrode was removed by handling the polythene stopper, the stem and bulb washed for about 10s from the appropriate wash-bottle, and placed in the new test-cell. Switch SW1 was set to 'ON' and the hydrogen-electrode-glass electrode emf tracked on the recorder, adjusting the potentiometer as necessary. This procedure was usually completed within 30s. Glass electrode compartments of cells not in use were closed with stoppers.

Cell values were continuously recorded at a chart speed of 0.5 in. per minute. Extrapolation could be readily made to the instant at which the electrometer was shorted, which, within a few seconds, equated to the moment of electrode transfer and the final value in previous test-cell.

4.3 THE pH OF THE AQUEOUS SOLUTIONS

Measurement of the emf of cell 2,

$$\text{Pt, H}_2 \mid \text{Solution X, Cl}^- \mid \text{AgCl, Ag} \qquad 2$$

in addition to checking its constancy and the correct functioning of the electrodes, also provided the acidity function $pa_H\gamma_{Cl}$.

Cell emfs were corrected to a dry hydrogen pressure of 101 325 Pa assuming the vapour pressure over the solution to be that of pure water, and ignoring the excess pressure of the solution above the gas-inlet jet, using Bates[71] tabulations.

Calculation of the $pa_H \equiv pm_{H+}\ \gamma_{H+}$ for the test solutions was carried out in the same manner as that adopted by e.g., Bates[83] for the establishment of the NIST pH scale.

Unlike pH or pa_H, where a_H is the activity of the hydrogen ion, $pa_H\gamma_{Cl}$, where γ_{Cl} is the activity coefficient of the chloride ion, is physically defined at all ionic strengths and can be determined precisely from the emf of cell 2, without liquid-junction,

$E = E^o - k \log m_{H+}\gamma_{H+} - k \log m_{Cl^-}\gamma_{Cl^-}$

where E^o is the standard potential of the cell,

$k = (RT \ln 10) / F$

m, the molality and γ, the activity coefficient.

$pa_H\gamma_{Cl} = -\log m_{H+}\gamma_{H+}\gamma_{Cl^-}$

$= (E - E^o)/k + \log m_{Cl^-}$

Values of pa_H for the aqueous test solutions were calculated from $pa_H\gamma_{Cl}$,

$pa_H = pa_H\gamma_{Cl} - \log\gamma_{Cl}$

using the Bates-Guggenheim[84] convention to evaluate $\log\gamma_{Cl}$,

$-\log \gamma_{Cl} = (A\sqrt{I}) / (I + B\text{å}\sqrt{I})$

where for an ion i, å the ion-size parameter, I the ionic strength, and A and B the Debye-Hückel constants,

$A = (1.825 \times 10^6 \times \sqrt{d}) / (\epsilon T)^{3/2}$, and

$B = (50.29 \times \sqrt{d}) / \sqrt{(\epsilon T)}$

where d is the density c, ϵ the dielectric constant of the solvent[85] and T the thermodynamic temperature.

The convention assigns a value of 4.56 Å to å, and is stated to be applicable to solutions with ionic strengths no greater than 0.1.

In establishing the NIST pH scale, $pa_H\gamma_{Cl}$ values for a buffer solution with different small concentrations of added chloride were obtained, and the limiting value of zero chloride ion concentration, $p(a_H\gamma_{Cl})^o$ evaluated[83].

For the aqueous acid and buffer solutions, the data are collected in Chapter 5, Tables 5.5 and 5.6 and Chapter 6, Table 6.5.

Cell 2 values for 0.01m and 0.1m hydrochloric acid solutions of 464.3 mV and 352.3 mV respectively, are in good agreement with values of 464.1 mV and 352.3 mV reported by Bates and Bower[86].

The emf of 738.0 mV obtained for 0.1m sulphuric acid solution employing the mercury,mercury(I) sulphate reference electrode is in excellent agreement with the value of 738.1 mV calculated from the data of Beck, Dobson and Wynne-Jones[76].

4.4 THE pH^* OF THE PARTIALLY-AQUEOUS SOLUTIONS

In the absence of a universal pH scale referred to the aqueous standard state, values for pa_H^* of the 50 and 95 wt % methanol-water mixture solutions, referred to their respective standard states, were determined in a similar manner to that described in the previous section for calculating pa_H values for aqueous solutions. This approach was adopted by Paabo, Robinson and Bates[87] in assigning reference values of $pH^*(S)$ to buffer solutions in 50 wt % methanol-water mixtures. Cell emfs were corrected to a dry hydrogen pressure of 1013.25 Pa. Corrections ΔE, defined by,

$\Delta E = (RT/2F) \ln (760/P_{H_2})$ and,

$P_{H_2} = P - P_s$

where P is the atmospheric pressure in mm Hg,

P_{H_2}, the pressure of dry hydrogen, and

P_s, the vapour pressure of the solvent medium

were added to the measured values.

For cell 2,

$E = {}_sE^\circ - k \log m_{H^+\,s}\gamma_{H^+} - k \log m_{Cl^-\,s}\gamma_{Cl^-}$

where the subscript s indicates referral to the standard state in the particular solvent, then,

$p_s(a_H\gamma_{Cl}) = -\log m_{H^+\,s}\gamma_{H^+\,s}\gamma_{Cl^-}$

and $pa_H^* = p_s(a_H\gamma_{Cl}) + \log {}_s\gamma_{Cl^-}$

The term $-\log {}_s\gamma_{Cl^-}$ was determined by modifying the convention used for the establishment of NIST aqueous pH scale.

For the 50 wt. % methanol-water mixtures, data for vapour pressure, density, ion-size parameter, dielectric constant and the solvent mixture standard reference electrode potential are those used by Paabo, Robinson and Bates[88]. Analogous values for the 95 wt. % methanol-water mixture solutions were interpolated from Oiwa's[89] tabulations. The data are collected in Chapter 6, Table 6.9. Cell 2 data for solutions in methanol-water mixtures are presented in Chapter 6, Tables 6.6 and 6.7.

For the DMF-water mixture solutions, cell emfs for the buffer solutions are given in Chapter 6, Table 6.8. Drifting values for hydrochloric acid solutions in this solvent medium, arising from the high solubility of silver chloride[90,91] precluded their measurement.

For hydrochloric acid solutions in 50 wt. % methanol-water mixtures, emfs observed were 0.2 to 0.5 mV greater than values calculated using the standard potential for the silver, silver chloride electrode reported by Paabo *et al.*[88]. Values for pa_H* calculated for the acetate buffer solutions were about 0.02 pa_H* lower than those reported by the same workers[87] for similar solutions with sodium chloride additions, but in this work the added salt was potassium chloride.

For the 95 wt. % methanol-water hydrochloric acid solutions, the observed emf for the 0.01m solution is in good agreement with that calculated from interpolation of Oiwa's[89] results, but that for the 0.1m solution differs by 2.5 mV. Observed and calculated results are presented in Table 4.1.

4.5 GLASS ELECTRODE RESISTANCE MEASUREMENT

As the resistance of a glass electrode is a function of temperature, decreasing by an order of magnitude for an approximately 25°C increase in temperature[92], d-c resistances of the electrodes were measured at 25°C by the method described by Eckfeldt and Perley[93].

The emf of the cell e.g.,

$$\text{glass electrode} \mid 0.1\text{m HCl} \mid \text{AgCl, Ag} \qquad 3$$

Table 4.1
Observed and Calculated Results for Methanol-Water Solutions.

Solution	**Parameter†**	**Observed**	**Calculated (ref)**
0.0100m HCl, 50% MeOH	emf, mV	436.1	435.6 (88)
0.1000m HCl, 50% MeOH	emf, mV	327.7	327.5 (88)
0.0150m HOAc + 0.015m NaOAc + 0.0500m KCl, 50% MeOH	pa_H*	5.527	5.550 (87)
0.0500m HOAc + 0.0500m NaOAc+ 0.0500m KCl, 50% MeOH	pa_H*	5.512	5.529 (87)
0.0100m HCl, 95% MeOH	emf, mV	331.4	331.6
0.1000m HCl, 95% MeOH	emf, mV	230.5	233.1 (89)

† emf of cell 2, Pt, H_2 | Solution X, Cl^- | AgCl, Ag

was measured. A voltage V, derived from a potentiometer connected between the reference electrode and the switch-connector box, and a resistance R_C, selected by switch SW4, were introduced into the circuit and the emf E_r, measured after about 15 minutes when the rate of emf drift was low. The resistance of the glass electrode R_g, was determined from the relationship,

$$R_g = (R_c/E_r)(V + E_g - E_r)$$

The resistance, R_C was chosen to be similar to that of the glass electrode. Applied voltages V, of 100 - 500 mV were used. The resistance measured was, of course, the resistance of the complete cell, but that of the solution is negligible compared with the resistance of the glass electrode. Accuracy of glass electrode resistances was probably about 5 %. After polarization electrodes were not used for at least a day.

4.6 CHARACTERIZATION OF THE TIME-POTENTIAL RESPONSES OF GLASS ELECTRODES

On transfer of low resistance glass electrodes between cells 4 and 5,

$$\text{glass electrode} \mid \text{HCl}, m_1 \mid \text{AgCl, Ag} \qquad 4$$

$$\text{glass electrode} \mid \text{HCl}, m_2 \mid \text{AgCl, Ag} \qquad 5$$

Covington and Prue[2] were able to extrapolate the slow linear variation of the emf of cell 4 to the moment of the glass electrode transfer. Their results for such transfers in dilute hydrochloric acid solutions supported the instantaneous potential concept that at the moment of transfer the glass electrode responded ideally to hydrogen ions and the subsequent drift could be attributed to a time-dependent asymmetry potential as the result of other potential-determining reactions at the electrode surface[1]. Applying the transfer technique with commercial, high-resistance glass electrodes for cells containing acid solutions of various concentrations, and hydrogen reference electrodes, Beck *et al.*[4] obtained various characteristic potential-time variations which they classified as transient features A, B and C. The classification was extended by Buck[5] to include time-response features D and E, and for this work, an additional feature F. The potential-time response characteristics are shown in Figure 4.1 which illustrates the difference in the glass electrode potentials between cells 6 and 7,

$$\text{Pt}, H_2 \mid \text{solution 1} \mid \text{glass electrode} \qquad 6$$

$$\text{Pt}, H_2 \mid \text{solution 2} \mid \text{glass electrode} \qquad 7$$

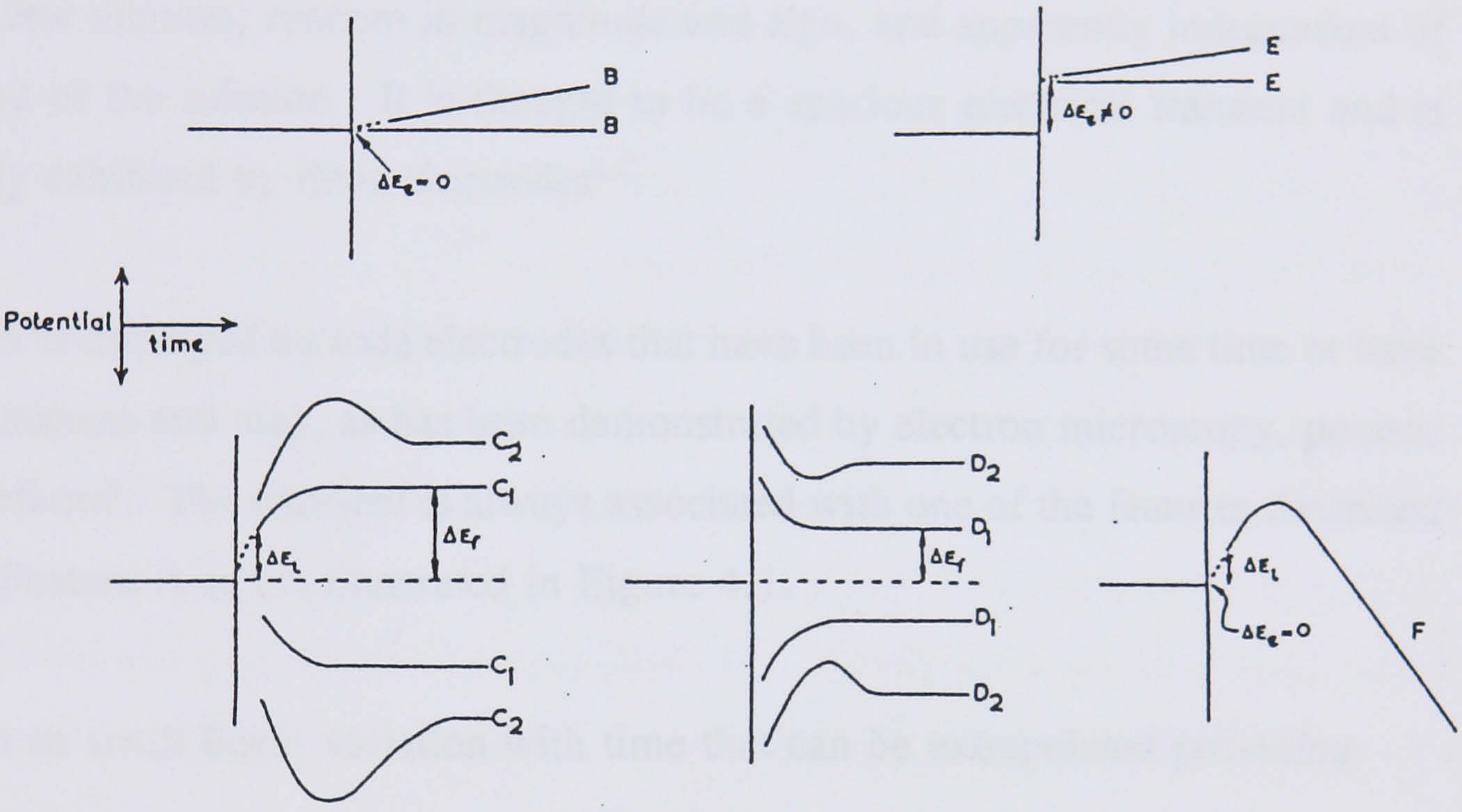


Fig. 4·1 Classification of Potential-Time Transient Forms.

ΔEi, the initial error, is the difference between the final potential in the first solution and the first measured potential in the second solution. ΔE_f, the final error, is the difference between final measurements in each solution. In some solutions stable potentials are not attained and ΔE_f is time-dependent.

ΔE_e, the extrapolated error, is the difference between the potential in the second solution extrapolated to the moment of transfer and the final potential in the first solution.

The characteristic time-potential features are, A, a rapid variation of potential over the first few minutes, random in magnitude and sign, and apparently independent of the nature of the solution. It is thought to be a spurious electrical transient and is invariably exhibited by lithia electrodes[3,4].

Feature A is displayed by soda electrodes that have been in use for some time or have high resistances and may, as has been demonstrated by electron microscopy, possess pitted surfaces[3]. The transient is always associated with one of the features described below. Feature A is not illustrated in Figure 4.1.

B, a zero or small linear variation with time that can be extrapolated providing ΔE_e = zero.

C, a rapid change of potential, the rate decreasing slowly C_1, occasionally exhibiting turning points C_2, and for which $/ \Delta E_f / > / \Delta E_i /$.

D, with the reverse characteristics of C, likewise subdivided in to D_1 and D_2, and for which $/ \Delta E_f / < / \Delta E_i /$

E, with the same characteristics as B, but with $\Delta E_e \neq$ zero.

F, observed in some partially aqueous solutions in this work for which ΔE_e = zero, exhibits a turning-point and at some time t, ΔE_t = zero.

Classification of transient response is not always clear, especially distinguishing between A + B or A + E and C, or D_1 transient features. Buck[5] has indicated that the D_1 transient may be regarded as a special form of a C_2 transient in which the initial portion of the transient and its turning point are too rapid to be detected. Similarly, a C_1 transient may be considered as a variant of a D_2 transient.

Inspection of transient features illustrated in Figure 4.1 indicates that the linear B and E time-potential responses are readily extrapolated to the moment of transfer at time t_o to provide ΔE_c. The non-linear portion of a C-type response, may lend itself, if the rate of change is not too large, to extrapolation to time t_o. The linear portion, which may vary with time indicates, of course, ΔE_t or ΔE_f. The non-linear part of a D-type response cannot be sensibly extrapolated to time t_o at least, for the purpose of testing the Beck and Wynne-Jones[1] hypothesis. Type F response has been observed only for electrode transfers between solutions in methanol-water mixtures. Inspection of e.g., Figures 6.10 and 6.11 suggest that this form of response is a C-type transient imposed on a continuous negative drift of the asymmetry potential of the glass electrode. Caudle[3] introduced the classification as a previous approach, reported by Simon and Wegmann[94] that ignored the first few minutes of the potential-time variation for a glass electrode on transfer, was an unsatisfactory basis upon which to test the instantaneous potential hypothesis.

Tabulations in Chapters 5, 6 and 7 for glass electrode transfer results include the transient response type.

CHAPTER FIVE

GLASS ELECTRODE ERRORS IN STANDARD AND OTHER BUFFER SOLUTIONS

5.1 INTRODUCTION

Although predominantly investigating the time response characteristics of glass electrodes in acid solutions, Caudle[3] made a limited study of their behaviour in NIST buffer solutions directly against hydrogen gas electrodes in a series of consecutive transfer runs, and obtained the results tabulated in Table 5.1.

He found the response characteristics for both the soda-based (EIL, GG) and the two lithia-based electrodes similar to those that he had observed for the same types of glass electrode in acid solutions at concentrations below the onset of negative error behaviour, that is B type for the soda-based electrode and A+B or E type for the lithia-based electrodes. Allowing for the experimental uncertainly of ± 0.1 mV, examination of the results discloses small, but significant errors, particularly for the lithia-based electrodes. The performance of the EIL GHS electrode was generally sluggish and somewhat erratic, a characteristic that Buck[5] also observed with EIL GHS and some other lithia-based electrodes, Beckman E2 and Pye-Ingold.

Surprising results were noted by Caudle[3] in transfers of glass electrodes between dilute hydrocholoric acid and amine-hydrochloric acid buffer solutions. Amines used were ethanolamine, pKa (25°C)=9.498[95] and tris(hydroxymethyl)amino methane (TRIS), pKa (25°C) 8.214[96]. His results are reproduced in Figure 5.1. The errors appear to be a function both of pH and buffer concentration but unrelated to the dissociation constants. Unfortunately he neither identified the glass electrode or electrodes used, nor recorded the time-emf data. The plots are presumably based on either ΔE_f or ΔE_c data.

Searching for a suitable high pH buffer to adopt as a standard solution from which to investigate glass electrode response characteristics in alkaline solutions, Buck[5] transferred both soda and lithia-based glass electrodes between 0.1m H_2SO_4 and buffer solutions of 0.05m amine - 0.05m amine- HCl (ethanolamine and TRIS). Both solutions proved satisfactory in that errors were negligible, other than the occasional erratic behaviour of some lithia-based electrodes referred to earlier. Buck's solutions were of higher concentration and at maximum buffer capacity, whereas Caudle's were

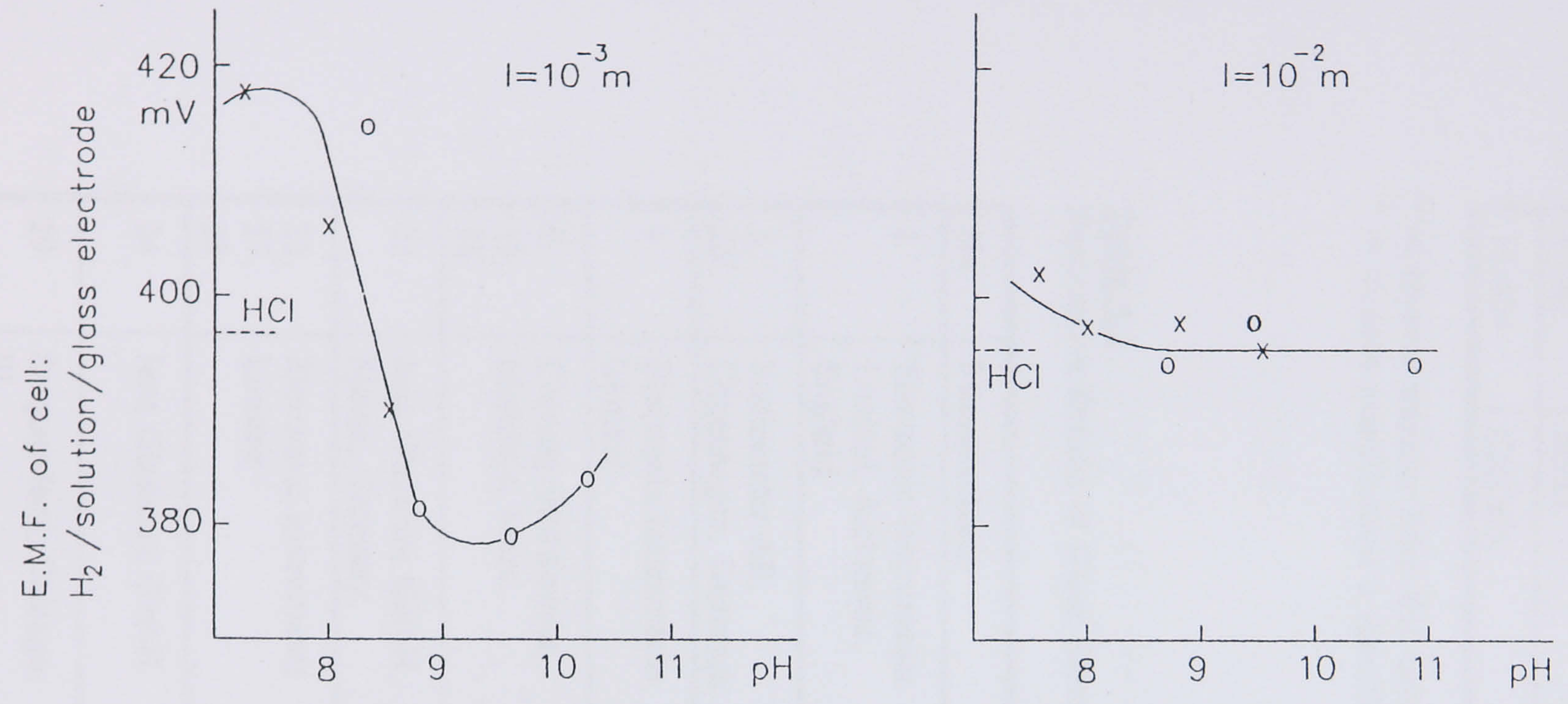


Fig.5.1 Transfers between HCl and HCl with TRIS (x) and Ethanolamine (o) (Caudle's data, Ref. 3).

Table 5.1
Errors of Glass Electrodes in NIST Buffer solutions (Caudle's averaged results)

pH(S) 25°C	Buffer	Molality, m	Error, mV		
			Jena, HA	EIL, GHS	EIL, GG
1.679	K tetroxalate	0.05	(-0.2)[a]	(-0.6)[a]	(-0.1)[a]
3.557	KH tartrate	satd. 25°C	0	0.4	0.1
4.008	KH phthalate	0.05	0.2	-0.9	-0.2
6.865	KH_2PO_4+ Na_2HPO_4	0.025 of each	-0.2	-0.2	-0.1
9.180	borax	0.01	0.3	0.5	-0.1
12.454	$Ca(OH)_2$	satd. 25°C	0.6	0.1	(15.0)[b]

[a] = reverse transfer from KH tartrate to K tetroxalate
[b] = outside manufacturer's specification of 1-10pH

Table 5.2
Descriptive Details of Glass Electrodes Used

No	Manufacturer	Designation	Specification
1	Electronic Instruments Limited, Richmond, England	GFH33	0-11pH, 0°-50°C, Flat-head
3, 25	Radiometer AB, Copenhagen, Denmark	242C	0-12pH, 10°-60°C, No.3 - Flat-head
4	Electronic Instruments Limited	GHS 33	0-14pH, 10°C-140°C
6, 19, 26	Corning Instruments, Medfield, Mass.	41263	0-14pH, -5°-100°C. Triple-purpose, No. 6 - 0.1m HCl filling
22	Jena Glaswerk GmbH, Mainz, Germany	HA 9401	1-14pH, 0°-70°C
23, 27, 28	Electronic Instruments Limited	GG 33	1-10pH, 10°-45°C
24	Jena Glaswerk GmbH	N 9000	1-10pH, 0°-40°C, 30mm bulb
29	Sargent-Jena, Chicago, Ill.	U530050-15C	1-14pH, -10° -70°C
30	Radiometer AB	202B	0-14pH, 20°-60°C
31	Beckman Inc., Fullerton, Calif.	41263	0-14pH, 15°-80°C. E2 glass
32	Sargent-Jena	HTA 530056-10	1-14pH, 20° - 120°C

more dilute, with consequent lower buffer capacity. Mattock[82] has indicated the difficulties in measuring pH in poorly buffered solutions, namely leaching of alkali from the glass electrode surface and ingress of carbon dioxide into the solution.

In this work the time-emf responses of a range of representative European and USA commercial glass electrodes were studied in a selection of widely used buffer solutions in the acidic to moderate pH range between pH 1 and pH 9.2. Buffer solutions used included NIST[97] Primary Standards and BS[98] Reference Value and Operational Standards of the two Institutions' pH scales.

5.2 EXPERIMENTAL

5.2.1 Glass Electrodes

Descriptive details of the glass electrodes used in this study are tabulated in Table 5.2 A full history of each electrode is given in Appendix A.

Electrode 24 was unscreened, it had been received from the supplier as a 'blank', i.e. as stem plus bulb and the assembly was completed with an internal filling solution of 0.1m hydrochloric acid and an electrolytic silver, silver chloride electrode. Due to the large bulb size it was mounted as described in Chapter 4 in a polythene bung and the bulb surrounded with a suspended protective circumferential glass guard ring. Although an obsolete variety, it was included as it was with this type of low resistance glass electrode that Covington and Prue[2] first demonstrated that precise measurements could be attained with glass electrodes. All other electrodes were screened, and apart from electrodes 1 and 3 that had flat membranes and electrode 24 described above, had conventional 10 mm diameter bulb membranes. Glass electrode 6 had been supplied as a blank, and was completed with a 0.1m hydrochloric acid internal filling and an electrolytic silver, silver chloride internal reference electrode; it had been previously used in similar studies that are presented in Chapter 6. Electrodes 25, 26, 27 and 28 were new for this work, electrodes 1, 3 and 6 had previously been used by the author[99], and Buck[5] had introduced electrodes 4, 19, 22 and 23 into his studies. Electrodes 29, 30, 31 and 32 had earlier been used by Covington and others[100], and electrode 24 had been previously used within the Department. All electrodes were mounted as described in Chapter 3. New electrodes were conditioned in distilled water for at least ten days prior to use, and when not in use all were stored in deionized water. Before use, the electrode stems were paraffin wax-coated to suppress electrical leakage.

The properties of a particular glass electrode type are determined by its composition, and in comparative studies of this nature, it would be helpful if the membrane glass compositions were known. Understandably, manufacturers are reluctant to disclose more than the barest information. Within the Department a limited flame photometric analysis of some membrane glasses had been made[5] , and this and other available data[101] are given in Table 5.3. The Jena N Electrode 24, is reported[102] to have a composite membrane comprising a bulb of high soda content with an applied surface layer of a higher durability pH responsive glass. The applied layer is almost certainly a soda-based glass because of the mixed alkali effect[42], i.e. the large increase of electrical resistivity of a glass when the alkali oxide is partially substituted by another alkali oxide. All other electrodes are assumed to be lithia-based, their wide pH and temperature specifications supporting this view.

All the glass electrodes had silver, silver-chloride internal reference electrodes. The filling solutions of the soda-based electrodes were 0.1m hydrochloric acid, those of the lithia-based electrodes either 0.1m hydrochloric acid, or a buffer solution containing chloride ions. During the course of this work, the d.c. resistances were measured as earlier described. The data are collected in Table 5.4

5.2.2 Solutions, Hydrogen and Reference Electrodes

Preparation of solutions and electrodes has been previously discussed. Glass

Table 5.3
Composition of Membrane Glasses

No	Type	Composition, mole %	Reference
1	GFH	Li_2O, BaO, UO_2, SiO_2	Manufacturer
4	GHS	Li_2O, 20.3, Cs_2O 0.2, CaO 2.6, SiO_2 76.9	5
22,8	HA	Li_2O 20.8, Cs_2O 1.5, CaO 1.3, SiO_2 76.4	5
23,27, 28	GG	Na_2O 21.37, CaO 6.44, SiO_2 72.19 (Corning 015)	Manufacturer
31	E2	Li_2O, BaO, SiO_2	101
6,19,16	Triple-purpose	Li_2O, Cs_2o, La_2O_3, Ta_20_5, UO_2, SiO_2	103,104

Table 5.4
Glass Electrode Details

No.	Manufacturer	Membrane Glass	pH range	Resistance, MΩ, 25°C	Internal Electrolyte	Reference
1	EIL	GFH	0-11	500	0.1m HCl	Manufacturer
3, 25	Radiometer	C	0-12	170,165	Citrate, Cl^-	105
4	EIL	GHS	0-14	510	0.1m HCl	Manufacturer
6†, 19, 26	Corning	Triple-purpose	0-14	170,250	Phosphate, Cl^-	5
22	Jena	HA	0-14	500	Acetate, Cl^-	5
23, 27, 28	EIL	GG	1-10	120,75,140	0.1m HCl	Manufacturer
24	Jena	N	1-10	< 1	0.1m HCl	—
29	Sargent-Jena	U	1-14	230	Acetate, Cl^-	5
30	Radiometer	B	0-14	400	Citrate, Cl^-	105
31	Beckman	E2	0-14	220	Phosphate, Cl^-	5
32	Sargent-Jena	HTA	1-14	555	Acetate, Cl^-	5

† Internal electrolyte, 0.1m HCl

Table 5.5
Data on Buffer Solutions containing Chloride

Buffer	Buffer moles kg^{-1}	Added chloride moles kg^{-1}	Ionic strength I	E† mV	$pa_H\gamma_{Cl}$	$-\log \gamma_{Cl}$	pa_H
Hydrochloric acid	0.1000	0.0000	0.1000	352.3	1.197	0.109	1.088
Sulphuric acid	0.1000	0.0000	-	738.0*	-	-	-
Potassium tetroxalate	0.1000	0.1000	0.240	379.0	1.643	0.144	1.504
	0.0500	0.1000	0.177	383.2	1.804	0.131	1.673
	0.0100	0.1000	0.113	416.9	2.239	0.116	2.173
Glycine-hydrochloric acid (equimolal)	0.1000	0.0000	0.100	435.0	2.598	0.109	2.406
	0.0500	0.0500	0.100	436.9	2.630	0.109	2.513
	0.0100	0.0900	0.100	446.3	2.629	0.109	2.685
Potassium hydrogen phthalate	0.1000	0.1000	0.206	520.5	4.043	0.138	3.902
	0.0500	0.1000	0.153	521.0	4.052	0.126	3.923
	0.0100	0.1000	0.110	523.4	4.092	0.113	3.976
Disodium hydrogen	0.0500	0.1000	0.800	687.9	6.877	0.154	6.716
Phosphate-potassium	0.0250	0.1000	0.200	690.1	6.914	0.137	6.770
Dihydrogen phosphate	0.0125	0.1000	0.150	691.6	6.935	0.125	6.807
(equimolal)	0.0025	0.1000	0.110	692.6	6.952	0.113	6.836
TRIS-hydrochloric acid (equimolal)	0.1000	0.0000	0.100	773.0	8.311	0.109	8.199
	0.0500	0.0500	0.100	773.1	8.314	0.109	8.201
	0.0100	0.0900	0.100	773.3	8.316	0.109	8.204
Borax	0.0500	0.1000	0.200	831.5	9.297	0.137	9.160
	0.0100	0.1000	0.120	827.9	9.236	0.116	9.120
	0.0050	0.1000	0.120	826.8	9.222	0.113	9.109

† emf of cell, Pt, H_2 | Solution X, Cl^- | AgCl, Ag

* measured against a mercury, mercury(I) sulphate electrode

Table 5.6
Data on Buffers with and without Added Chloride used in Transfers from 0.1m Sulphuric Acid

Buffer	Buffer moles kg^{-1}	Added salt	Salt moles kg^{-1}	Ionic strength I	pa_H
Potassium hydrogen phthalate	0.1000	none	-	0.1060	-
	0.0500	none	-	0.0533	4.008
	0.0100	none	-	0.010	-
	0.0100	KCl	0.1000	0.110	3.976
	0.0100	$KClO_4$	0.1000	0.110	-
Disodium hydrogen phosphate-potassium dihydrogen phosphate (equimolal)	0.0500	none	-	-	6.775
	0.0250	none	-	-	6.865
	0.0025	none	-	-	7.068
	0.0500	KCl	0.1000	0.300	6.716
	0.0250	KCl	0.1000	0.200	6.770
	0.0125	KCl	0.1000	0.150	6.807
	0.0025	KCl	0.1000	0.110	6.836
	0.0025	$KClO_4$	0.1000	0.110	-

electrodes were transferred from 0.1m hydrochloric acid into one of a series of weak acid buffer system solutions and returned to the acid. Each series of a buffer system comprised a sequence of solutions of decreasing buffer concentration with a constant chloride strength of 0.1m, made up, if necessary with the addition of potassium or tetramethyl ammonium chloride.

Glass electrode potentials were measured against platinized-platinum hydrogen gas electrodes, except in the phthalate buffer solutions, in which the less catalytically active palladized-platinum electrode was used as the inert base.

Thermoelectrolytic silver, silver chloride reference electrodes were used in these solutions periodically to check the consistency of the cells:

$$\text{Pt, H}_2 \;|\; \text{Solutions, 0.1m Cl}^- \;|\; \text{AgCl, Ag} \qquad 1$$

and provided cell emf data for the calculation of the pa_H of the buffer solutions.

For a number of the experimental runs, transfers were made from 0.1m sulphuric acid, in which mercury, mercury(I) sulphate reference electrodes were used. In one series of these runs potassium chloride was replaced by potassium perchlorate, and in another, the buffer solutions contained no added salt.

Details of the solutions used in the 0.1m hydrochloric acid transfers are collected in Table 5.5. Those of the 0.1m sulphuric acid transfer series are presented in Table 5.6.

Details of the calculation of the pa_H of the solutions have been described in Chapter 4. Ionic strengths of the potassium tetroxalate buffers were taken from Bates[106] data and those of the potassium hydrogen phthalate buffers calculated from the acid dissociation constants[107,108]. For the equimolal phosphate buffer solutions, ionic strengths were virtually identical with the

Table 5.7
Record of Transfers in Aqueous Buffer Solutions

Run	Acid	Buffer Series	Added Salt	Electrode Number															
				1	3	4	6	19	22	23	24	25	26	27	28	29	30	31	32
1	HCl	Phosphate	KCl		x		x	x											
2	HCl	Borax	KCl		x		x	x											
3	HCl	TRIS	KCl		x		x	x											
4	HCl	Tetroxalate	KCl		x		x	x											
6	HCl	Glycine	KCl		x		x	x											
7	HCl	Glycine	KCl	x		x			x	x									
8	HCl	Glycine	KCl								x								
9	HCl	TRIS	KCl		x		x	x			x								
10	HCl	TRIS	KCl	x		x			x	x									
11	HCl	Phosphate	KCl		x		x	x			x								
12	HCl	Phosphate	KCl	x		x			x	x									
13	HCl	TRIS	$(CH_3)_4NCl$		x		x	x			x								
14	HCl	TRIS	$(CH_3)_4NCl$	x	x	x			x	x									
15	HCl	Phthalate	KCl		x	x		x			x								
16	HCl	Phthalate	KCl	x		x			x	x									
17	H_2SO_4	Phosphate	KCl	x				x											
18	H_2SO_4	Phosphate	KCl		x				x	x	x								
29	HCl	Phthalate	KCl											x					x
30	HCl	Phthalate	KCl		x				x								x	x	
31	HCl	Phthalate	KCl	x				x				x				x			
32	HCl	Phosphate	KCl	x				x				x							
33	HCl	Phosphate	KCl						x									x	
34	HCl	Phosphate	KCl		x					x				x		x			x
35	HCl	Phosphate	KCl			x							x						
36	HCl	Mixed	KCl	x	x	x			x										
37	HCl	Mixed	KCl						x										
38	HCl	Mixed	KCl							x		x	x	x		x	x	x	x
39	HCl	Mixed	KCl				x	x			x								
41	H_2SO_4	Phosphate	None		x										x				
42	H_2SO_4	Phthalate	None		x					x					x				
43	H_2SO_4	Phosphate	None							x					x				
44	H_2SO_4	Phthalate	KCl, $KClO_4$		x					x					x				
45	H_2SO_4	Phosphate	KCl, $KClO_4$		x					x					x				

stoichiometric composition. The ionic strengths of the glycine-hydrochloric acid and TRIS-hydrochloric acid buffers are stoichiometric.

pa_H values for the 0.05m, 0.0125m and 0.0025m phosphate buffer solutions were calculated from $pa_H\gamma_{Cl}$ data of Bates[109].

5.3 RESULTS AND DISCUSSION

A chronological listing of the transfer experiments is presented in Table 5.7. The majority of the experiments were of stepwise transfer of the glass electrodes from either 0.1m hydrochloric acid or 0.1m sulphuric acid into each solution of a buffer series, and back into the acid solution. Runs 36-39, however, were of consecutive transfers of the glass electrodes from 0.1m hydrochloric acid through a series of buffer solutions of increasing pH, then returned to the acid from the final borax buffer solution.

Inspection of Table 5.7 shows that transfer runs from 0.1m hydrochloric acid were conducted in three stages. Initially three electrodes that had been previously used within the Department were studied. During run 6, five other electrodes that had earlier been used were inserted into the experiments, and finally three new electrodes and four that had formerly been used in the NBS laboratories were incorporated.

Experimental runs in which glass electrodes were transferred from 0.1m sulphuric acid were made with a selection of these electrodes together with one new electrode.

The detailed time-emf data of the electrode transfer runs are collected in Appendix B. Error results for transfers from 0.1m hydrochloric acid are collected in Tables 5.8 and 5.9, and those from 0.1m sulphuric acid in Table 5.10 and 5.11. Results are expressed in separate tables in mV or ΔpH and represent the emf or pH difference of the cells:

$$\text{Pt,H}_2 \mid 0.1\text{m HCl} \mid \text{glass electrode} \qquad 2$$

$$\text{and, Pt,H}_2 \mid \text{buffer solution} \mid \text{glass electrode} \qquad 3$$

Table 5.8
Transfer from 0.1m HCl into Buffer Solutions containing 0.1m Chloride (Total)

Buffer + Chloride	Buffer Molality	Run	Errors, mV														
			Electrode Number														
			1	3	25	4	6	19	26	22	23	27	24	29	30	31	32
K tetroxalate + KCl	0.10	4		0			0	0									
	0.05	4		0			0	0									
	0.05	36-39	-0.5	0	0.1	0.1	0	0	0	0	0.1	0.1	0	0	0	0	0.1
	0.01	4		0			0	0.2									
Glycine + HCl + KCl	0.10	6-8	0	0		0	0	0		0	0.2		0.1				
	0.05	6-8	0.1	0		0	0	0		0.2	0.8		0.1				
	0.01	6-8	0.1	0		0	0	0.1		0	0.9		0.2				
KH phthalate + KCl	0.10	15-16	0	0		0.3	0.1			0.1	0.4		0				
	0.10	29-31	0	0.1	0.1			0.1		0.1	0.5	0.1		0.4	0.1	0.1	0.1
	0.05	15-16	0	0.1	-	0.2	0.1	0		0	0.8		0.1				
	0.05	29-31		0.2	0.1			0.1		0.1	0.7	0.1		0.3	0	0.3	0.1
	0.01	15-16	0.3	0		0.7	0.5	0		0.6	1.2		0.3				
	0.01	29-31		0.5	0.4			0.4		0.5	1.2	0.4		0.6	0.4	0.3	0.4
1:1 Phosphates + KCl	0.05	32-34	0.4	0.1	0.1	1.6		0.4	1.3	0.3	0.6	0.2		0.5		0.2	0.2
	0.025	1		0.2			0.5	0.2									
	0.025	11-12	0.2	0.3		0.5	0.5	0.3		0.3	0.7		1.3				
	0.025	32-35	0.3	0.1	0.3	0.4		0.2	1.5	0.3	0.4	0.4		0.4		0.3	0.3
	0.0125	1		0.3			0.6	0.2									
	0.0125	11-12	0.3	0.3		1.0	0.7	0.4		0.4	0.9		1.4				
	0.0025	1		0.5			1.0	0.6									
	0.0025	11-12	1.7	1.1		1.9	1.7	1.1		2.0	2.0		2.8	1.9		0.7	1.2
	0.0025	32-35	0.6	1.0	0.7	1.8		0.9	2.6	1.4	1.7	1.3					
TRIS + HCl + KCl	0.10	3					0.5	0.1									
	0.10	9-10	0	0		0	0.4	0.1		0.1	0.7		0				
	0.05	3		0.4			1.1	0.7									
	0.05	9-10	0.7	0		0.2	0.4	0.2		0.2	1.2		1.8				
	0.01	3		0			0.5	0									
	0.01	9-10	1.3	0.2		1.7	0.8	0.4		1.0	2.3		3.5				
TRIS + HCl + Me₄NCl	0.10	13-14	0.1	0		0.1	0.5	0		0.1	0.7		0				
	0.05	13-14	0.5	0		0.2	0.4	0		0.3	0.8		0.1				
	0.01	13-14	1.2	0.1		1.5	1.4	0.4		1.3	1.7		0.8				
Borax + KCl	0.05	2		0.3			0.4	0									
	0.01	2		0.2			0.3	0.3									
	0.01	36-39	1.3	0.3	0.2	2.2	1.1	0	2.2	0.3	2.2	1.5	7.0	1.4	1.2	0.8	0.9
	0.005	2		0.4			0.7	0.3									

Table 5.9
Transfer from 0.1m HCl into Buffer Solutions containing 0.1m Chloride (Total)

Buffer + Chloride	Buffer Molality	Run	Errors, ΔpH														
			Electrode Number														
			1	3	25	4	6	19	26	22	23	27	24	29	30	31	32
K tetroxalate + KCl	0.10	4		0			0	0									
	0.05	4		0			0	0									
	0.05	36-39	0.008	0	0.002	0.002	0	0.002	0	0	0.002	0.002	0	0	0	0	0.002
	0.01	4		0			0	0.003									
Glycine + HCl + KCl	0.10	6-8	0	0		0	0	0		0	0.003		0.002				
	0.05	6-8	0.002	0		0	0	0		0.003	0.014		0.002				
	0.01	6-8	0.002	0		0	0	0.002		0	0.015		0.003				
KH phthalate + KCl	0.10	15-16	0	0		0.005	0.002			0.002	0.007		0				
	0.10	29-31	0	0.002	0.002			0.002		0.002	0.008	0.002		0.007	0.002	0.002	0.002
	0.05	15-16	0	0.002		0.003	0.002	0		0	0.014		0.002				
	0.05	29-31		0.003	0.002			0.002		0.002	0.012	0.002		0.005	0	0.005	0.002
	0.01	15-16	0.005	0		0.012	0.008	0		0.010	0.020		0.005				
	0.01	29-31		0.008	0.007			0.007		0.008	0.020	0.007		0.010	0.007	0.005	0.007
1:1 Phosphates + KCl	0.05	32-34	0.007	0.002	0.002	0.027		0.007	0.022	0.005	0.010	0.003		0.008		0.003	0.003
	0.025	1		0.003			0.008	0.013									
	0.025	11-12	0.003	0.005		0.008	0.008	0.005		0.005	0.012		0.022				
	0.025	32-35	0.005	0.002	0.005	0.007		0.003	0.025	0.005	0.007	0.007		0.007		0.005	0.005
	0.0125	1		0.005			0.010	0.003									
	0.0125	11-12	0.005	0.005		0.007	0.012	0.007		0.007	0.015		0.024				
	0.0025	1		0.008			0.017	0.010									
	0.0025	11-12	0.029	0.019		0.032	0.029	0.019		0.034	0.034		0.047				
	0.0025	32-35	0.010	0.017	0.012	0.030		0.015	0.044	0.024	0.029	0.022		0.032		0.012	0.020
TRIS + HCl + KCl	0.10	3					0.008	0.003									
	0.10	9-10	0	0		0	0.007	0.003		0.007	0.012		0				
	0.05	3		0.007			0.019	0.012									
	0.05	9-10	0.012	0		0.003	0.007	0.003		0.003	0.020		0.030				
	0.01	3		0			0.008	0									
	0.1	9-10	0.022	0.003		0.029	0.014	0.007		0.017	0.039		0.059				
TRIS + HCl + Me$_4$NCl	0.10	13-14	0.002	0		0.002	0.008	0		0.002	0.012		0				
	0.05	13-14	0.008	0		0.003	0.007	0		0.005	0.014		0.002				
	0.01	13-14	0.020	0.002		0.025	0.024	0.007		0.022	0.029		0.014				
Borax + KCl	0.05	2		0.005			0.007	0									
	0.01	2		0.003			0.005	0.005									
	0.01	36-39	0.002	0.005	0.003	0.037	0.019	0	0.037	0.005	0.037	0.025	0.018	0.024	0.020	0.014	0.015
	0.005	2					0.005	0.005		0.005							

Recorded errors are final error values, ΔE_f and as cell emfs were generally stable following any initial transient are usually identical to either extrapolated error values ΔE_e ignoring feature A or initial error values ΔE_i. Examples of emf drift are rare, but when observed the linear change could reasonably be extrapolated to the instant of transfer. Errors reported for stepwise transfers are for transfer from acid to buffer solution, with the exception of runs 36-39, where the results for 0.01m borax are based on transfers from that buffer solution into acid. Errors observed on the reverse electrode transfer from buffer to acid are of equal magnitude and opposite sign, and above about pH 4 generally have a more rapid initial transient. Examination of the results presented in Tables 5.8 and 5.9 shows that within the experimental error of ± 0.1 mV or 0.002 pH, glass electrode potentials are error free in the tetroxalate and glycine buffer solutions used. The errors shown by the soda based EIL GG electrode 23 in the glycine buffer solutions are anomalous and the overall performance of this particular electrode will be discussed later.

Above about 2.5 pH, small but significant positive errors are apparent with all glass electrodes tested. The errors are independent of both pH and total ionic strength of the buffer solutions, but are a function of the buffer composition and its molality, increasing markedly with decreasing buffer strength. The magnitude of the error of a particular electrode can be attributed to both the membrane glass composition and its past use. Perley[110] observed that pH measurements in poorly buffered solutions are inconsistent and Schwabe[111] demonstrated that variations apparent in static solutions, could be avoided with a flowing sample. He regarded the effect as due to leaching of alkali from the glass electrode surface. To test this idea, a magnetic stirrer was introduced into cells of the weakest phosphate buffer solution, but no change of glass electrode potential was noted. As the errors were independent of total ionic strength they may be deduced to be independent of the nature of the cation, and this was confirmed in the TRIS buffer series experiments where potassium chloride additions were replaced with tetramethyl ammonium chloride. Similar errors were shown with all electrodes except the Jena N electrode, 24 which exhibited a slight response to potassium ion at pH 8.2. The alkali cation response of this electrode is also apparent in the 0.01m borax buffer solution containing 0.1m potassium chloride.

Using radiotracer techniques, Schwabe *et al.*[31] demonstrated that whilst chloride ions are absorbed into the surface layers of the glass electrode from hydrochloric acid solutions, sulphate ions from sulphuric acid solutions are not. To ascertain whether or not the errors observed could be ascribed to carryover of absorbed hydrochloric acid by leaching into the buffer solutions, which effect would be greater the lower the buffer molality, transfer runs 17 and 18 were made from 0.1m sulphuric acid into a series of equimolal phosphate buffer solutions containing 0.1m potassium chloride. The results are included in Tables 5.10 and 5.11 and comparison with those obtained in similar buffer solutions on transfers from 0.1m hydrochloric acid recorded in Tables 5.8 and 5.9 indicate that this effect, whilst not accounting for the errors noted, may contribute in part at the lowest buffer molalities.

To test the possibility that the errors could perhaps be due to the presence of chloride in the buffer solutions, transfers were made from 0.1m sulphuric acid into a series of chloride-free phthalate and equimolal phosphate buffers, and solutions of the same buffers containing 0.1m potassium perchlorate. A new EIL GG electrode 28, that had never previously been used was introduced in to these transfer runs. The results are collated in Tables 5.10 and 5.11 and confirm that neither chloride addition nor total ionic strength affected electrode response.

On completion of the stepwise transfer runs from 0.1m hydrochloric acid into the buffer solutions containing 0.1m chloride, all the glass electrodes tested were consecutively transferred from 0.1m hydrochloric acid through a series of NIST standard buffer solutions of increasing pH containing 0.1m potassium chloride and returned from the final buffer solution to the acid. The buffers selected were 0.05m potassium tetroxalate, 0.05m potassium hydrogen phthalate, 0.025m equimolal phosphates and 0.01m borax. Results of the time-emf response are tabulated in Appendix B, and are summarized in Table 5.12. As Caudle[3] has reported, the individual electrode errors of the buffer series proved to be substantially additive. The electromotive efficiencies, α, and practical slopes, k_g, of the electrodes (see Chapter 2, section 2.6.2) exhibited in these transfer runs are presented in Table 5.13. Those for the lithia-based electrodes are marginally higher than the values reported for comparable electrode transfers by Baucke[61] for cells with liquid-junctions, which

Table 5.10
Transfer from 0.1m H_2SO_4 into Buffer Solutions with and without Added Salt

Buffer Solution	Buffer Molality	Added Salt	Salt Molality	Run	Error, mV						
					Electrode Number						
					1	3	19	22	23	28	24
K H Phthalate	0.1000			42		0			0	0	
	0.0500			42		0			0	0	
	0.0100			42		0			0.1	0.1	
	0.0100			44		0			0.3	0	
	0.0100	KCl	0.1000	44		0			0.3	0	
	0.0100	$KClO_4$	0.1000	44		0			0	0.1	
1:1 Phosphates	0.0500	KCl	0.1000	17-18	0.2	0.2	0.3	0.1	0.3		1.4
	0.0250	KCl	0.1000	17-18	0.4	0.3	0.4	0.3	0.3		1.4
	0.0125	KCl	0.1000	17-18	0.3	0.3	0.3	0.3	0.5		1.3
	0.0025	KCl	0.1000	17-18	1.2	0.8	0.6	1.2			
	0.0500			41		0.3				0.1	
	0.0250			43		0			0.2	0.2	
	0.0250			45		0			0.1	0.3	
	0.0025			45		0.8			0.5	0.7	
	0.0025	KCl	0.1000	45		0.8			0.8	0.6	
	0.0025	$KClO_4$	0.1000	45		0.6			0.9	0.4	

Table 5.11
Transfer from 0.1m H_2SO_4 into Buffer Solutions with and without Added Salt

Buffer Solution	Buffer Molality	Added Salt	Salt Molality	Run	Error, ΔpH						
					Electrode Number						
					1	3	19	22	23	28	24
K H Phthalate	0.1000			42		0			0	0	
	0.0500			42		0			0	0	
	0.0100			42		0			0.002	0.002	
	0.0100			44		0			0.005	0	
	0.0100	KCl	0.1000	44		0			0.005	0	
	0.0100	$KClO_4$	0.1000	44		0			0	0.002	
1:1 Phosphates	0.0500	KCl	0.1000	17-18	0.003	0.003	0.005	0.002	0.005		0.024
	0.0250	KCl	0.1000	17-18	0.007	0.005	0.007	0.005	0.005		0.024
	0.0125	KCl	0.1000	17-18	0.005	0.005	0.005	0.005	0.008		0.022
	0.0025	KCl	0.1000	17-18	0.020	0.014	0.010	0.020			
	0.0500			41		0.005				0.002	
	0.0250			43		0			0.003	0.003	
	0.0250			45		0			0.002	0.005	
	0.0025			45		0.014			0.008	0.012	
	0.0025	KCl	0.1000	45		0.014			0.014	0.010	
	0.0025	$KClO_4$	0.1000	45		0.010			0.015	0.007	

Table 5.12
Consecutive Transfer of Glass Electrodes from 0.1m HCl through a Series of Buffer Solutions
Errors in mV

Buffer Solution		0.05m K tetrox. + 0.1m KCl (1)	0.05m KH phth.+ 0.1m KCl (2)	0.025m 1:1 phosphates + 0.1m KCl (3)	0.01m borax + 0.1m KCl (4)	0.1m HCl (5)	Sum (1+2+3 +4-5)
No.	Run pa_H	1.680	3.930	6.777	9.127	1.088	-
1	36	0	-	0	1.2	- 1.3	- 0.1
3	36	0	0.2	0.2	0.1	- 0.3	0.2
25	38	0	0.4	0.1	0.3	- 0.2	0.6
4	36	0	-	0.2	1.0	- 2.2	-
6	39	0	0.4	- 0.1	0.7	- 1.1	- 0.1
19	37	- 0.1	0.2	0.1	0	0	0.2
26	38	- 0.1	0.5	0.5	1.0	- 2.2	- 0.3
22	37	0	0.3	0.1	0.3	- 0.3	0.4
23	38	0	0.4	0.1	1.5	- 2.2	- 0.2
27	38	0	0.2	0.1	1.0	- 1.5	- 0.2
24	39	- 0.1	0.1	0.4	5.7	- 7.0	- 0.9
29	38	0	0.3	0.3	0.6	- 1.4	- 0.2
30	38	0	0	-	0	- 1.2	
31	38	0	0.2	0.1	0.6	- 0.8	0.1
32	38	- 0.1	0.4	0	0.6	- 0.9	0

Table 5.13

Electromotive Efficiencies, α, and Practical Slopes, k_{μ}, for Glass Electrodes Transferred through a Series of Buffer Solutions into 0.1m HCl (Runs 36-39).

Buffer Solution	0.05 m KH phth. + 0.1 m KCl	0.025 m 1:1 phosphates + 0.1 m KCl	0.01 m borax + 0.1 m KCl	0.1 m HCl
pa_H	3.930 into 6.777 into 9.127 into 1.088			
No.		α	α	α
1		1.0000	0.9914	0.9973
3		0.9988	0.9993	0.9994
25		0.9994	0.9978	0.9996
4		0.9988	0.9928	0.9954
6		-	0.9950	0.9977
19		0.9988	1.0000	1.0000
26		0.9970	0.9928	0.9996
22		0.9988	0.9978	0.9994
23 (soda)		0.9988	0.9892	0.9954
27 (soda)		0.9988	0.9928	0.9968
24 (soda)		0.9976	-	-
29		0.9982	0.9957	0.9971
30		-	1.0000	0.9975
31		0.9988	0.9957	0.9983
32		1.0000	0.9957	0.9981
$\bar{\alpha}$		0.9988	0.9954	0.9980
$\bar{k}_{\mu}$, mV		59.09	58.89	59.04
$\bar{\alpha}$ (lithia electrodes)		0.9989	0.9966	0.9984
$\bar{k}_{\mu}$, mV (lithia electrodes)		59.09	58.96	59.07
$\bar{\alpha}$ overall, lithia electrodes.	0.9980			
$\bar{k}_{\mu}$, mV, lithia electrodes.	59.04			

Table 5.14

Electromotive Efficiencies, α, and Practical Slopes, k_{μ}, for Schott N1120 Glass Electrodes Transferred Between NIST Buffer Solutions (Baucke's Results, Ref. 61).

Buffer Solution	0.05 KH_2 citrate	0.025 m 1:1 phosphates	0.025 m 1:1 carbonates	0.05 m KH_2 citrate
pH	3.776 into 6.865 into 10.012 from 3.776			
N1120, No.		α	α	α
1		0.9986	0.9967	0.9976
2		0.9978	0.9975	0.9976
3		0.9976	0.9969	0.9972
$\bar{\alpha}$		0.9980	0.9971	0.9975
$\bar{k}_{\mu}$, mV		59.04	58.99	59.02
$\bar{\alpha}$ overall	0.9976			
	59.02			

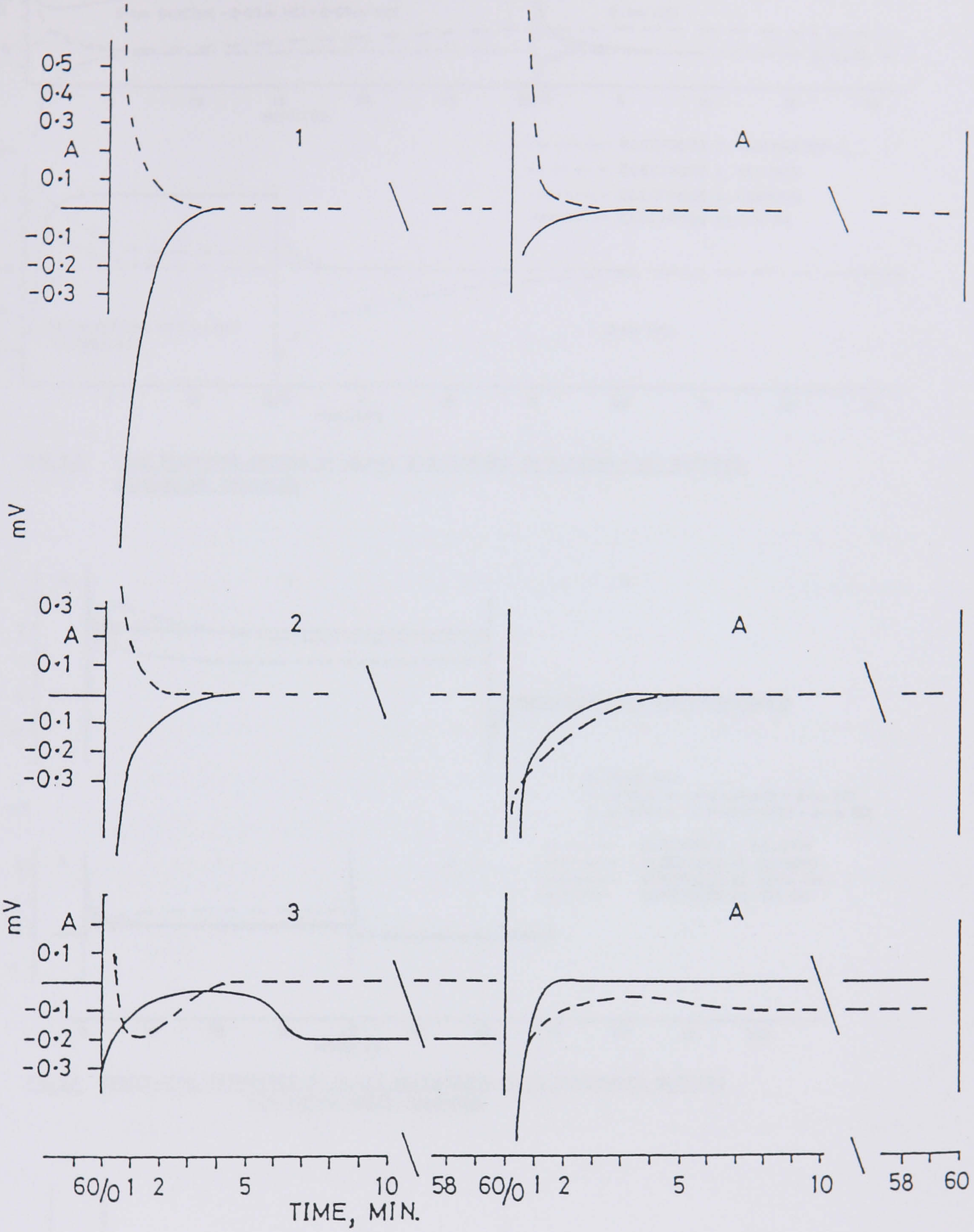
are collected in Table 5.14. As with Baucke's data, electromotive efficiencies, for all electrodes examined, are lowest in the neutral pH phosphate buffer solutions.

Electrode 23, an EIL GG electrode that had been in use for some three years, initially exhibited comparatively large errors in all buffer solutions tested with the exception of the tetroxalate buffer. Its performance in both phthalate and phosphate buffers improved markedly after prolonged storage in distilled water, presenting reduced errors similar to those of newly introduced electrodes of the same type 27 and 28. Manov and others[112] have reported that old or mishandled Corning 015 composition glass electrodes exhibit errors of 3.5 mV or 0.06 pH, in 0.05m borax buffer solutions, a rather larger error than those exhibited in this work by the EIL GG electrode 23 of the same glass formulation.

The Corning Triple Purpose electrode 26 displayed much larger errors in the phosphate and higher pH buffers than the older electrodes of the same type, 6 and 19. It is probable that it had suffered from extended storage and the surface had been earlier hydrated by condensation. The performance of the Radiometer C electrode 3 was virtually identical to that of the similar new electrode, 25.

Jena-Sargent electrodes 29 and 32 that had previously been used within the NBS laboratories[100] were conditioned by immersion for a week in distilled water. On use in buffer solutions they were found to be extremely sluggish, with indeterminate drifting over five hours. They were rejuvenated[113] by soaking in 1M sodium hydroxide solution for half an hour followed by overnight storage in 0.1M hydrochloric acid. The process was repeated three times. The electrodes were then stored in distilled water for a week prior to use. The rejuvenation process was successful, removing the outer exhausted or dehydrated surface layer, and generating a new, conditioned surface. It is, perhaps, interesting to note that Covington had found these electrodes satisfactory, but that later, Paabo regarded them as being rather sluggish[114]. It would appear that they were exhibiting relatively rapid-response deterioration.

Stable potentials were generally established by the glass electrodes within three to five



A. 0·1m HCl
1. 0·1m K TETROXALATE + 0·1m KCl
2. 0·05m " + 0·1m KCl
3. 0·01m " + 0·1m KCl

SOLID LINE ——— ELECTRODE 19, CORNING
DASHED LINE - - - ELECTRODE 3, RADIOMETER C

FIG 5.2 ERROR—TIME RESPONSE OF ELECTRODES 3 AND 19 IN TETROXALATE BUFFERS CONTAINING CHLORIDE.

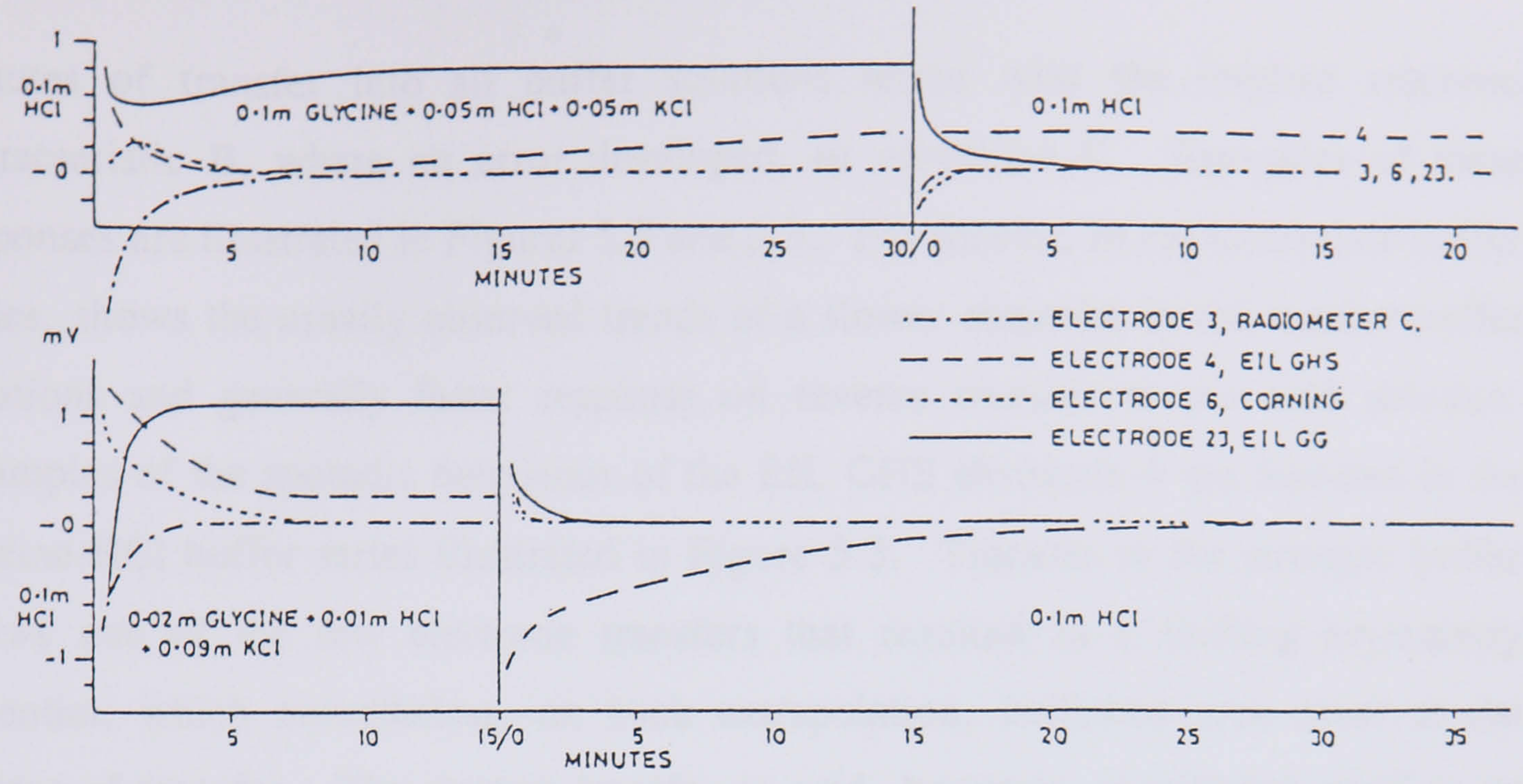


FIG 5.3. TIME RESPONSE ERRORS OF GLASS ELECTRODES IN GLYCINE – HCl BUFFERS CONTAINING CHLORIDE.

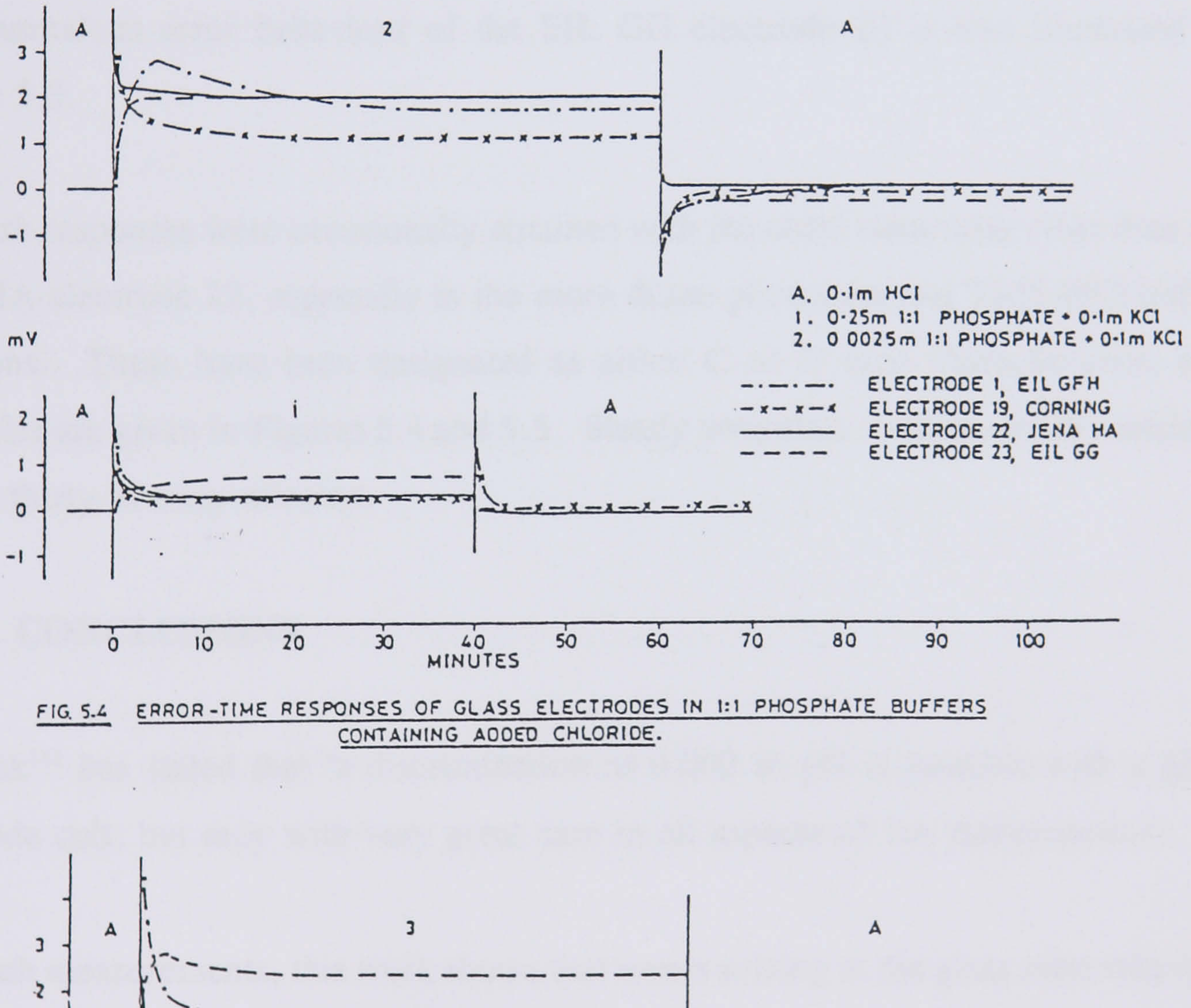


FIG. 5.4 ERROR-TIME RESPONSES OF GLASS ELECTRODES IN 1:1 PHOSPHATE BUFFERS CONTAINING ADDED CHLORIDE.

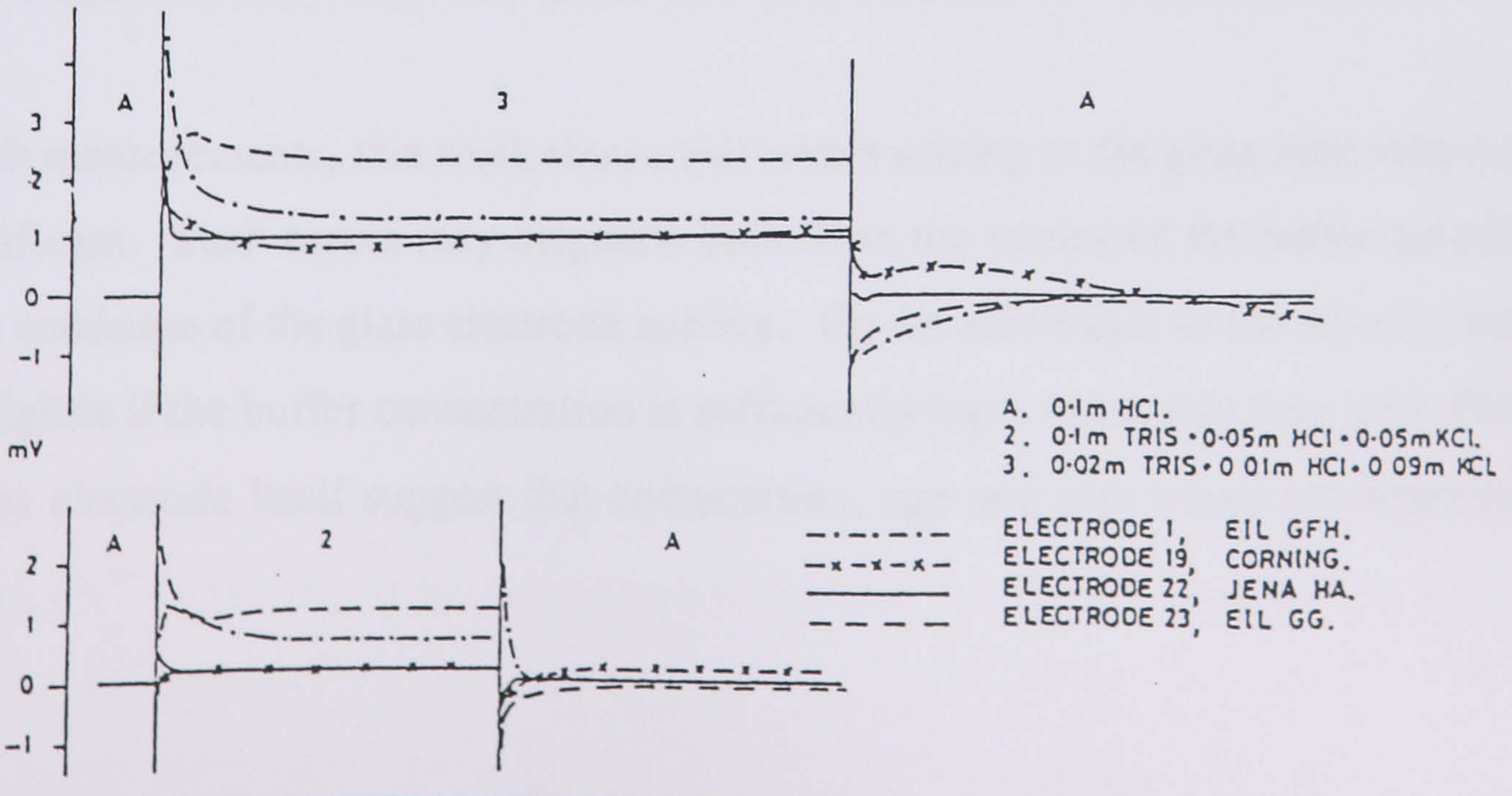


FIG. 5.5 ERROR-TIME RESPONSES OF GLASS ELECTRODES IN TRIS-HCl BUFFERS CONTAINING ADDED CHLORIDE.

minutes of transfer into all buffer solutions tested with the implied response characteristic B, where no error developed, or otherwise E. Examples of these responses are illustrated in Figures 5.2 and 5.3. The former, in the tetroxalate buffer series, shows the usually observed trends of a slower response in the weaker buffer solutions and generally faster response on reverse transfer to the acid solution. Examples of the sporadic behaviour of the EIL GHS electrode 4 are featured in the glycine-HCl buffer series illustrated in Figure 5.3. Transfer to the stronger buffer shows one of the few electrode transfers that resulted in a drifting asymmetry potential, which nevertheless, on back extrapolation, indicated zero error at the instant of transfer. The reverse transfer to acid, however, manifested itself as an error-free B response with no initial A transient. A subsequent similar transfer from a more dilute glycine-HCl buffer exhibited a very sluggish decay to a steady potential. The anomalous error behaviour of the EIL GG electrode 23 is also illustrated in Figure 5.3.

Sluggish responses were occasionally obtained with the older electrodes other than the Jena HA electrode 22, especially in the more dilute phosphate and TRIS-HCl buffer solutions. These have been designated as either C or D type characteristics, and examples are given in Figures 5.4 and 5.5. Steady potentials were invariably attained within thirty to sixty minutes.

5.4 CONCLUSIONS

Mattock[115] has stated that 'a discrimination to 0.002 in pH is possible with a glass electrode cell, but only with very great care in all aspects of the measurement'.

For such measurements, this work shows that errors arising at the glass electrode may be significant. Such errors may originate both from the nature of the buffer solution and the condition of the glass electrode surface. Errors ascribable to the solution may be negligible if the buffer concentration is sufficiently high, those that may arise from the glass electrode itself suggest that composition, age and past usage are important factors.

Baucke[61] has proposed that the hydrogen-ion response of pH glass electrodes is sub-Nernstian and independent of glass composition. Whilst those results for electrode electromotive efficiences in comparable buffer solutions of this present work are in qualitative agreement with his data obtained in NIST buffer solutions, the totality of the results do not substantiate his argument.

The individual buffer concentrations selected for the NIST pH scale are a compromise to permit the adoption of an acceptable dilute solution convention to calculate the value of the single ion activity coefficient of the chloride ion in order to assign a pH(s) value to a primary or secondary pH standard buffer to three decimal places. If the concentration of the buffer were too low, its buffer properties would be poor, if too high, a simple means for the calculation of a single ion activity is not available. The results imply that above pH 4 the concentration of the NIST primary buffers are too low for precise measurements with glass electrodes. The magnitude of the errors observed may be significant in measurements where high precision is necessary. Of importance are the many routine measurements of the pH of body fluids, in which quite small changes have indicative clinical implications. A further application in which the results noted in this study could result in erroneous values is in the electrometric determination of the dissociation constants of acids and bases, which are essentially pH measurements at high discrimination in Harned cells.

The technique adopted in this study suggests a method by which the performance of glass electrodes may be ascertained in cells without either liquid junctions or hydrogen-gas electrodes. The emf difference between any two solutions in Table 5.5 is the theoretical emf change for an ideal glass electrode transferred between the two chloride containing solutions, each with a silver, silver chloride reference electrode. If the electrode may be regarded as being error-free in one of these solutions, any deviation from the theoretical emf difference in the other is an error of the glass electrode in that solution. Obviously from the results obtained, only the higher concentration buffers should be used. Covington and co-workers[116,117] have described such a procedure using this approach with a range of amine-HCl buffer solutions for the range 0-14 pH that has been adopted as the test procedure for the British Standard for Glass Electrodes[118].

CHAPTER SIX

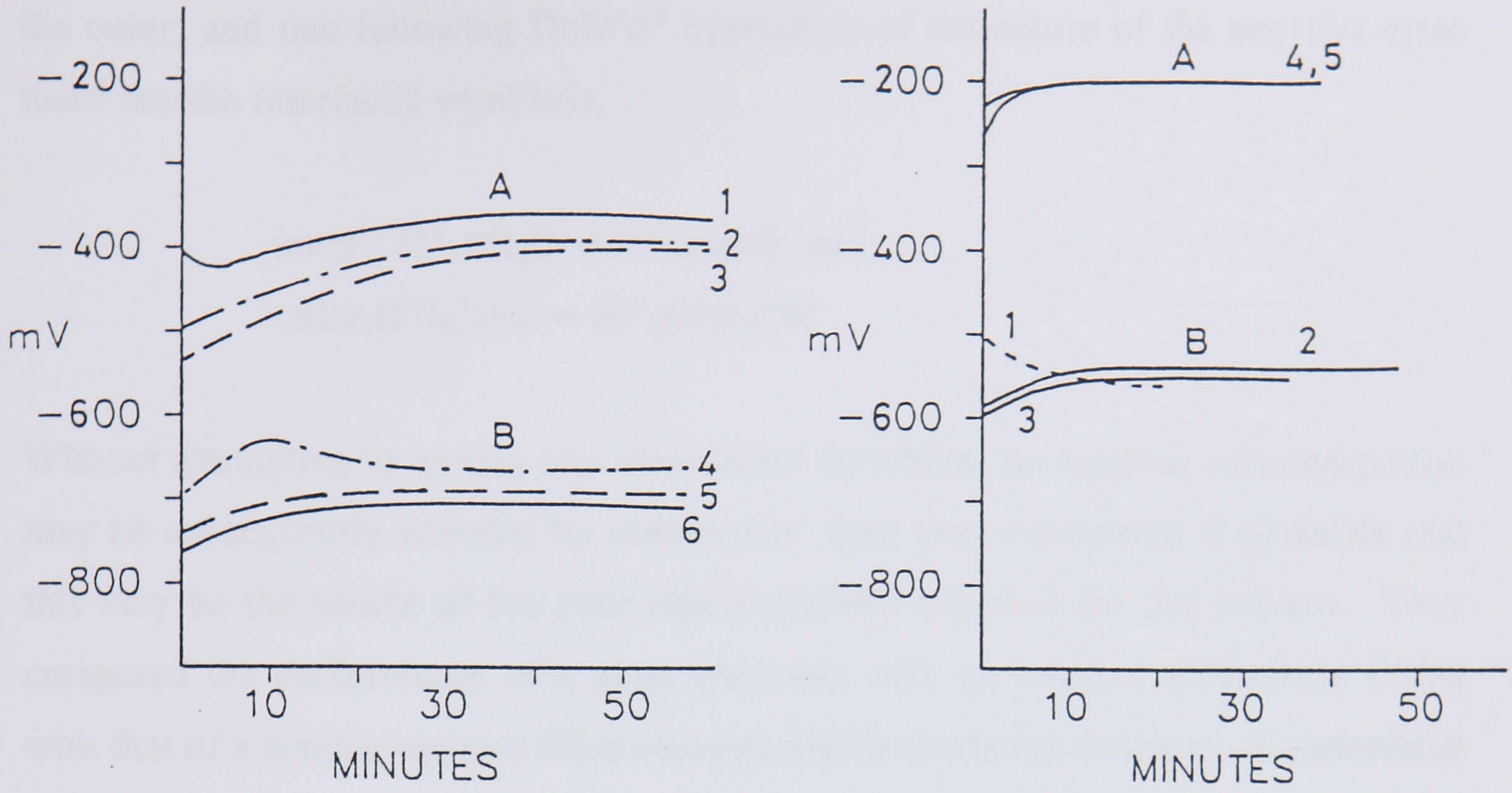
THE EFFECT OF THE NATURE OF THE SOLVENT OF THE INNER REFERENCE SYSTEM ON THE RESPONSE CHARACTERISTICS OF THE pH GLASS ELECTRODE IN AQUEOUS AND NON-AQUEOUS BUFFER SOLUTIONS

6.1 INTRODUCTION

The hypothesis of Dole[7] that the potentials at the inner and outer glass-solution interfaces are developed independently, though founded on a rather questionable experiment, has long been accepted. On the basis of this supposition, the nature of the internal construction is immaterial to the electrode function. Thus, other than providing a stable or only slowly varying potential, the criteria[119] for the selection of a particular internal filling solution and reference electrode have been regarded as the selection of the zero-point with some stated reference half-cell. Their resultant temperature coefficient allows pH cell temperature compensation with pH meters, employing the isopotential pH concept of Jackson[120]. The temperature variation of pH cells has recently been extensively reviewed by Midgley[121].

That such fillings are invariably aqueous is hardly surprising, as glass electrodes, admittedly with aqueous fillings have long been considered to be subject to negative errors and drifting potentials in partially and non-aqueous solvent media[122]. There is substantial evidence that the presence of a certain amount of water is necessary to develop and maintain the hydrogen-ion function of the glass membrane and that the response of the electrode degenerates as the membrane is dehydrated or used in non-aqueous media[123]. Although these characteristics are unsuitable for direct potentiometry, glass electrodes have been widely used for titrimetry in a wide range of organic solvent media. Drifting potentials and degraded response do not necessarily preclude distinct potential jumps with resultant clear end-points. Potential drifts reported can be high, for example, in DMF (*N,N*-dimethylformamide) solutions, Deal and Wyld[124] regarded stability after an aliquot of titrant as a drift of no greater than 4 mV per minute. In sulpholane, equilibrium took some 30-40 minutes to be established after titrant addition, and potentials exhibited negative errors in solutions of strong acids, features that Coetzee and Bertozzi[125] ascribed to dehydration. Haphazard potentials and indeterminate end-points were apparent in butanol[123] and benzene-propanol[126] media unless a small amount of water was present, and drifting potentials have been reported in 95% methanol-water mixtures[127].

The poor reproducibility of glass electrode potentials in acetonitrile solutions led



AQUEOUS FILLED ELECTRODES. ACETONITRILE FILLED ELECTRODES.

FIG. 6.1 TIME-EMF RESPONSE OF GLASS ELECTRODES IN ACETONITRILE SOLUTIONS OF PYRIDINE (A) AND DIPHENYLGUANIDINE (B)-PICRIC ACID BUFFERS. (FROM REF. 6)

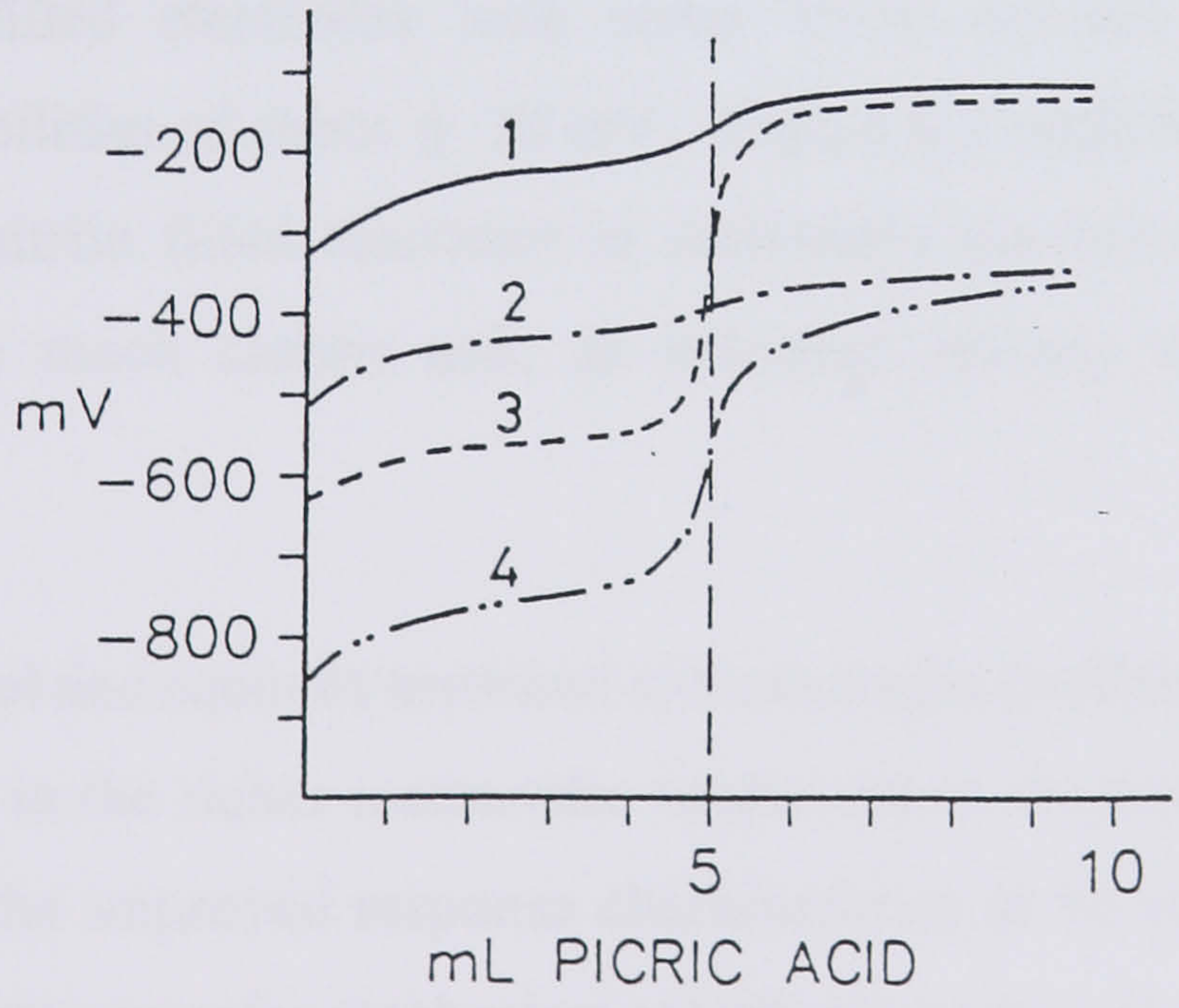


FIG. 6.2 ACID-BASE TITRATIONS IN ACETONITRILE SOLUTIONS WITH ACETONITRILE (1, 3.) AND AQUEOUS (2, 4.) FILLED GLASS ELECTRODES. (FROM REF. 6.)

Badoz-Lambling[6] to consider that the glass membrane separates two different solvent media, an aqueous solution at the inner glass surface and an acetonitrile solution at the outer, and that following Dole's[26] hypothesis of the nature of the negative error there are the interfacial equilibria,

$$\text{inner, } H^+,nH_2O \rightharpoonup H^+(\text{glass}), \text{ and}$$
$$\text{outer,} H^+(\text{glass}) \rightharpoonup H^+,pCH_3CN$$

Without attempting to specify any mechanism by which 'an aqueous solvated proton may be subsequently solvated by acetonitrile' (sic) they considered it plausible that this may be the source of the poor reproducibility reported for this solvent. They compared the performance of a glass electrode with an internal acetonitrile filling with that of a similar aqueous filled commercial electrode for titrations of acetonitrile solutions of pyridine and diphenyl guanidine with picric acid. Contrary to the general practice of storing electrodes in water or aqueous solutions, but following the recommendation of Grunwald[128], the glass electrodes were stored in acetonitrile before and during measurements as this procedure resulted in equilibria being established much more rapidly. Acetonitrile filled electrodes attained equilibria within 5-10 minutes and were reproducible to about 10 mV as shown in Figure 6.1, whereas the aqueous filled electrodes took some 10-30 minutes to equilibrate with poorer reproducibilities of about ± 30 mV. Figure 6.2 depicts the superior performance of the acetonitrile filled electrode in titrimetry; the horizontal portions and potential jumps are much clearer and, as indicated earlier, titrations were effected more rapidly.

In methanol and aqeuous methanol solvent media Douhéret[129] found similar behaviour, especially in the richer methanolic media and at the extremes of the pH* scales. He regarded the improved response characteristics to be the result of a similar solvent-related proton transfer mechanism at both glass-electrolyte interfaces. Very rapid and correct response in hydrazine solutions was reported by Goudeau *et al.*[130] if the internal solvent medium was hydrazine, whereas aqueous filled electrodes displayed both degraded hydrogen-ion function and prolonged equilibration times. Aqueous solution filled glass electrodes conditioned in DMF were found by Tézé and Schaal[90] to possess fast response times in DMF solutions, however, because of significant changing asymmetry potentials they regarded them as useful for general titrimetry, but only with frequent calibration suitable for quantitative direct potentiometry. Ritchie and Megerle[131], however, using glass electrodes with internal DMF fillings obtained stability within 5 minutes of aliquot addition and were able to determine dissociation constants for substituted 4-picolinium ions in good agreement with other data. The performances of aqueous and DMF solvent filled glass electrodes were compared in DMF solutions by Juillard[132]. Steady, ideal and reproducible potentials were attained quite quickly with the DMF filled electrodes, but the aqueous filled ones exhibited limited reversibility and wandering, non-reproducible responses that were much improved with the addition of 2% methanol.

Fast equilibration times in non-aqueous solvent mixtures were also obtained[133] if the filling of the glass electrode was replaced simply by mercury. Ritchie and Uschold[133] used such electrodes to determine the dissociation constants of a number of weak acids in dimethyl sulphoxide, reporting reversible response over some 25 orders of magnitude. Linear, but non-theoretical response of mercury filled electrodes in *N*-methylpyrolidone, glycol and methanol has been described by Bréant and Georges[134] who found some difficulties in using this type of electrode for the determination of acidity constants, but of little significance for general acid-base titrimetry. Mercury-filled electrodes had been earlier used by Thompson[135] in aqueous solutions, but Bates[136] reported that these and other metal-filled electrodes were not particularly satisfactory.

The various studies cited were titrimetric. No examination has been made of the time response characteristics in partially and non-aqueous media similar to those described by Caudle[3] and testing the instantaneous potential concept of Beck and Wynne-Jones[1]. As an initial investigation, this Chapter describes an examination of the potential-time response behaviour in acid and buffer solutions in aqueous and partially aqueous solutions, of glass electrodes with differing internal filling media, conditioning and storage. Partially aqueous, rather than non-aqueous solutions were chosen for this work because of the difficulties in maintaining dryness. Methanol was chosen as it is known from Haugaard's[37] work to be absorbed by, and may perhaps solvate the glass surface. DMF was selected, as being non-hydroxylic, it is unlikely to solvate the glass surface.

6.2 EXPERIMENTAL

6.2.1 Glass Electrodes

Glass electrodes used in this study were prepared from unused commercial blanks, i.e. complete glassware with bulb membranes only, kindly donated by Corning Glassworks, Medfield, Mass., USA, and W.G. Pye and Co. Limited, of Cambridge. Two types of blank were provided by Corning; a yellow glass, that used for their Type 476020 'Triple Purpose' electrode, and a 'white' glass[137]. The Pye blanks were of their 'Combi' glassware, rejected for production use because of dimensional error. Each type of glass blank came from a single production batch, thus ensuring as far as practical, identical composition and history. Corning had cautioned that they had received reports that electrodes of the yellow glass, possibly of specific batches, were sluggish[114]. The bulbs of the Pye blanks were inhomogenous, with obvious striation. Qualitative spectrographic and XRF analyses of the glasses, kindly performed by Miss J. Metcalfe[103], are presented in Table 6.1.

Assembly and mounting of the glass electrodes has been previously described in Chapter 3. Prior to assembling the Pye 'Combi' electrodes, the porous ceramic plugs in the stems were removed and the holes sealed.

Three sets of glass electrodes were prepared with internal fillings pertinent to the three series of transfer experiments.

Table 6.2 details the internal fillings of the Pye and Corning yellow glass electrodes used in transfer experiments between 0.1m hydrochloric acid and a series of aqueous buffer solutions. The electrodes were conditioned and stored in distilled water. Electrode 6 was later used in the aqueous buffer time-response study reported in Chapter 5.

Table 6.1
Qualitative Composition of Electrode Glasses

Glass	Composition
Pye 'Combi'	Li_2O, CaO, BaO, La_2O_3, Cs_2O, CeO_2, SiO_2
Corning 'yellow'	Li_2O, La_2O_3, Ta_2O_5, Cs_2O, UO_2, SiO_2
Corning 'white'	Li_2O, La_2O_3, Dy_2O_3, Ta_2O_5 SiO_2

Table 6.2
Glass Electrodes used in Aqueous Buffer Solutions

No.	Type	Internal construction	(R,MΩ,25°C)
5	Corning yellow	Mercury/Pt contact	-
6	Corning yellow	0.1m HCl, aqueous/Ag,AgCl	170
7	Corning yellow	0.1m HCl, D_2O/Ag,AgCl	110
8	Corning yellow	0.05m HOAc, 0.05m NaOAc, 0.1m NaCl, aqueous/Ag,AgCl	155
9	Corning yellow	0.1m HCl, 60 % ethanol/Ag,AgCl	160
12	Pye 'Combi'	Mercury/Pt contact	-
13	Pye 'Combi'	0.1m HCl, aqueous/Ag, AgCl	260
14	Pye 'Combi'	0.1m HCl, 20% ethanol/Ag, AgCl	105
15	Pye 'Combi'	0.1m HCl, 60% ethanol/Ag, AgCl	-
16	Pye 'Combi'	0.1m HCl, 80% ethanol/Ag, AgCl	-
17	Pye 'Combi'	0.1m HCl, 50% dioxan/Ag, AgCl	110

Table 6.3
Glass Electrodes used in Methanol-Water Solutions

Conditioning Medium	Internal assembly with Ag, AgCl electrodes (R,MΩ,25°C)		
	0.1m HCl, water	0.1m HCl, 50% methanol	0.1m HCl, 95% methanol
Water	C1 (R, 370)	C2 (R, 370)	C3 (R, 360)
50% Methanol	C4 (R, 20)	C5	C6
95% Methanol	C7	C8	C9

Table 6.4
Glass Electrodes used in 95% DMF - Water Solutions

Conditioning Medium	Internal assembly with Ag,AgCl electrodes (R, MΩ,25°C)	
	0.1m HCl, water	0.075m HOAc, 0.02 m KOAc, satd. KCl, 95% DMF
Water	C11, (R, 400)	C12 (R,220)
95% DMF	C13	C14

Corning yellow glass electrodes were used in the transfer experiments in methanol-water solutions. Their internal fillings, conditioning and storage details are given in Table 6.3. These electrodes were first used in the 95% methanol-water solution experiments then stored for four weeks in their respective conditioning media prior to use in the 50% methanol-water solutions.

The Corning 'white' glass electrodes were used in the 95% DMF-water solutions, their details are given in Table 6.4. They were stored in their respective conditioning media for three weeks prior to and between use.

The stems of glass electrodes used in the methanol-water and DMF-water solvent media were not waxed.

6.2.2 Hydrogen and Silver-Silver Chloride Electrodes

As in the glass electrode transfer studies previously described, glass electrode potentials were measured against hydrogen-gas electrodes, and silver-silver chloride electrodes, where practical, used to check cell constancy. The preparation of these electrodes has been described in Chapter 3. Both hydrogen-gas and silver-silver chloride electrodes have been shown to behave reversibly in methanol and methanol-water mixtures containing hydrochloric acid up to 0.1m concentration by e.g. Oiwa[89] and Paabo *et al.*[88], and in acetate buffer solutions by Paabo *et al.*[87], and Bates *et al.*[138].

In the determination of the activity coefficients of sodium chloride in a series of DMF-water mixtures up to 90% DMF with a sodium responsive glass electrode, Lanier[91] used silver-silver chloride electrodes. Discrepancies were apparent in the richer DMF solvents that he ascribed to increasing solubility of silver chloride with increasing DMF content. Equilibration of the electrodes required some hours, even if presaturated with silver chloride. The electrode has been found to have a satisfactory response in hydrochloric acid solutions in DMF below 0.03m by Kumar and Pantony[139] and below 0.05m by Tézé and Schaal[90], but above this concentration the much enhanced solubility of silver chloride, probably due to complex formation, prevents its use. A satisfactory stable reference half-cell was developed for polarographic studies using the electrode[139] in an electrolyte of saturated potassium chloride in 0.8m potassium perchlorate.

No reference was sourced on the use of the hydrogen-gas electrode in DMF-water mixtures. Few problems are reported in the literature regarding its use in DMF solutions. Kumar and Pantony[139] and Tézé and Schaal[90] have shown it to be reversible in hydrochloric acid solutions up to 0.03m and 0.05m respectively, and the latter have also used it in acetate buffer solutions in DMF, although indicating prolonged stabilization times of some hours and recommending replacement after two days use. Ivanovskaya and Shul'ts[35] reported difficulties were experienced in 0.1m hydrochloric acid solutions in DMF over extended periods of time, but did not elaborate on the nature of the problem.

In this work both hydrogen electrode bases and silver, silver chloride electrodes were immersed overnight in solutions in which they were to be used to ensure equilibration.

6.2.3 Solutions

Details of the aqueous buffer solutions used are listed in Table 6.5.

Data for the 95% and 50% methanol-water solutions used are tabulated in Tables 6.6 and 6.7 respectively, and those for the 95% DMF-water mixture solutions in Table 6.8.

Pressure corrected emfs of the cells,

$$\text{Pt, H}_2 \mid \text{solution, Cl}^- \mid \text{AgCl, Ag} \qquad 1$$

were used to calculate the pa_H of the aqueous solutions and $pa_H{}^*$ of the

Table 6.5
Data on Aqueous Buffer Solutions

Buffer	Buffer molality moles kg^{-1}	Added KCl moles kg^{-1}	Ionic strength	E† mV	$pa_H\gamma_{Cl}$	$-\log\gamma_{Cl}$	pa_H
Hydrochloric acid	0.1000	0	0.1000	352.3	1.117	0.109	1.088
Potassium hydrogen tartrate	saturated	0.1000	0.134	496.8	3.640	0.121	3.519
Disodium hydrogen phosphate - Potassium dihydrogen phosphate (equimolal)	0.0250	0.1000	0.150	690.1	6.907	0.125	6.782
Borax	0.0100	0.1000	0.120	827.3	9.226	0.116	9.110
Calcium hydroxide	saturated	0.1000	0.149	1026.4	12.592	0.125	12.467

† emf of cell, Pt, H_2 | Solution X, Cl^- | AgCl, Ag

Table 6.6
Data for 95 wt % Methanol-Water Acid and Buffer Solutions

Buffer	Buffer molality moles kg^{-1}	Added KCl moles kg^{-1}	Ionic strength	E† mV	$pa_H\gamma_{Cl}$	$-\log\gamma_{Cl}$	pa_H*
a_1 Hydrochloric acid	0.0150	-	0.0100	331.4	2.249	0.126	2.123
a_2 Hydrochloric acid	0.1000	-	0.1000	230.5	1.544	0.292	1.252
b_1 Acetic acid - sodium acetate	0.0490 0.0490	0.0500	0.0990	624.5	7.903	0.292	7.611
b_2 Acetic acid - sodium acetate	0.0300 0.0300	0.0500	0.0800	624.4	7.901	0.273	7.628
b_3 Acetic acid - sodium acetate	0.0150 0.0150	0.0500	0.0650	624.4	7.901	0.255	7.646
b_4 Acetic acid - sodium acetate	0.0050 0.0050	0.0500	0.0550	624.3	7.900	0.241	7.659

† emf of cell, Pt, H_2 | Solution X, Cl^- | AgCl, Ag

Table 6.7
Data for 50 wt % Methanol-Water Acid and Buffer Solutions

Buffer	Buffer molality moles kg^{-1}	Added KCl moles kg^{-1}	Ionic strength	E† mV	$pa_H\gamma_{Cl}$	$-\log \gamma_{Cl}$	$pa_H{}^*$
a_1 Hydrochloric acid	0.0100	-	0.0100	436.1	2.150	0.069	2.081
a_2 Hydrochloric acid	0.1000	-	0.1000	327.7	1.317	0.165	1.152
b_1 Acetic acid - sodium acetate	0.0500 0.0500	0.0500	0.1000	603.4	5.677	0.165	5.512
b_2 Acetic acid - sodium acetate	0.0150 0.0150	0.0500	0.0650	603.0	5.670	0.143	5.527

† emf of cell, Pt, H_2 | Solution X, Cl^- | AgCl, Ag

Table 6.8
Data for 95wt % DMF-Water and Aqueous Solutions

Solution		Molality moles kg^{-1}	KCl moles kg^{-1}	Ionic strength	E† mV
a1w	Hydrochloric acid	0.0100	-	0.0100	464.3
a2w	Hydrochloric acid	0.1000	-	0.1000	352.3
a1	Hydrochloric acid	0.0095	-	-	-
a2	Hydrochloric acid	0.0950	-	-	-
b1	Acetic acid + potassium acetate	0.0075 0.0020	saturated (*ca.* 0.02)	-	815.5
b2	Acetic acid + potassium acetate	0.0750 0.0200	saturated (*ca.* 0.02)	-	790.3

† emf of cell, Pt, H_2 | Solution X, Cl^- | AgCl, Ag

methanol-water mixture solutions as discussed in Chapter 4. For the 50% methanol-water mixtures, data for vapour pressure, density, ion-size parameter, dielectric constant and the solvent standard electrode potential are those used by Paabo *et al.*[88]. Analogous values for the 95% methanol-water mixture solutions were interpolated from Oiwa's[89] collations. Little information is available for 95% DMF-water mixtures, consequently only pressure corrected emfs are tabulated. Vapour pressure was interpolated assuming Raoult's Law from those for DMF[140] and water[141]. The data are collected in table 6.9.

6.3 RESULTS AND DISCUSSION

The three series of transfer experiments are conveniently considered separately. For clarity, the emf-time results are illustrated graphically, and the transfer details tabulated.

6.3.1 Transfers in Aqueous Buffer Solutions

All electrodes were subjected to the same sequence of consecutive transfers from 0.1m hydrochloric acid through a series of standard buffer solutions of increasing pH each containing 0.1m potassium chloride and finally returned to 0.1m hydrochloric acid.

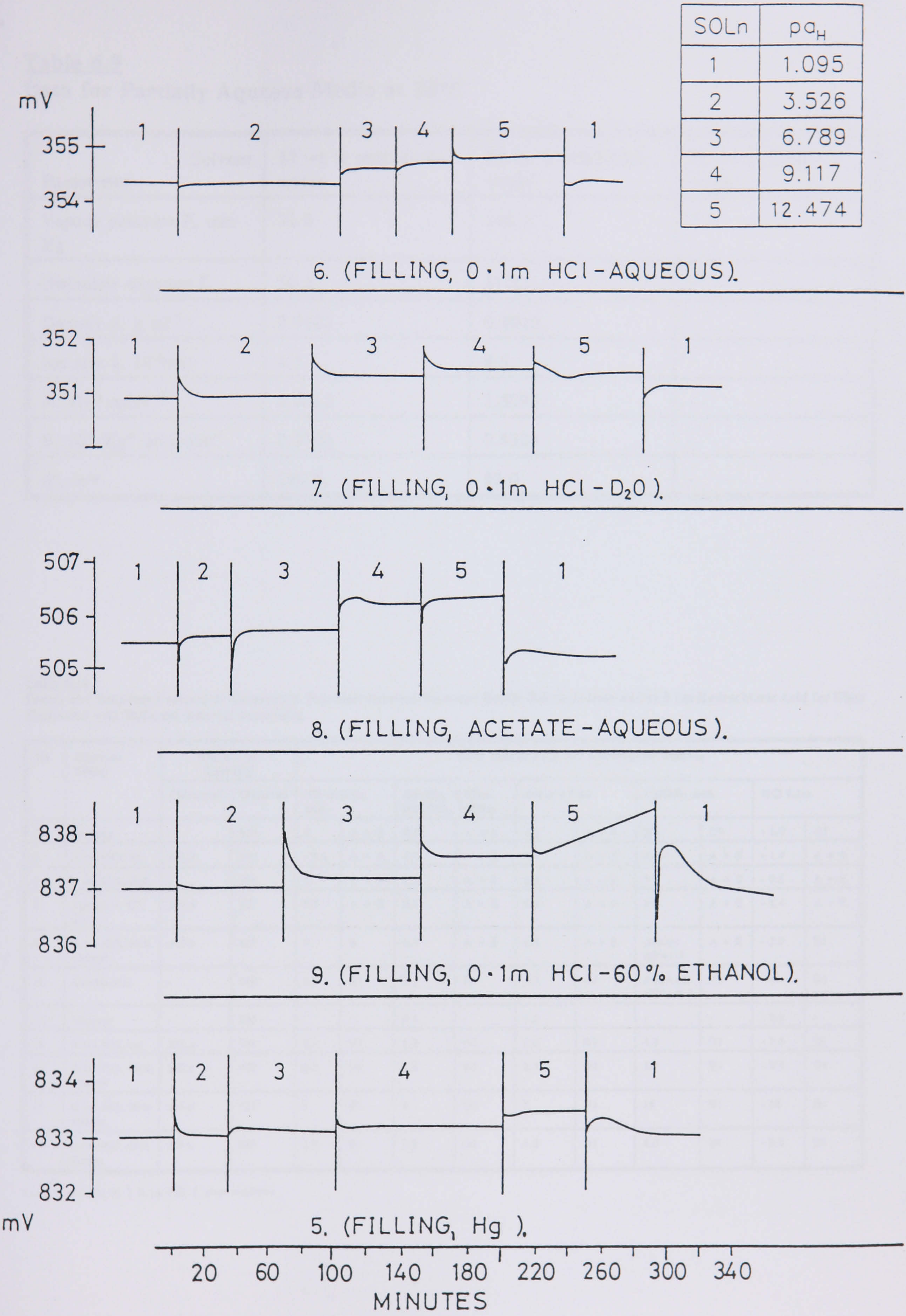
Inspection of the error potential-time plots of the Corning electrodes in Figure 6.3 shows very similar performance for electrodes 5 to 9. Transient A is commonly exhibited, dissipating to the characteristic B or E type response, occasionally examples of a type D_2 transient response are displayed.

Mercury and aqueous filled electrodes 5 and 6 establish stable potentials within about three minutes, rather more rapidly than the deuterium oxide and aqueous acetate filled electrodes C7 and C8. The response of the 60% ethanol-water mixture filled electrode 9 differs from those only on transfer to the calcium hydroxide buffer solution at about pH 12.47 in which a positive linear drift to higher pH of 1.5 mV/h is established. Back extrapolation to the instant of transfer, however, suggests initial zero error. Subsequent transfer to 0.1m hydrochloric acid results in a sluggish, drifting, type D_2 response.

A new commercial Corning electrode 10 of the same type, believed to have an internal aqueous phosphate buffer filling containing added chloride, that had been similarly conditioned in deionized water to the 'home-made' varieties, was introduced for comparison. Surprisingly, this electrode's performance was undoubtedly the poorest of the Corning electrodes tested. All transfers exhibited sluggish D_1 type responses with stable potentials being established only after some 30 minutes in solutions of intermediate pH. In the calcium hydroxide buffer solution, however, a negative drift of 2 mV per hour was established.

Electrode 6 was later widely used throughout the more extensive transfer study described in Chapter 5. Its performance in this series of experiments was very similar to its behaviour and that of the commercial Corning electrode of the same membrane type 19, in that study, and much better than the similar electrode 26 newly introduced towards the end of that work. Whilst all the transfers of electrodes 5-9 exhibited some, often rapid initial transient, steady potentials were developed with varying degrees of reasonable rapidity that could be back extrapolated to the instant of transfer. As the majority of transfers resulted in steady readings, the extrapolated error ΔE_e was identical to the final error of ΔE_f. Such errors were small, the largest between solutions being into the mixed phosphate buffer solution, behaviour that was generally observed in this buffer for all types of glass electrode used in the study described in Chapter 5.

As previously mentioned, the behaviour of the commercial electrode 10 was markedly different to that of the 'home-made' electrodes in having a very sluggish response, and exhibiting much greater errors in all solution transfers. Corning Glassworks had received reports from users that glass electrodes of this type were regarded as sluggish. It is probable that the source of



SOLn	pa_H
1	1.095
2	3.526
3	6.789
4	9.117
5	12.474

6. (FILLING, 0·1m HCl-AQUEOUS).

7. (FILLING, 0·1m HCl-D_2O).

8. (FILLING, ACETATE-AQUEOUS).

9. (FILLING, 0·1m HCl-60% ETHANOL).

5. (FILLING, Hg).

FIG. 6.3 RESPONSE OF CORNING ELECTRODES IN AQUEOUS BUFFER SOLUTIONS.

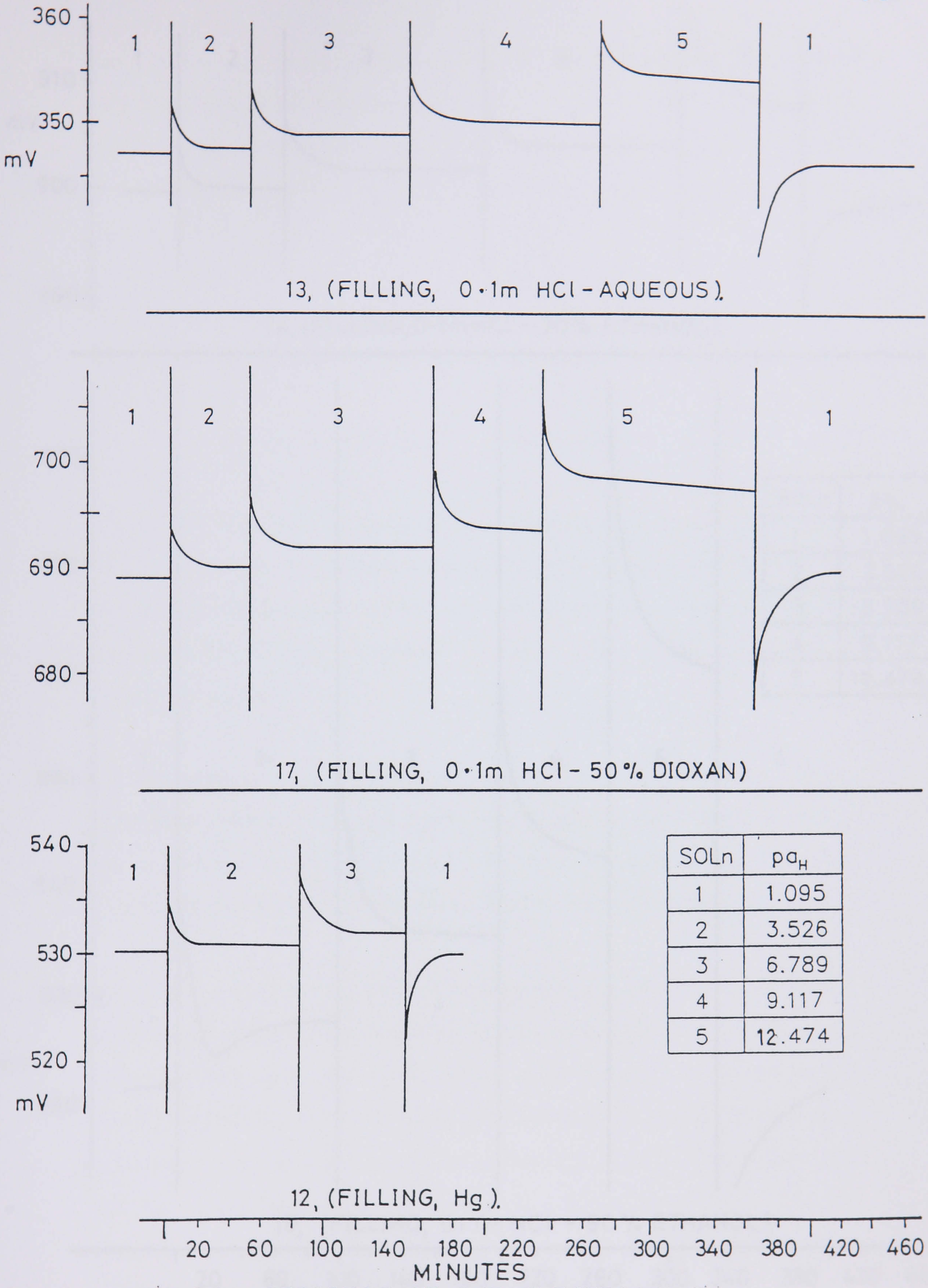
Table 6.9
Data for Partially Aqueous Media at 25 °C

Solvent Parameter	50 wt % methanol-water	95 wt % methanol-water	95 wt % DMF-water
Vapour pressure P, mm Hg	71.8	118.5	7.5
Dielectric constant Σ	56.3	35.35	-
Density d, g ml^{-1}	0.9125	0.8010	-
Ion size å, 10^{-8}cm	4.3	4.5	-
A, Kg$^{1/2}$ mole$^{-1/2}$	0.8015	1.5095	-
B, 10^{-8} Kg$^{1/2}$ mole cm^{-1}	0.3708	0.4384	-
E°, mV	190.6	80.0	-

Table 6.10
Errors and Response Features of Consecutive Transfers between Standard Buffer Solutions from and to 0.1m Hydrochloric Acid for Glass Electrodes with Different Internal Assemblies

No.	Electrode Filling	Emf,mV in 0.1m HCl		Error (ΔEf or ΔEe), mV and Response Features									
		Calculated	Observed	KH tartrate, satd.		KH_2PO_4, 0.025m Na_2HPO_4, 0.025m		Borax 0.01m		$Ca(OH)_2$ satd.		HCl 0.1m	
5	Mercury	-	835	0	A + B	0.2	A + B	0.2	A + B	0.2	D2	- 1.0	D2
6	0.1m HCl, aq.	352.3	361	- 0.1	A + B	0.7	A + E	0.3	A + B	0.4	A + E	- 1.4	A + E
7	0.1m HCl, D_2O	-	351	0	A + B	0.6	A + E	0.3	A + B	0	A + B	- 0.5	A + E
8	Acetate + Cl$^-$, aq.	559.6	557	0.5	A + E	0.5	A + E	0.8	A + E	0.4	A + E	- 2.4	A + E
9	0.1m HCl, 60% ethanol	317.6	837	0	B	0.4	A + E	0.8	A + E	ΔEe=0 ΔE=1.8	A + E	- 3.0	D2
10	Commercial	-	665	0.8	D1	2.1	D1	1.9	D1	ΔEe=1.0 ΔEf=-0.8	D1	- 4.4	D1
12	Mercury	-	530	-	-	0.5	-	1.5	-	-	-	- 2.2	-
13	0.1m HCl, aq.	352.3	356	0.4	D1	1.2	D1	1.0	D1	4.2	D1	- 7.8	D1
14	0.1m HCl, 20% ethanol	340.4	900	0.2	D1	1.8	D1	2.2	D1	3.7	D1	- 8.4	D1
15	0.1m HCl, 60% ethanol	317.6	922	6	D1	8	D2	7	D1	16	D1	- 38	D1
17	0.1m HCl, 50% dioxan	269.4	693	1.0	D1	2.0	D1	1.2	D1	4.0	D1	- 8.2	D1

† emf of cell, Pt, H_2 | 0.1m HCl | glass electrode



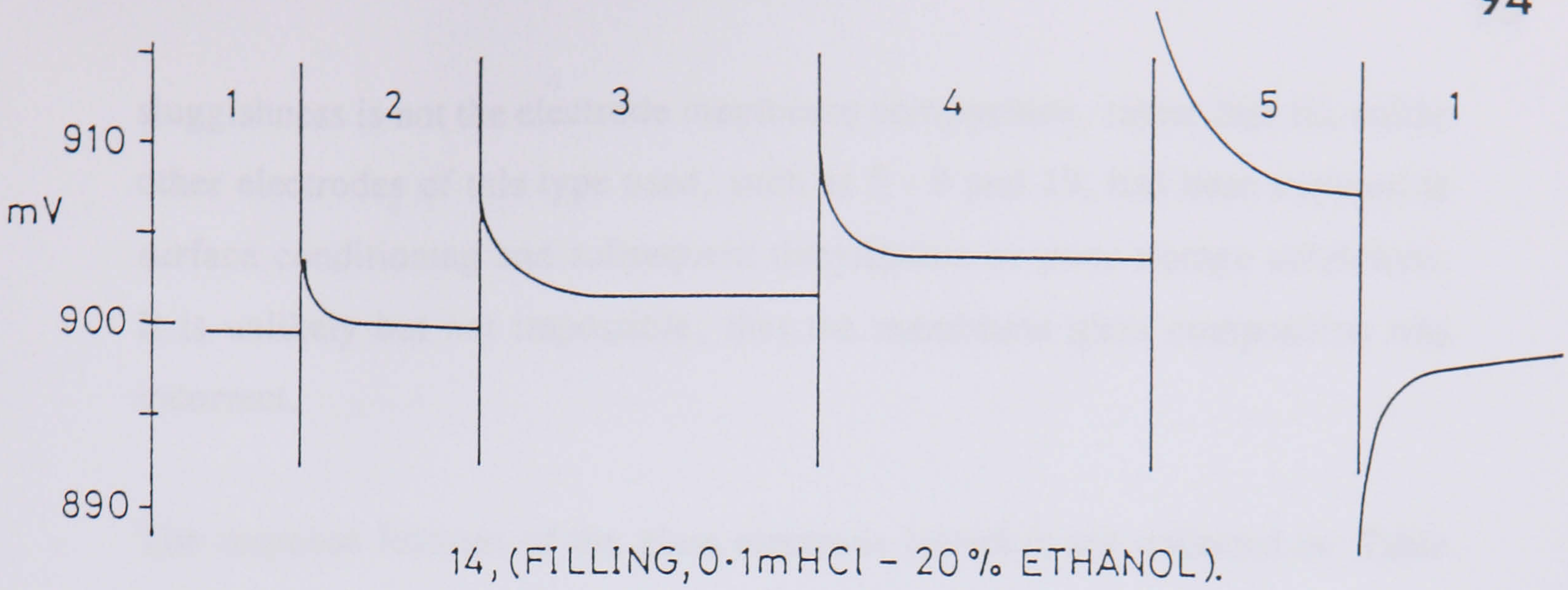
13, (FILLING, 0·1m HCl - AQUEOUS).

17, (FILLING, 0·1m HCl - 50% DIOXAN)

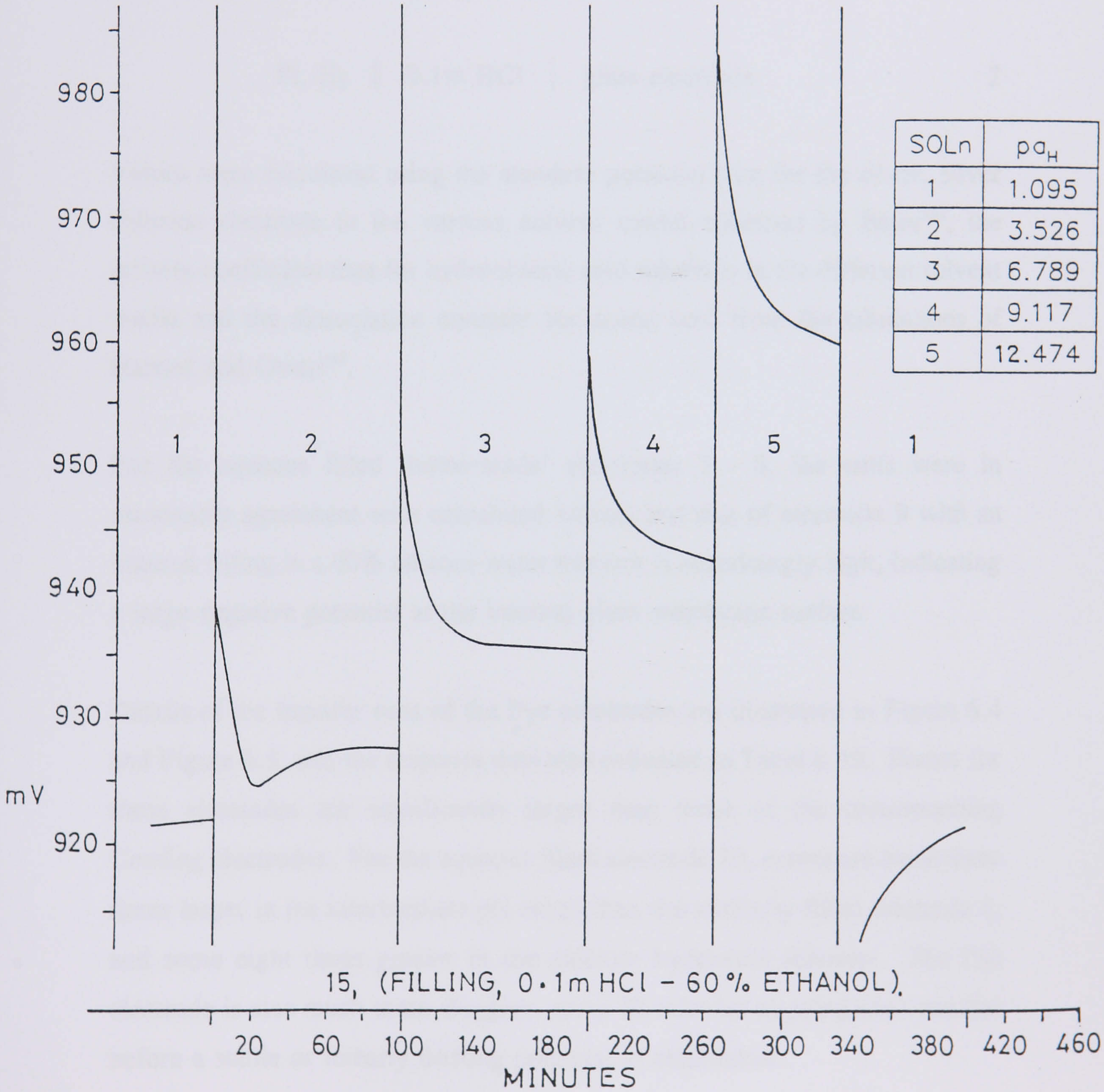
12, (FILLING, Hg).

SOLn	pa_H
1	1.095
2	3.526
3	6.789
4	9.117
5	12.474

FIG. 6.4 RESPONSE OF PYE ELECTRODES IN AQUEOUS BUFFER SOLUTIONS.



14, (FILLING, 0·1mHCl – 20% ETHANOL).



SOLn	pa_H
1	1.095
2	3.526
3	6.789
4	9.117
5	12.474

15, (FILLING, 0·1m HCl – 60% ETHANOL).

FIG. 6.5 RESPONSE OF PYE ELECTRODES IN AQUEOUS BUFFER SOLUTIONS.

sluggishness is not the electrode membrane composition, rather that 10, unlike other electrodes of this type used, such as 5 - 9 and 19, had been exposed to surface conditioning and subsequent dehydration or poor storage conditions. It is unlikely but not impossible, that the membrane glass composition was incorrect.

The response features of the glass electrode transfers are collected in Table 6.10. Listed in this table are the emfs of the cell,

$$\text{Pt, } H_2 \mid 0.1\text{m HCl} \mid \text{glass electrode} \qquad 2$$

Values were calculated using the standard potential data for the silver, silver chloride electrode in the various solvent media collected by Bates[142], the activity coefficient data for hydrochloric acid solutions in the different solvent media and the dissociation constant for acetic acid from the tabulations of Harned and Owen[143].

For the aqueous filled 'home-made' electrodes 5 - 8, the emfs were in reasonable agreement with calculated values, but that of electrode 9 with an internal filling in a 60% ethanol-water mixture is surprisingly high, indicating a large negative potential at the internal glass membrane surface.

Details of the transfer runs of the Pye electrodes are illustrated in Figure 6.4 and Figure 6.5, and the response data also collected in Table 6.10. Errors for these electrodes are significantly larger than those of the corresponding Corning electrodes. For the aqueous filled electrode 13, errors are some three times larger in the intermediate pH range than the similarly filled electrode 6, and some eight times greater in the calcium hydroxide solution. The Pye electrode is also much more sluggish, some 20 minutes elapsing after transfer before a stable or linearly drifting potential is established.

The performances of the Pye electrodes with fillings of mercury, 12, the water-based, 13, dioxan-water mixture, 17, and the 20% ethanol-water mixture, 14, are very similar. The latter, however, only very slowly recovers its initial potential in 0.1m hydrochloric acid on transfer from the calcium hydroxide buffer solution. The response of the 60% ethanol-water mixture filled electrode, 15, is quite different; errors for all transfers are much greater, and even an hour after transfer, a stable potential was established only in the potassium hydrogen tartrate buffer solution. In the neutral and alkaline buffer solutions, linear, drifting potentials are found after about an hour's immersion, the negative rate of drift increasing with increasing pH of the buffer solution. As noted earlier for the 20% ethanol-water filled electrode, 14, electrode 15 shows a very slow recovery after transfer to 0.1m hydrochloric acid from the calcium hydroxide buffer solution towards its original potential in that solution at the commencement of the transfer series run. For all transfers with the Pye electrodes, a type D_1 response characteristic was exhibited. A Pye electrode had been made with a filling of 0.1m hydrochloric acid in an 80% ethanol-water mixture, but its use was abandoned as, due to a rapidly changing potential, measurements were impractical.

As noted earlier for the partially aqueous filled Corning electrode, 9, the emfs of the non-aqueous solution filled Pye electrodes measured against the hydrogen gas electrode in 0.1m hydrochloric acid were unexpectedly high.

The emfs of similar cells with the mercury filled electrodes 5 and 12 cannot be commented on as there is the imponderable metal-glass interfacial potential. There is a difference between these two electrodes of some 300 mV, possibly arising from different degrees of hydration of their inner surfaces. When first used, electrode 5 showed some instability, initially possessing an unstable potential some 500 mV less than that to which it suddenly settled and remained.

6.3.2 Transfers in Methanol-Water Mixture Solutions

After conditioning in their respective solvent media for about four weeks, the glass electrodes were transferred between hydrochloric acid and acetate buffer solutions in 95% methanol-water media. They were subsequently stored for at least two weeks in the same storage solvent prior to being similarly transferred between 50% methanol-water solutions of the same electrolytes. Time-emf responses of the electrodes are illustrated in Figures 6.6-6.9, and Figures 6.10-6.12 for the 95% and 50% methanol-water mixtures series respectively, and the response details collected in Tables 6.11 and 6.12.

Each glass electrode was transferred from its storage solution into one of the test solutions; and the emf of the hydrogen-gas electrode-glass electrode pair followed until it had either settled to a steady value, or linearly drifting emf. It was then transferred between the test solutions and the emf against the hydrogen gas electrode recorded.

In the 95% methanol solutions, the most satisfactory performance is seen to be displayed by the 50% methanol filled and conditioned electrode C5 on the basis of A + B or E type transients. It may reasonably be argued that the transient type shown is C_2, rather than a slow A since the initial non-linear response, prior to the turning point after some ten minutes, suggests that it may be extrapolated to the instant of transfer with a resultant error approaching zero. If the latter argument were correct, the two aqueous filled electrodes C1 and C7 conditioned in water and 95% methanol respectively could also be usefully used by extrapolation of the initial non-linear portion with the suggestion of possibly, zero error. The stable or slowly drifting potentials established by these electrodes, however, result in final or extrapolated errors that would be unacceptable for precise direct potentiometry. Interestingly, electrode C1 exhibits the first observation of transient type F. The performance of the 50% methanol filled, 95% methanol conditioned electrode C8 is much poorer. With the exception of C5, the behaviour of these electrodes over the duration of their transfer runs imply continuously changing asymmetry potentials, and excluding C1 an indication of negative errors in 95% methanol hydrochloric acid solutions that may be dependent upon the conditioning medium, being absent with water, but

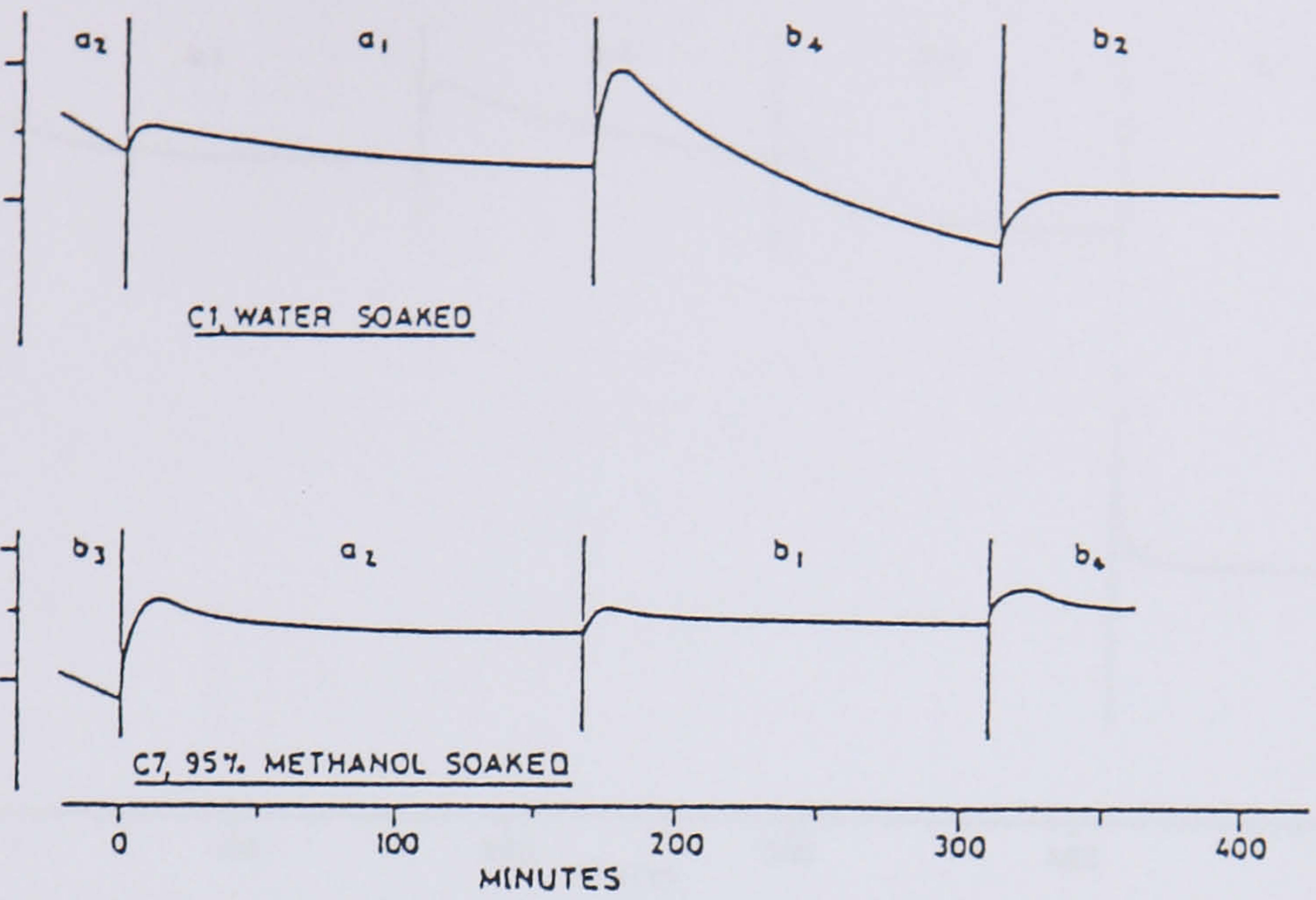


FIG 6.6 RESPONSE IN 95% METHANOL-WATER SOLUTIONS OF AQUEOUS FILLED ELECTRODES.

KEY TABLE 6-6

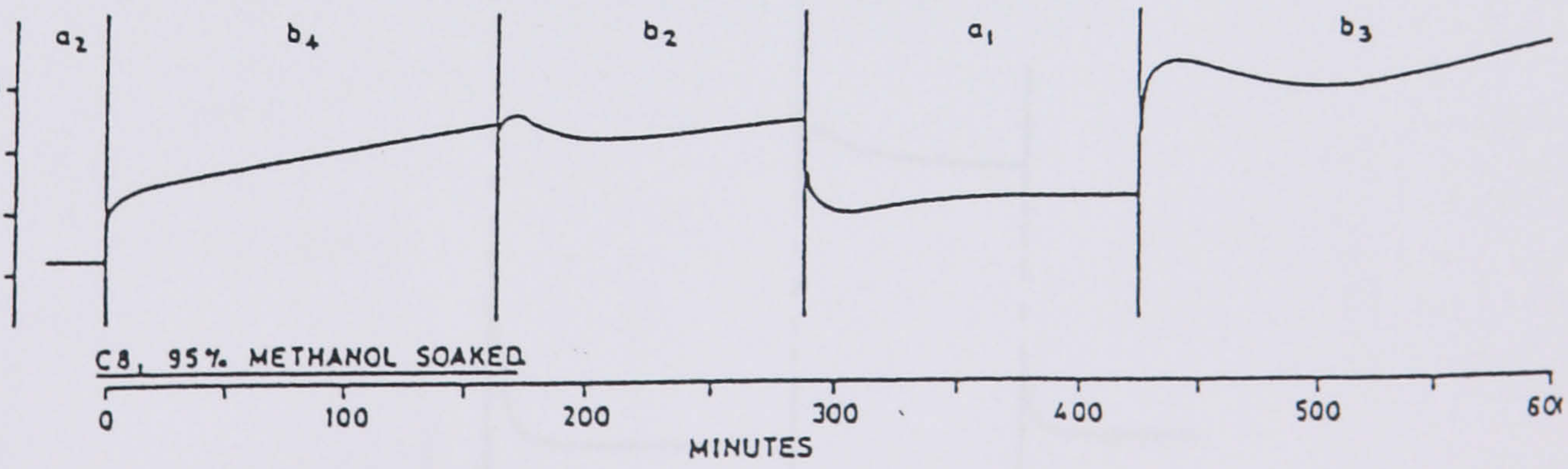


FIG. 6.7 RESPONSE IN 95% METHANOL-WATER SOLUTIONS OF 50% METHANOL-WATER FILLED ELECTRODES.

KEY TABLE 6-6

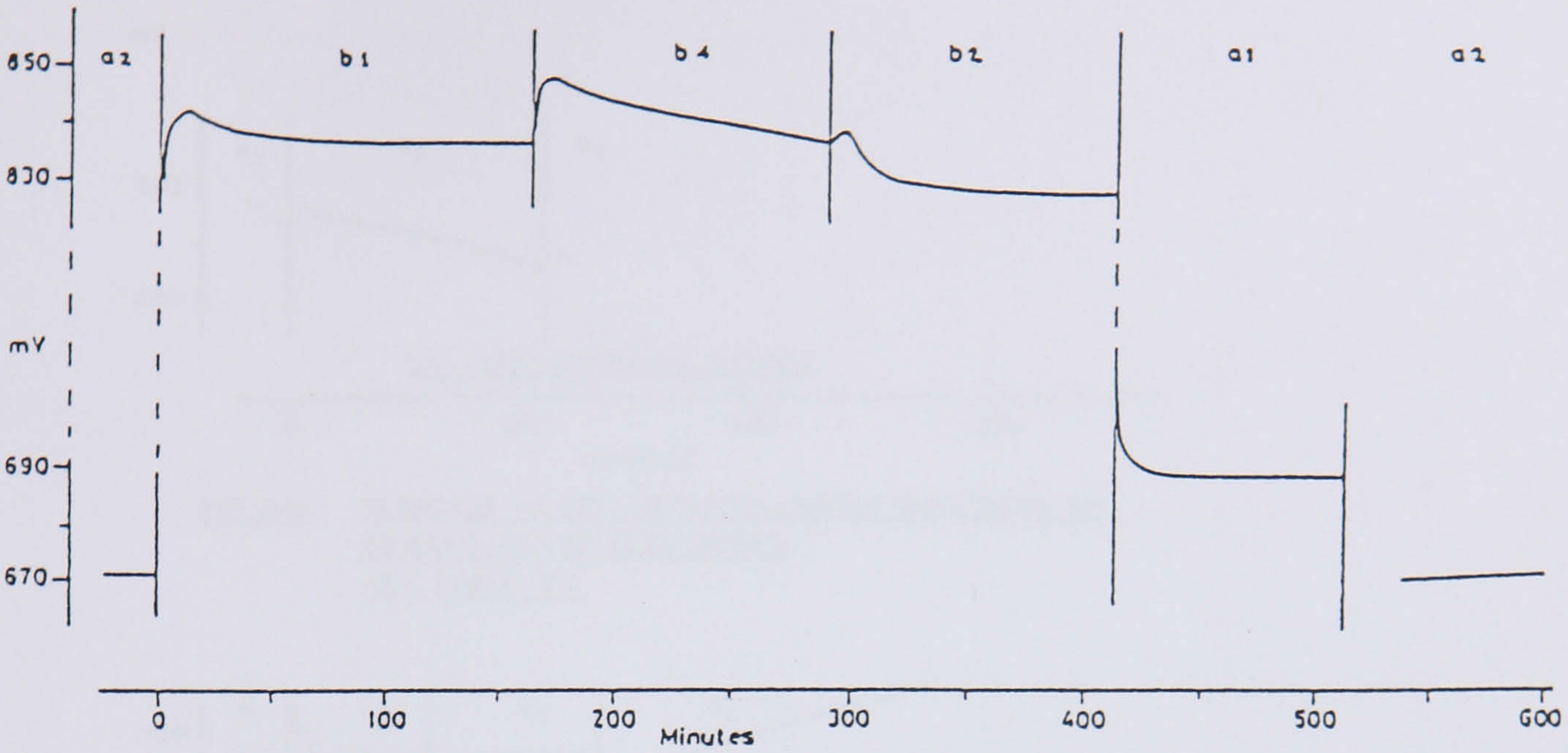


FIG 6.8 RESPONSE IN 95% METHANOL-WATER SOLUTIONS OF ELECTRODE C6.
(95% METHANOL FILLED, 50% METHANOL SOAKED).
KEY, TABLE 6-6

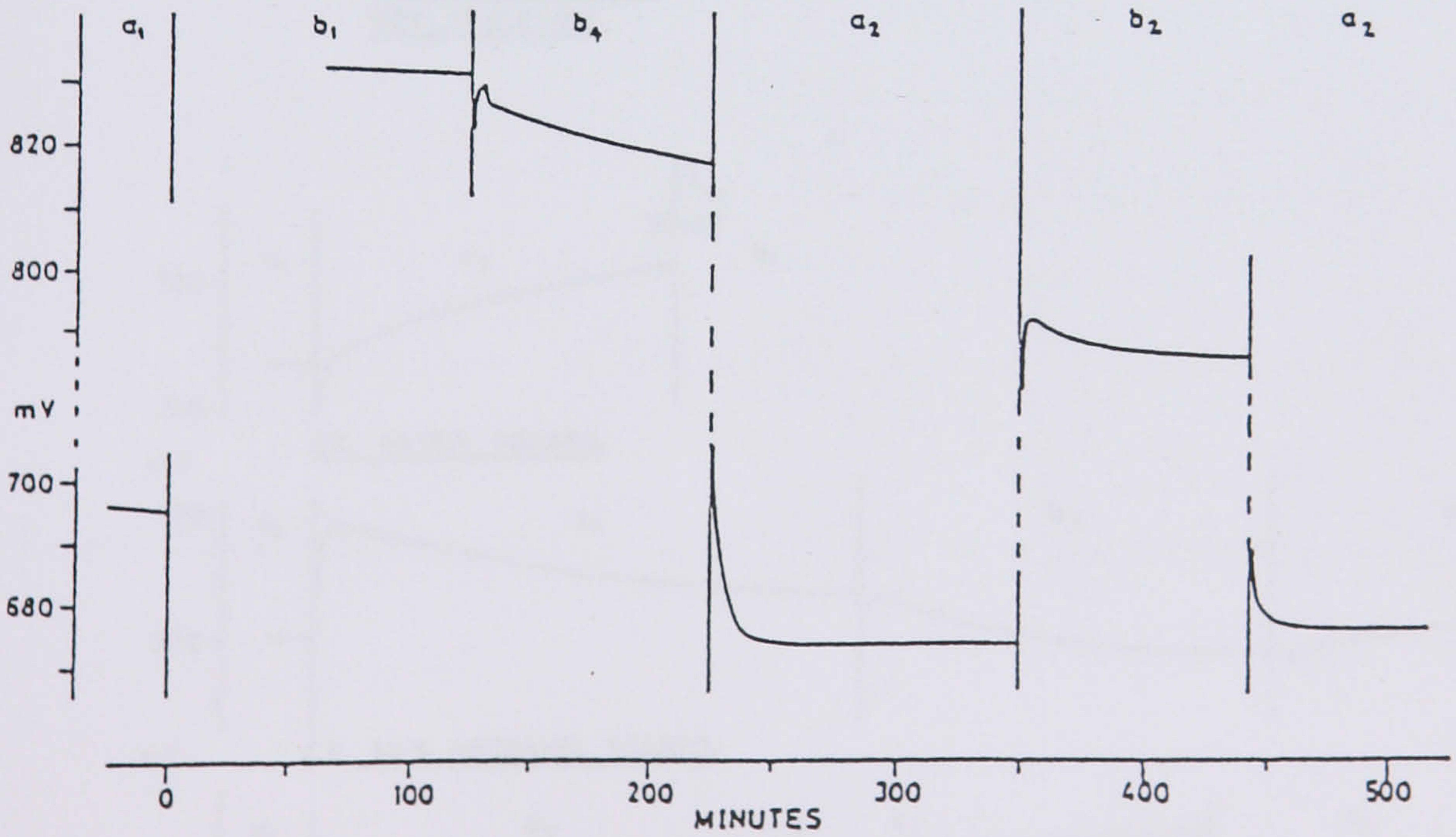


FIG 6.9 RESPONSE IN 95% METHANOL-WATER SOLUTIONS OF ELECTRODES C9
(95% METHANOL FILLED AND SOAKED).
KEY, TABLE 6-6

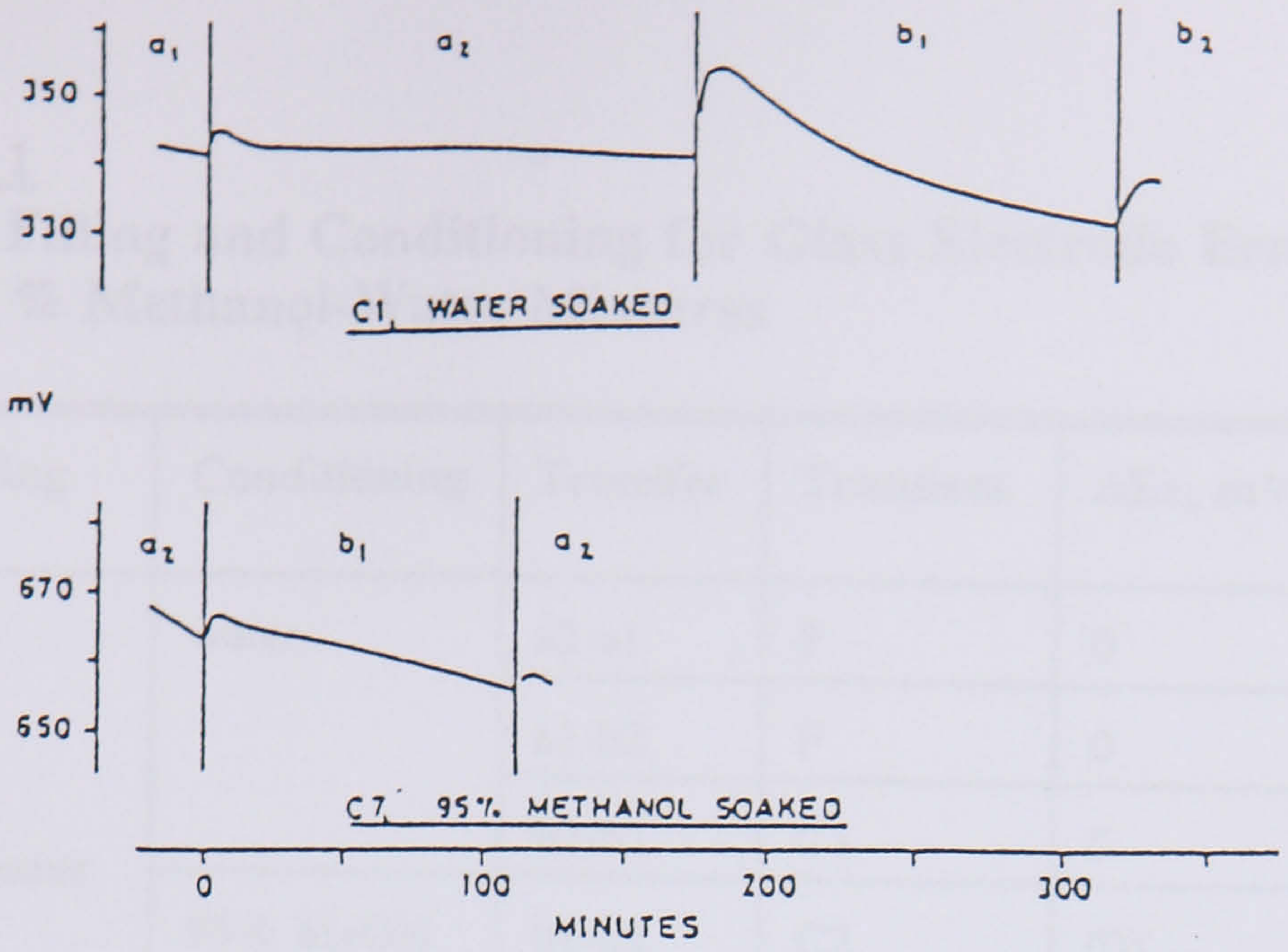


FIG 6.10 RESPONSE IN 50% METHANOL-WATER SOLUTIONS OF AQUEOUS FILLED ELECTRODES.
KEY, TABLE 6·7

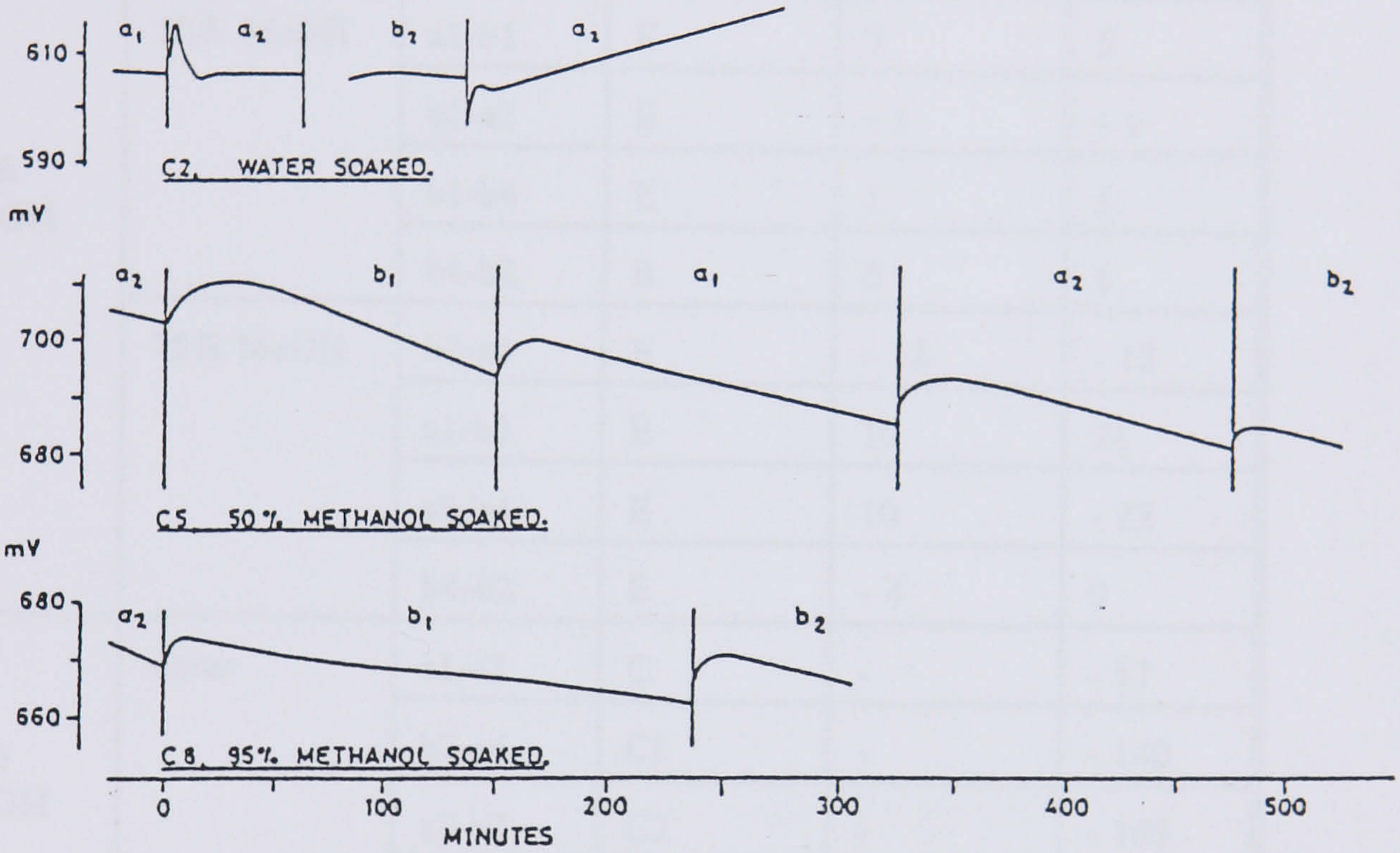


FIG 6.11 RESPONSE IN 50% METHANOL-WATER SOLUTIONS OF 50% METHANOL-WATER FILLED ELECTRODES,
KEY, TABLE 6·7

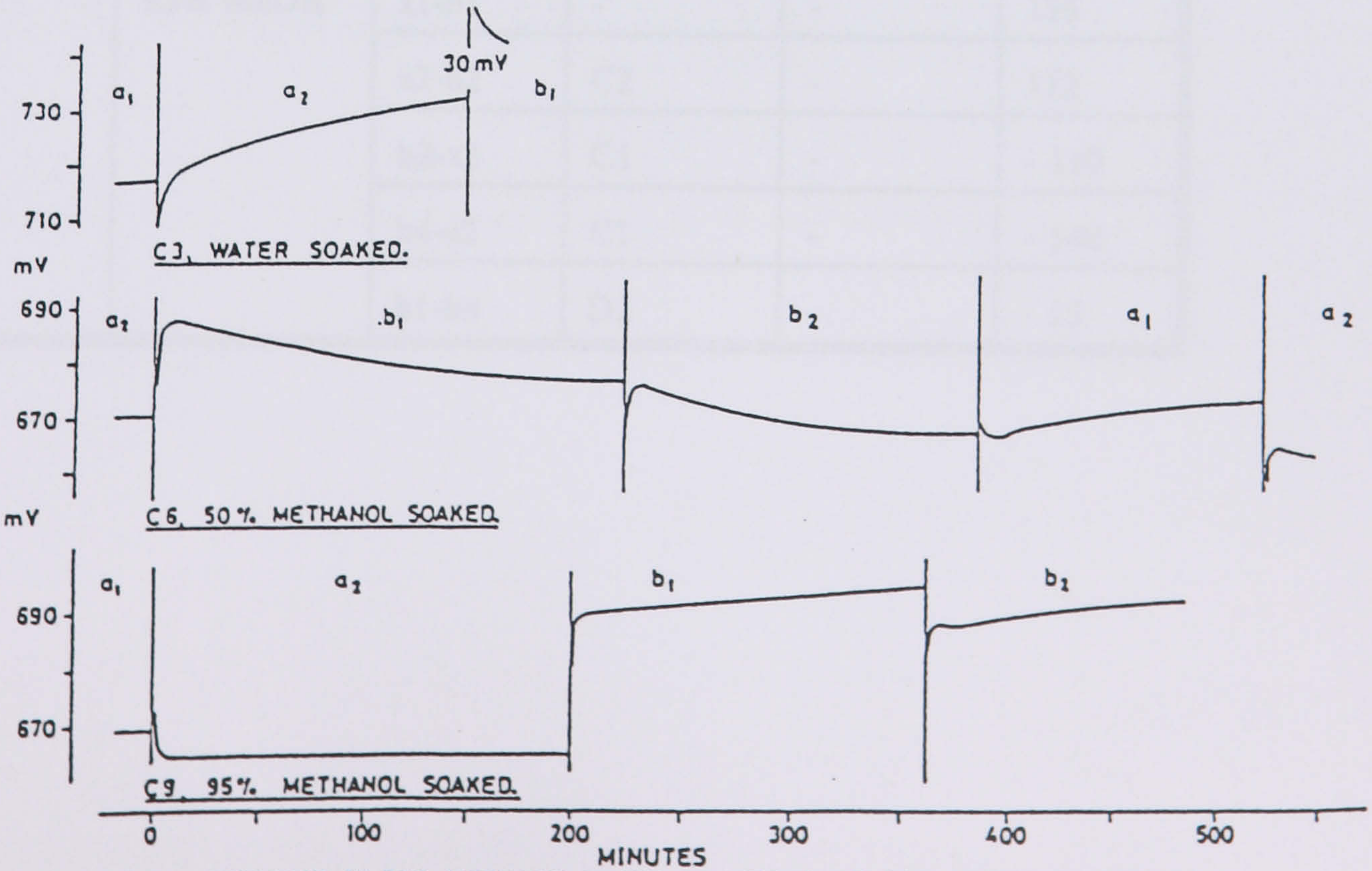


FIG. 6.12 RESPONSE IN 50% METHANOL-WATER SOLUTIONS OF 95% METHANOL-WATER FILLED ELECTRODES.
KEY, TABLE 6·7

Table 6.11
Effect of Filling and Conditioning for Glass Electrode Errors in 95 wt. % Methanol-Water Mixtures

No	Filling	Conditioning	Transfer	Transient	ΔEe, mV	ΔEf,mV
C1	aqueous	water	a2-a1	F	0	
			a1-b2	F	0	
			b2-b1	C1	0	8
C7		95% MeOH	b1-a2	C2	(0)	10
			a2-b1	C2	(0)	2
			b1-b2	C2	(0)	2
C5	50% MeOH	50% MeOH	a1-b1	E	7	5
			b2-a2	E	- 1	- 1
			b1-b4	E	1	1
			b4-b2	B	0	1
C8		75% MeOH	b2-a4	E	- 12	- 12
			a1-b3	E	10	24
			a2-b4	E	10	- 22
			b4-b2	E	- 4	0
C6	95% MeOH	water	a1-a2	C	-	- 17
			b2-a4	C1	-	- 140
			a2-b2	C2	-	- 165
			b1-b4	C2	-	0
			b4-b2	C2	-	- 9
C9		95% MeOH	a1-b1	-	-	135
			a2-b2	C2	-	112
			b2-a2	C1	-	- 110
			b4-a2	C1	-	- 140
			b1-b4	D2	-	- 15

Table 6.12
Effect of Filling and Conditioning for Glass Electrode Errors in 50 wt % Methanol-Water Mixtures

No	Filling	Conditioning	Transfer	Transient	ΔEf mV
C1	aqueous	water	a1-a2	F	0
			a2-b1	F	0
			b1-b2	F?	0
C7		95% MeOH	a2-b1	F	0
			b1-a2	F	0
C2	50% MeOH	water	a1-a2	C2B	0
			a2-b2	CB	1
			b2-a2	?	4?
C5		50% MeOH	a1-a2	F	0
			b1-a1	F	0
			a2-b1	F	0
			a2-b2	F	0
C8		95% MeOH	a2-b1	F	0
			b1-b2	F	0
C3	95% MeOH	water	a1-a2	E	0
			a2-b1	D1	
C6		50% MeOH	a1-a2	E	- 6
			b2-a1	D2	- 6
			a2-b1	F	0
			b1-b2	D2	- 8
C9		95% MeOH	a1-a2	E	- 7
			a20-b1	C1	28
			b1-b2	D2	- 5

increasing with increasing methanol content.

The responses of the 95% methanol filled electrodes C6 and C9 conditioned in 50% and 95% methanol respectively were unexpected. As Figures 6.8 and 6.9 illustrate, very large errors are apparent between acid and buffer solutions, the effect being rather greater with C9. This electrode also exhibited significant errors between the buffer solutions. Emfs displayed suggest that liquid junction potentials are developed at the outer glass-solution interface of these electrodes, but this cannot be the case as these same electrodes did not exhibit similar gross errors in the subsequent transfer experiments in 50% methanol solutions.

In the 50% methanol-water solution transfer series, the aqueous conditioned electrodes C1 and C7 possess very similar response characteristics to those that they displayed in the 95% methanol solutions. That of C1 is virtually identical, whilst C7 exhibits rather larger changing asymmetry potential with definite F type transients. Their time-emf responses are shown in Figure 6.10.

Unlike their behaviour in the 95% methanol solution transfer series, the 50% methanol filled electrodes did not display negative errors in the 50% methanol acid solutions. Electrode C2 that had been abandoned in the 95% methanol solution study as it had exhibited unstable potentials, after further conditioning in water, presented initially B type transfer characteristics in the 50% methanol solution run, but, after some two hours use, developed a steady, increasing, positive drift. Its overall behaviour suggests perhaps, a dry-soldered cable connection. Electrodes C5 and C8 both exhibited F-type transient behaviour.

Negative errors in acid solutions are shown in Figure 6.12 for the three 95% methanol-filled electrodes. The aqueous soaked electrode C3 that had inadvertantly not been used in the 95% methanol solutions, is seen to possess a very sluggish response that, even after some 90 minutes, has not settled to either a steady or linearly drifting potential. Although sluggish, the 50% methanol conditioned electrode C6 does settle to steady or constant drifting potentials, with C or E type transients, but displays errors for most transfers. The 95% methanol conditioned electrode C9 also exhibits errors in all solution transfers, but steady or linearly drifting potentials were established relatively rapidly, within five to ten minutes.

6.3.3 Transfers in 95% Dimethylformamide-Water Mixture Solution

For this series of transfer experiments aqueous 0.01m and 0.1m solutions of hydrochloric acid were included with the 95% DMF hydrochloric acid and acetate buffers. There is no record in the literature of glass electrode transfer between these media, other than that of Ivanovskaya and Shul'ts[35] in which electrodes were successively transferred between 0.1m hydrochloric acid solutions in both water and DMF, and the potentials measured against quinhydrone electrodes over four to five weeks.

Four 'white' Corning glass electrodes, two with aqueous 0.1m hydrochloric acid fillings, C11 and C13, and two with 95% DMF acetate buffer fillings, C12 and C14, were prepared. Electrodes C11 and C12 were conditioned and stored in water, and electrodes C13 and C14 in 95% DMF, for four weeks prior to use. The results of the transfers are collected in Table 6.13.

The time-emf transfer characteristics for three separate transfer runs of the aqueous filled, aqueous conditioned electrode C11 are shown in Figure 6.13. Following the first transfer run the electrode was stored overnight in water prior to the second. The final set of transfers was made after a further two days storage in water.

In all solutions A + B or E type transients were displayed with equilibria being usually established within three to five minutes. Exposure to the 95% DMF hydrochloric acid solutions appears to degrade the electrode response in subsequent transfers in the 95% DMF acetate buffer and aqueous hydrochloric acid solutions. Comparison of the results of the first experimental run that include 95% DMF 0.0095m hydrochloric acid, with the final run from which 95% DMF acid solutions were excluded, shows that the effect of the 0.0095m acid solution is small in comparison with that of the 0.095m acid solution displayed in the second run. Surprisingly, the approximately 30 mV error in 95% DMF 0.095m hydrochloric acid solution is positive, however, the subsequent transfer to the 95% DMF 0.0095m acid solution results in a negative error. Whilst such electrodes could not be used for precise direct potentiometry, the results indicate that they may prove very satisfactory for general analytical titrimetry.

Results of the responses of the 95% DMF filled, aqueous conditioned electrode obtained in experimental runs on consecutive days with intervening storage in water are graphically illustrated in Figure 6.14. Positive errors of about 10-20 mV between 0.0095m hydrochloric acid and acetate buffers in 95% DMF are exhibited, and very large negative errors of some 150 mV shown in the 0.095m hydrochloric acid solution. The results obtained in the second run show the development of a continuous negative drift of some 15 mV/h. It is conceivable that immersion in acid solutions, particularly the stronger solution, develops a consequent, degraded response. After the first run of some four hours duration, overnight storage in water was perhaps too short a period of time to enable response recovery.

Figure 6.15 presents the performance of the aqueous filled, 95% DMF soaked electrode C13 obtained in transfer runs on three successive days with intermediate storage in that solvent mixture. The behaviour is unsatisfactory. Lower potentials of the glass electrode are apparent in the 95% DMF 0.0095m acid solution than in the 0.095m solution. The results, though not readily understandable, do, however, suggest that they cannot be ascribed to a cracked membrane and resultant liquid junctions.

The transfer characteristics of the 95% DMF filled and conditioned electrode C14 on three consecutive days are illustrated in Figure 6.16. The time

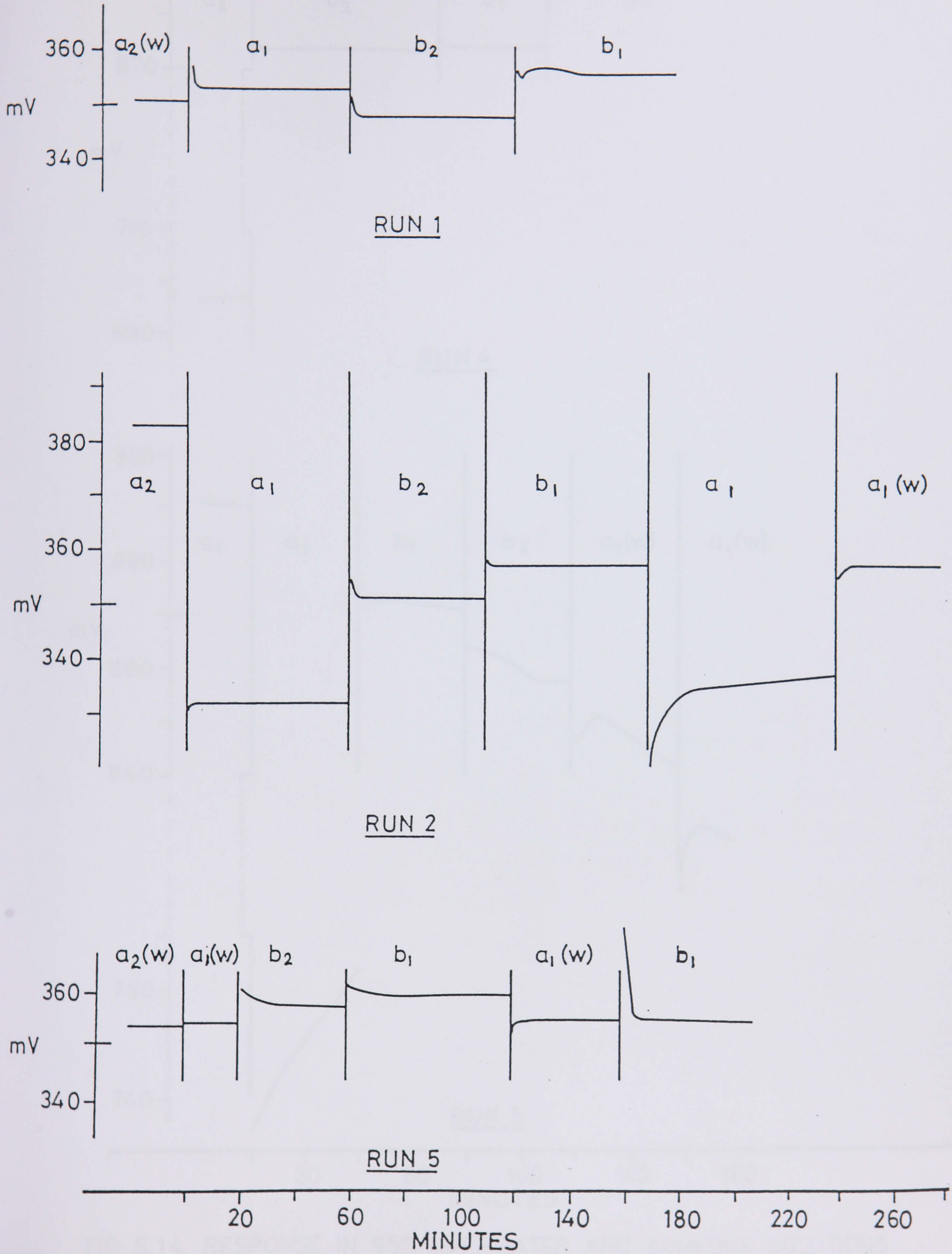


FIG 6.13. RESPONSE IN 95% DMF–WATER AND AQUEOUS SOLUTIONS OF ELECTRODE C11 (AQUEOUS FILLED, WATER SOAKED).

KEY. TABLE 6.8.

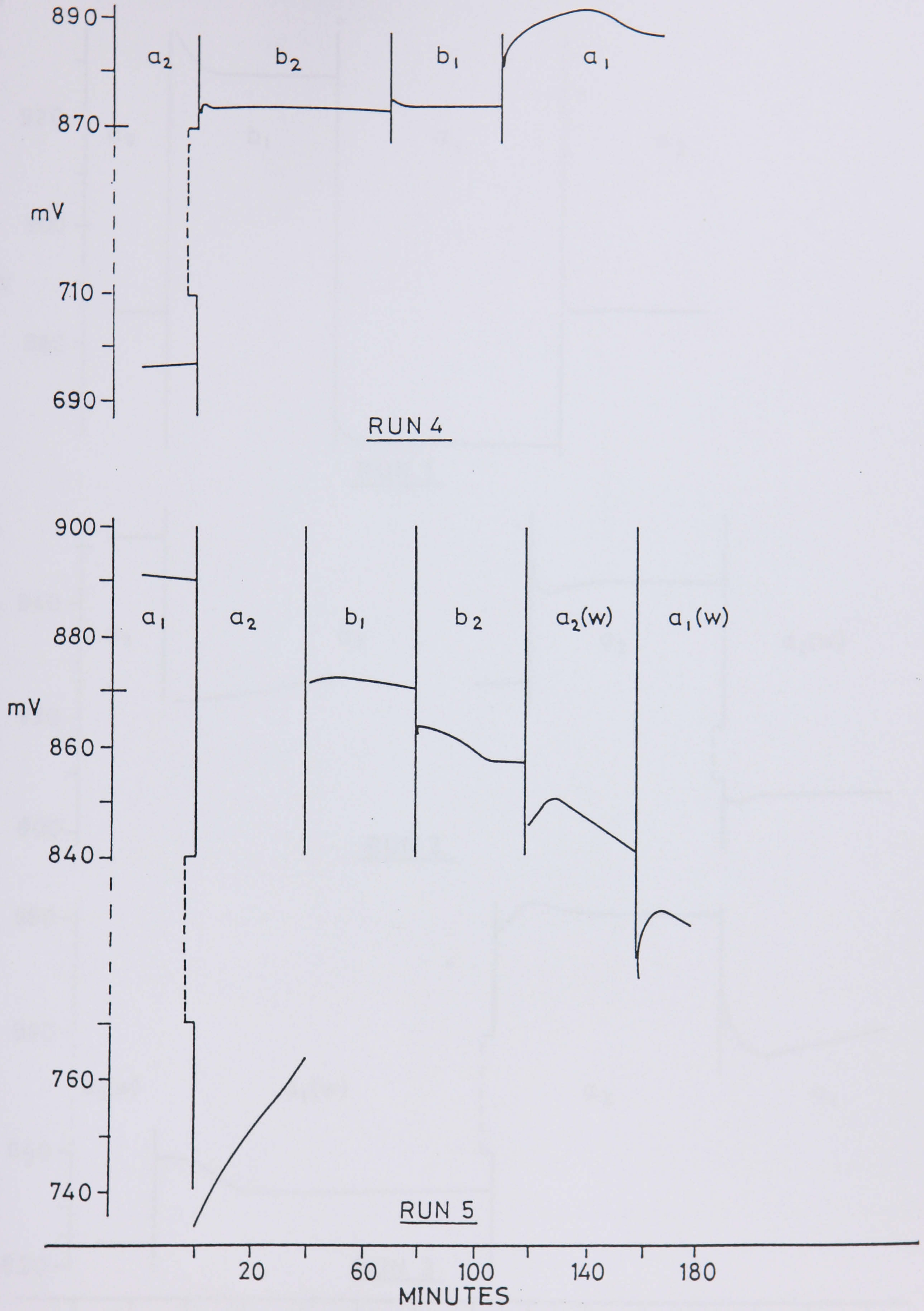


FIG 6.14. RESPONSE IN 95% DMF–WATER AND AQUEOUS SOLUTIONS OF ELECTRODE C12 (95% DMF FILLED, WATER SOAKED).

KEY. TABLE 6.8.

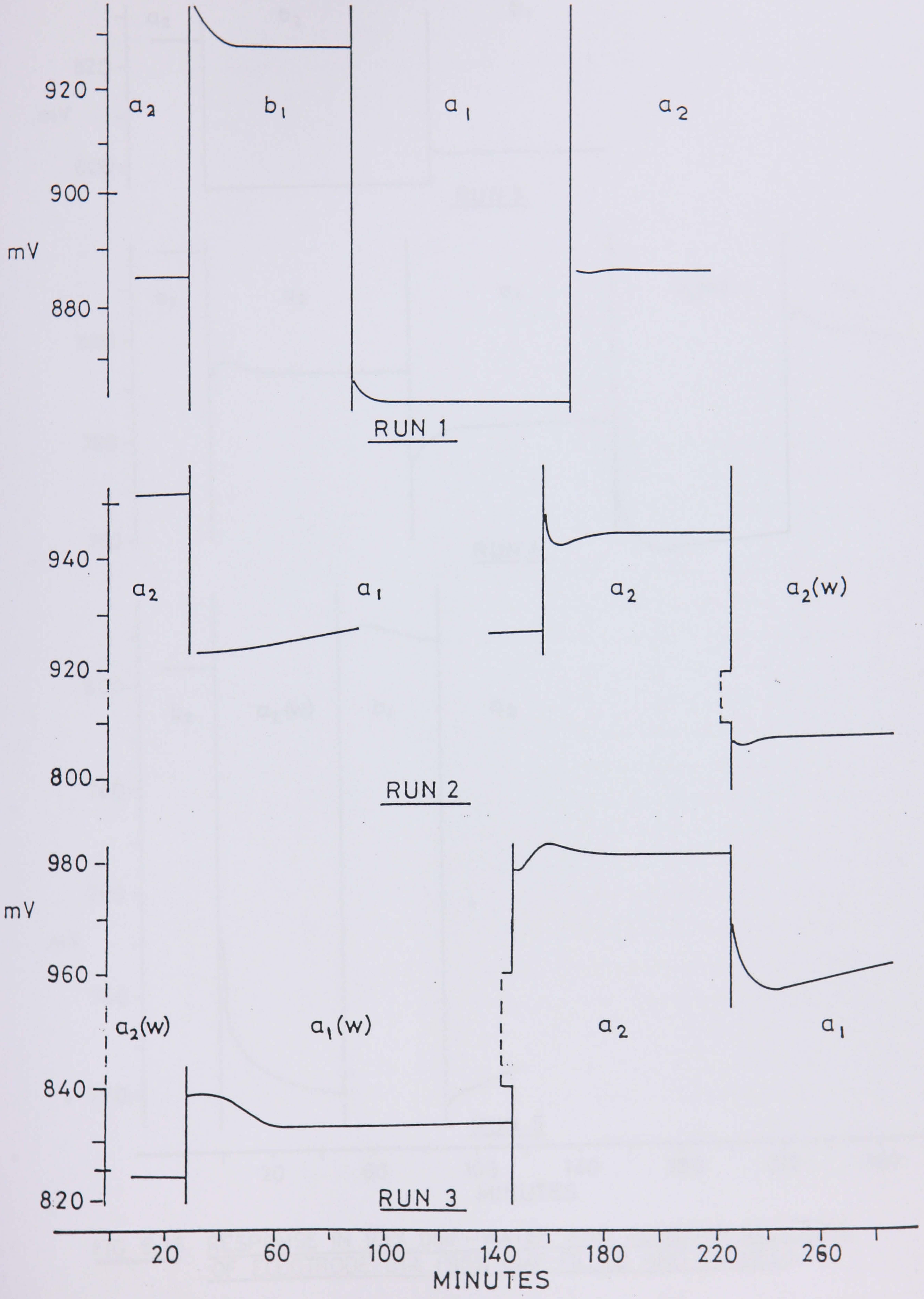


FIG 6.15. RESPONSE IN 95% DMF–WATER AND AQUEOUS SOLUTIONS OF ELECTRODE C13 (AQUEOUS FILLED, 95% DMF SOAKED).

KEY. TABLE 6.8.

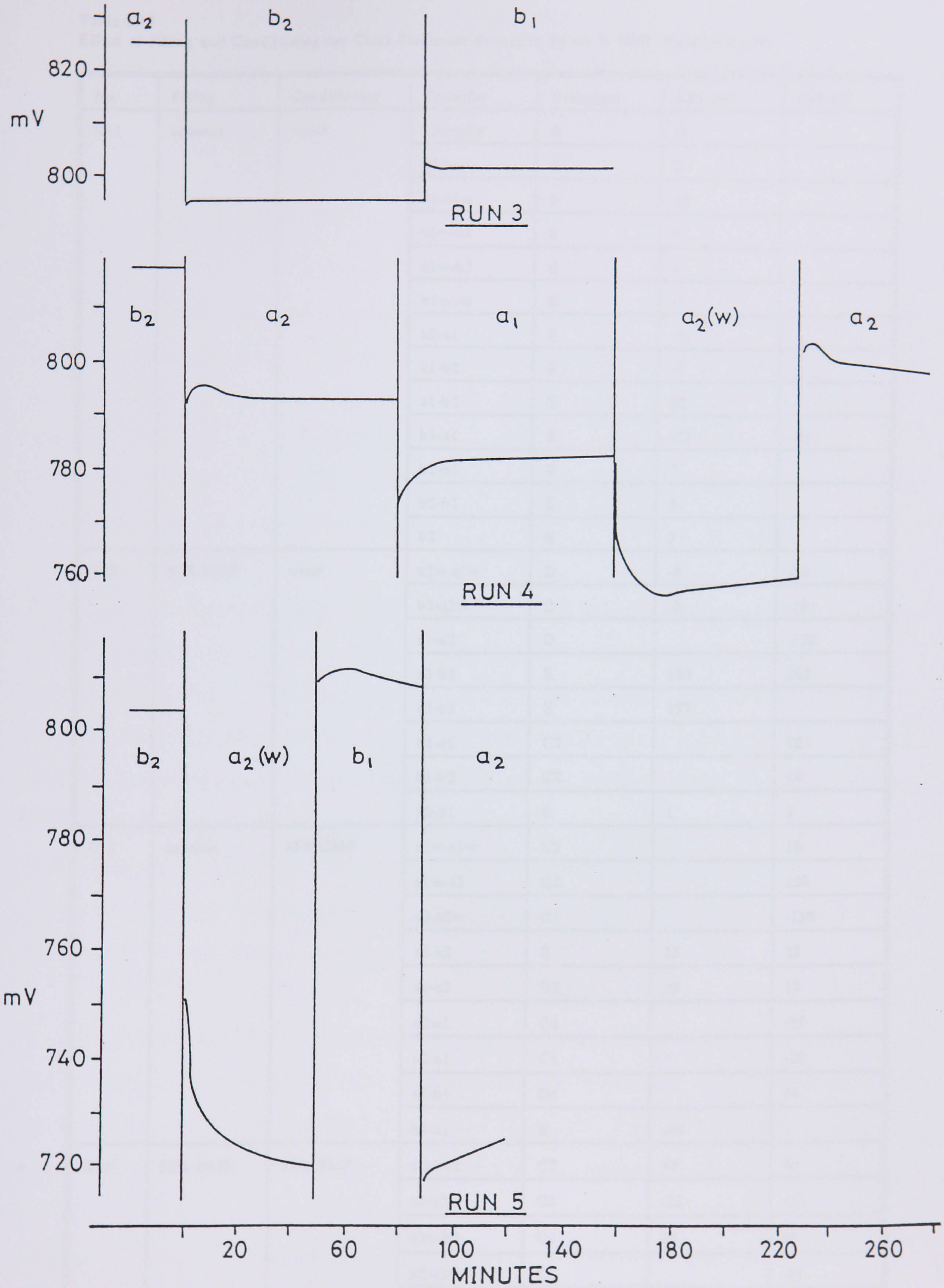


FIG 6.16. RESPONSE IN 95% DMF–WATER AND AQUEOUS SOLUTIONS OF ELECTRODE C14 (95% DMF FILLED AND SOAKED).

KEY. TABLE 6.8.

Table 6.13
Effect of Filling and Conditioning for Glass Electrode Errors in 95 wt % DMF-Water Mixtures

No.	Filling	Conditioning	Transfer	Transient	ΔEe mV	ΔEf mV
C11	aqueous	water	a2w-a1w	B	0	
			a2w-a1	E	2	
			a1-a1w	E	20	
			a1w-b1	E	0	
			a1w-b2	E	4	
			b1-a1w	E	-5	
			a2-a1	E	-51	
			a1-b2	E	-5	
			a1-b2	E	20	
			b1-a1	E	-23	-21
			b2-b1	E	7	
			b2-b1	E	6	
			b2	E	5	
C12	95% DMF	water	a2w-a1w	D	-8	-14
			b2-a2w	D	-2	-16
			a1-a2	D		-120
			a2-b1	E	110	105
			a2-b2	E	157	
			b1-a1	C2		12
			b1-b2	C2		14
			b2-b1	E	1	2
C13	aqueous	95% DMF	a2w-a1w	C2		10
			a1w-a2	C2		150
			a2-a2w	C1		-130
			a1-a2	E	25	25
			a1-a2	D2	19	19
			a2-a1	D1		-25
			a2-a1	C1		-20
			a2-b1	D1		44
			b1-a1	E	-60	
C14	95% DMF	95% DMF	a2w-a2	C2	42	40
			a1-a2w	C1	-28	-22
			a2w-b1	C1	95	90
			b2-a2w	C1		-85
			a2-a1	D1	12	10
			a2-b2	E	-30	
			b2-a2	D2	-24	
			b2-b1	E	5	

responses progresively degenerate from a rapid invariant E type characteristic to more laggardly C and D types. The performance between solutions is similar to that of electrode C13, but the errors exhibited while large, are much less.

6.4 CONCLUSIONS

This study has demonstrated that the time responses and errors of nominally similar glass electrodes are affected both by changing the aqueous internal filling to partially aqueous media and to partially aqueous solvent conditioning. Reports[128,129] that much improved time response and negligible or zero error is attained if glass electrodes have internal fillings of, and are conditioned, in the solvent medium in which they are to be used, have not been corroborated.

The results are also at variance with the long accepted hypothesis that the inner and outer interfacial potentials of the glass electrode are developed independently. The behaviour could be ascribed to hydrogen ion diffusion through the glass membrane as proposed by Badoz-Lambling *et al.*[6], yet this mechanism is inconceivable as it conflicts with Haugaard's[37] three layer model of the glass electrode based on the electrical and surface properties of glass, unless, of course, the central bulk glass were totally solvated, which for these glass compositions is barely credible. The possibility that the effects may be due to liquid-junction potentials at cracked membranes is not considered likely.

In both the methanol-water and DMF-water mixtures used there was evidence that the performance of the electrodes was degraded by immersion in hydrochloric acid solutions and that the magnitude of the effect increased with both increasing acid concentration and increasing organic content of the solvent. There was some evidence that the effect could be removed and the response restored by prolonged soaking in water. These observations are analogous to those reported by Schwabe *et al.*[22] for glass electrode errors in aqueous hydrochloric acid solutions in which the negative error was unequivocally ascribed to acid absorption by the gel layer, but the error behaviour is quite different.

It is clearly apparent that further investigations are necessary to clarify the nature of the effects of partially and non-aqueous solvent media at the glass-solution interfaces of the glass electrode. As pH membrane glasses are hygroscopic it would be prudent to complete the internal construction of the glass electrode with, and immerse it in, the particular solvent medium in which it is to be used immediately after the membrane bulb is fused to the electrode body. Alternatively, if this were not practical, both inner and outer surfaces of the membrane should be renewed by etching[90] immediately prior to assembly.

CHAPTER SEVEN

THE DURABILITY AND HYDROGEN-ION FUNCTION OF SODA-LIME AND LITHIA-LIME GLASSES: AN INITIAL STUDY

7.1 INTRODUCTION

The essential role of water in the development of the hydrogen-ion function at a glass membrane surface was apparent in the earliest applications of the glass electrode. Haber and Klemensiewicz[67] obtained satisfactory pH response with electrodes prepared from a soda-rich Thuringian glass[144] and noted that if they were allowed to become dry, their pH function was degraded. Electrodes prepared from a chemically resistant Jena borosilicate glass were devoid of a useful pH response unless initially subjected to prolonged steam autoclaving at 250°C, after which they displayed a pH function, somewhat reduced due, at least partially, to a mixed-ion response.

Unconditioned Corning 015 electrodes annealed before use were found by Hubbard and Rynders[145,146] to possess a normal pH response, whereas similar electrodes that were conditioned prior to annealing subsequently displayed both severely degraded response and potential shift. These unfortunate features were removed by etching the electrode surface with dilute hydrofluoric acid and both correct pH response and potential were restored.

These observations amply demonstrated the importance of the surface structure of the glass electrode membrane to its response and intimated the degradation of conditioned electrode properties, subsequent to annealing, to be due to the formation during heat-treatment of a non-hygroscopic, silaceous, surface layer.

In comparing the hygroscopicities of powdered samples of a selection of commercial glasses exposed to constant humidity conditions, Hubbard[147] identified a qualitative correlation with the pH function of electrodes fabricated from the glasses. Highly hygroscopic glasses such as Corning 015 possessed an excellent pH function over a wide pH range, but those of electrodes prepared from chemically resistant glasses, for which water absorption was barely detectable, such as 'Vycor' and 'Pyrex' were scarcely discernible. Moderately hygroscopic glasses displayed unsatisfactory, intermediate pH functions.

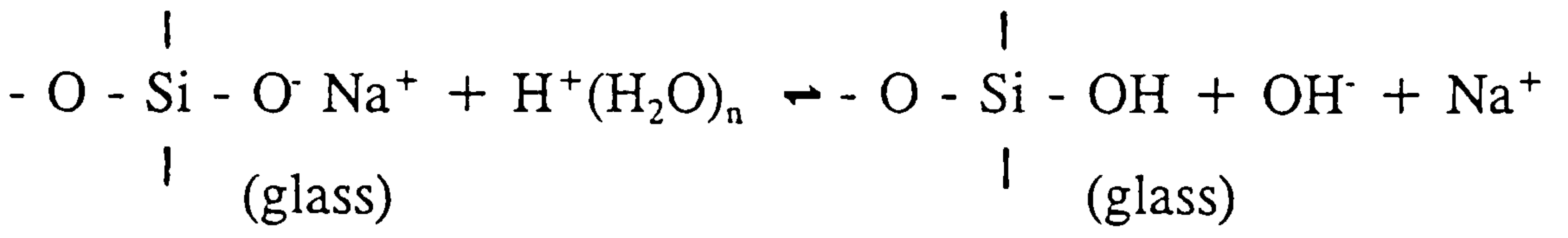
A comparison of the pH response of glasses with their durabilities in a range of mineral acid and buffer solutions was made by Hubbard and his co-workers[17,148] by an optical technique. Interference bands under an optical flat fused quartz plate of flat-ground plates of the glasses were noted. The plates were removed and partially immersed in the test solutions, usually at 80°C for up to six hours. On removal the plates were replaced under the optical flat and any consequent band displacement recorded. In the pH range in which an electrode exhibited proper pH function, glasses were observed to have swollen slightly. Where negative errors were displayed, e.g. below about pH 1 for Corning 015, swelling was repressed. Above some pH value, which with Corning 015 was coincident with the onset of the positive error of the electrode, the glass surface was attacked by the solution. Hubbard and Rynders[149] proposed that some minimum hygroscopicity is necessary for a glass to develop a pH function and that the theoretical response will only be exhibited in solutions over the pH range in which uniform swelling is displayed, albeit that the durability tests were effected at 80°C and the pH responses determined at 25°C.

The reaction of a glass with water is not, as Morey[150] has stated, simply dissolution, rather 'a highly complex one involving the penetration of glass by water and the subsequent decomposition of the complex silicate mixture, with formation of substances wholly different from those originally present'.

A parabolic relationship of the water extraction of alkali from glass with time observed by e.g. Bacon and Burch[151] was regarded by Keppeler and Thomas-Welzow[152] to infer a diffusion mechanism. Lyle[153] endorsed this view and suggested that a hydrated silaceous layer develops at the surface across which alkali ions diffuse to the attacking solution at a rate proportional to the concentration gradient (Co-Ci)/x, where x is the layer thickness. If the reaction were diffusion controlled extraction of alkali Q from a glass with time t, it would be expressed by $Q^2=Kt$, however, he found the index was rarely 2 and proposed a general relationship $Q^{\alpha}=Kt$. For the glasses that he studied, α was observed to depend on the glass composition and to be independent of temperature. Douglas and Isard[154] established a $\sqrt{t}$ correlation for a commercial soda-lime glass and regarded the rate of the ion-exchange reaction at the glass surface to be controlled by the self-diffusion coefficient of sodium ions in the glass. They considered the silica network of the glass to remain intact.

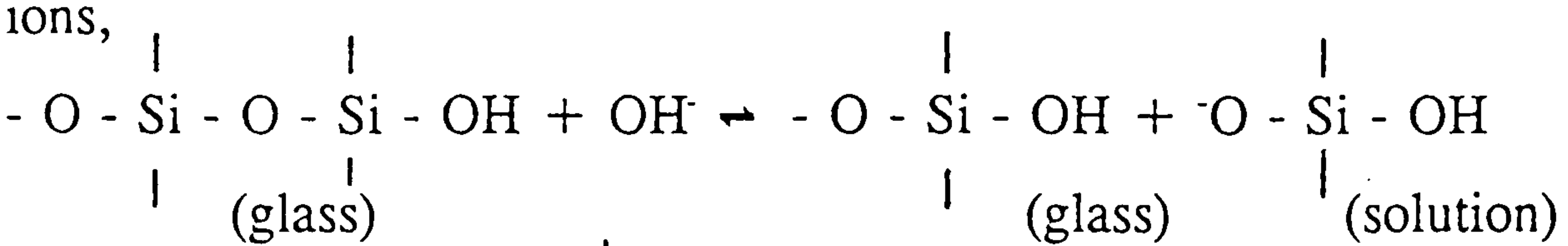
The kinetics of reaction for a range of alkali and alkali-lime glasses were studied by Rana and Douglas[44] who showed that alkali diffusion coefficients for the water leaching reaction generally differed markedly from the self-diffusion coefficients determined for the glasses from conductivity measurements. They concluded that, for the glasses studied, the rate of alkali extraction at short times and adequately low temperatures varies linearly with $\sqrt{t}$, and that, at sufficiently high temperatures and long times, a second mechanism dominates in which the amount of alkali extracted varies linearly with time. They showed that silica is extracted at all stages of the reaction, the rate probably, as with alkali extraction, varying with $\sqrt{t}$ during the first mechanism and with t in the second. The mechanisms were found to be dependent on composition and temperature, the least durable glasses exhibiting the $\sqrt{t}$ mechanism only at sufficiently low temperatures.

Decomposition of a glass by water was visualized by Douglas and El-Shamy[59] to involve preferential alkali extraction at the glass surface by ion-exchange leaving an alkali-deficient leached layer,



$$-O-\underset{|}{\overset{|}{Si}}-O^- Na^+ + H^+(H_2O)_n \rightarrow -O-\underset{|}{\overset{|}{Si}}-OH + OH^- + Na^+ \tag{1}$$
$$\text{(glass)} \qquad\qquad\qquad\qquad \text{(glass)}$$

Silica will pass into solution as a result of cleavage of the siloxane bond by hydroxyl ions,



$$-O-\underset{|}{\overset{|}{Si}}-O-\underset{|}{\overset{|}{Si}}-OH + OH^- \rightarrow -O-\underset{|}{\overset{|}{Si}}-OH + {}^-O-\underset{|}{\overset{|}{Si}}-OH \tag{2}$$
$$\text{(glass)} \qquad\qquad\qquad \text{(glass)} \qquad \text{(solution)}$$

the negatively charged $^-O-\underset{|}{\overset{|}{Si}}-OH$ groups separating from the network and passing into solution when other bridging oxygen bonds to the network are ruptured. As equation (2) shows silica removal is promoted with increasing hydroxyl ion activity of the attacking solution. The accompanying decrease in hydrogen ion activity will repress the removal of alkali ions into solution as shown in equation (1).

At the leached layer-solution interface, reaction sites will be available for ion-exchange with ions in solution, that may be represented as:

$\equiv Si - O^-$, $\equiv Si - O^- Na^+$, $\equiv Si - OH$

the equilibrium being determined by the concentrations and solvation energies of the ions in the solution and the interfacial layer. An alkali ion concentration gradient will exist across the leached layer to its interface with the bulk glass that may vary between a uniform concentration gradient as envisaged by Lyle[153] for a constant diffusion coefficient, or for a concentration dependent diffusion coefficient, a rapid change at the glass-leached layer interface.

They identified two reaction zones, that of the surface sites at the leached layer-solution interface where equilibrium is established with ions in solution and that at the glass-leached layer interface comprising counter ion exchange with hydrogen ions that diffuse across the layer from the solution. The leached layer thickness will depend upon the composition of the glass and the conditions to which it is subjected. It will be thicker for low durability glasses and may include the whole bulk of the glass.

In an attempt to find if there is a quantitative correlation between the durability of a glass and its pH function, the durabilities using the Rana and Douglas[44] method, and the hydrogen-ion functions of a number of simple ternary glasses were studied.

7.2 SELECTION AND PREPARATION OF THE GLASSES

7.2.1 Selection of Glasses

Two series of glasses were chosen for study and are identified in Tables 7.1 and 7.2.

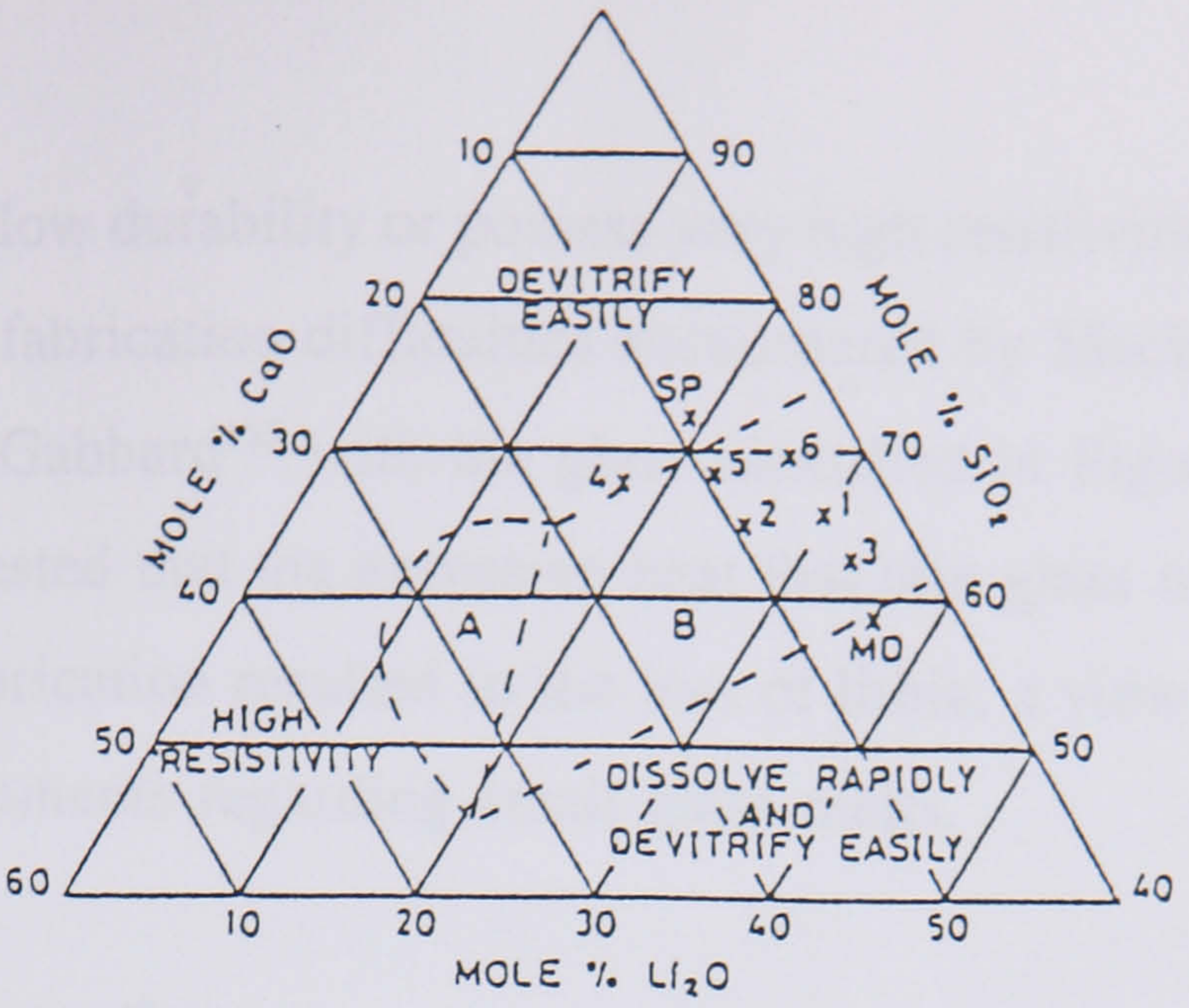
Soda lime glasses selected included the classic pH glass compositions of Hughes[11] N1, MacInnes and Dole[13] (Corning 015) N2 and N3, and the better pH glasses noted by Hubbard, Cleek and Rynders[148] in the hygroscopicity-pH response study, N4-N10. Lithia-lime glasses studied lay within the composition range recommended by Cary and Baxter[19] illustrated in Figure 7.1. Formulations lying outside this range were found by them to be subject

Table 7.1
Soda-lime Glasses

Glass no.	Wt %			Mol %		
	Na_2O	CaO	SiO_2	Na_2O	CaO	SiO_2
N1	20	8	72	19.4	8.6	72.0
N2	22	6	72(Q)	21.4	6.4	72.2
N3	22	6	72(S)	21.4	6.4	72.2
N4	25	10	65	24.2	10.7	65.1
N5	25	5	70	24.3	5.4	70.3
N6	30	5	65	29.2	5.4	65.4
N7	20	5	75	19.4	5.4	75.2
N8	15	10	75	14.5	10.7	74.8
N9	15	15	70	14.5	16.0	69.6
N10	20	10	70	19.4	10.7	69.9

Table 7.2
Lithia-lime Glasses

Glass no.	Wt %			Mol %		
	Li_2O	CaO	SiO_2	Li_2O	CaO	SiO_2
L1	17.5	5	77.5	29.8	4.5	65.7
L2	15	10	75	26.0	9.3	64.7
L3	20	5	75	33.4	4.4	62.2
L4	10	15	75	18.1	14.4	67.5
L5	12.5	10	77.5	22.2	9.4	68.4
L6	15	5	80	26.1	4.6	69.3



1-6, PREPARED GLASSES, L1 - L6.
SP, SOKOLOF AND PASSYNSKY GLASS
MO, MACINNES AND DOLE GLASS
A&B, USEFUL pH GLASS COMPOSITIONS
A, HIGH RESISTIVITY COMPOSITIONS.

FIG 7·1 Li_2O - CaO - SiO_2 GLASS COMPOSITIONS (AFTER CARY AND BAXTER(19))

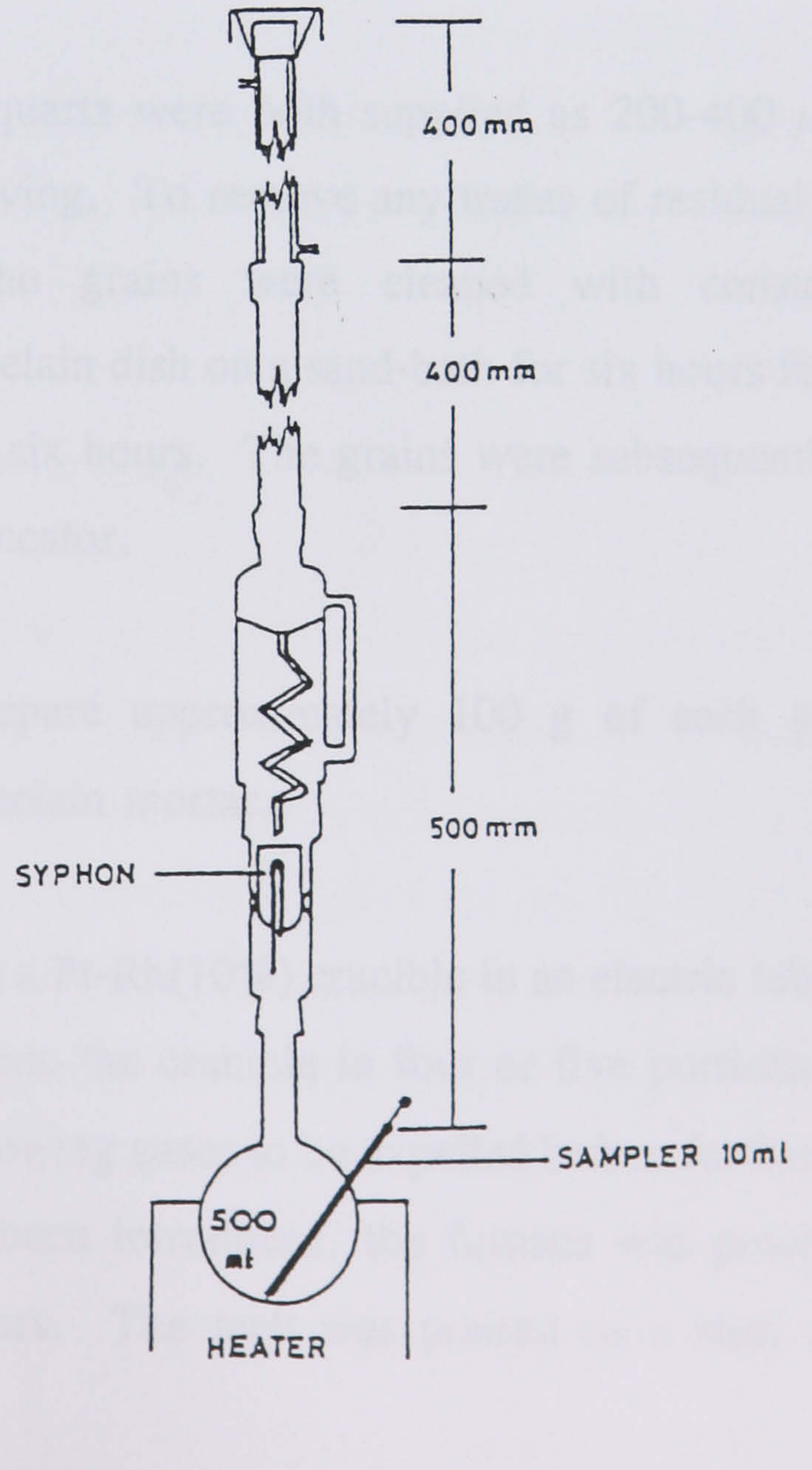


FIG 7.2 WATER LEACHING UNIT

to devitrification, low durability or possess very high resistivities, observations confirmed by the fabrication difficulties encountered by MacInnes and Dole[13] and by Dole and Gabbard[155] with the glass identified in Figure 7.1. as MD. Perley[20] has suggested that the excessive heat that thin glass membranes were subjected to in fabrication resulted in the loss of lithia, a view consistent with Eisenman's[156] comments regarding small glass melts.

7.2.2 Glass Preparation

Soda based glasses, N1-N4 were prepared within the Department of Glass Technology, University of Sheffield from 'AnalaR' grade sodium and calcium carbonate obtained from BDH, Poole, crushed Indian quartz (Q) from that Department's stock or crushed 'Spectrosil'(S) donated by Thermal Syndicate, Wallsend.

The anhydrous carbonates were dried in an air bath at 120°C for two hours, cooled and stored in a desiccator.

Crushed 'Spectrosil' and quartz were both supplied as 200-400 μm grains, fines were removed by sieving. To remove any traces of residual iron from the crushing process, the grains were cleaned with constant-boiling hydrochloric acid in a porcelain dish on a sand-bath for six hours followed by boiling water for a further six hours. The grains were subsequently dried at 120°C and stored in a desiccator.

Materials sufficient to prepare approximately 100 g of each glass were thoroughly mixed in a porcelain mortar.

Glass batches were fused in a Pt-Rh(10%) crucible in an electric tube furance. Powders were introduced into the crucible in four or five portions and fired initially at 900°-1000°C, allowing gases to be expelled before further addition. When all the powder had been introduced, the furnace was powered up to 1450°C-1500°C for six hours. The melt was poured on a steel marver as crude rods. When cool, these were broken into small pieces in brown paper, remelted for four hours, then cast into rods of some 3 - 6 mm diameter. On cooling they were stored in a dessicator.

Soda-based glasses, N5-N10 and the lithia-based glasses L1-L6 had previously been prepared for the Department in Newcastle using analytical grade chemicals where available and a high purity silica. Analytical grade lithium carbonate was not then available within the UK, but a low sodium content material had been obtained from the USA. These glasses were broken up, remelted and subsequently treated as the other glasses.

Although it is general practice to compare glasses on a mol % basis, at the time that, e.g. Hubbard Cleek and Rynders[148] studied these soda-lime glasses, compositions were commonly expressed in weight per cent. Both soda and lithia-based glasses of this study were prepared as weight per cent compositions. Mol % formulations are included in Tables 7.1 and 7.2.

Glass batch analyses were not undertaken, under the conditions in which the glasses were prepared analyses of alkali oxide and lime for glasses of similar compositions have been reported to be within 1 and 3% respectively of make-up component[44].

7.2.3. Glass-leaching Sample Preparation

Glass grains were prepared in the manner described by Rana and Douglas[44]. Glass rods were broken down into small pieces within folded brown paper. An approximately 10 g portion was crushed in a porcelain mortar by vertical pounding and sieved on phosphor-bronze BS sieves nos. 25 (0.635 mm) and 36 (0.421 mm) by gentle swirling, retaining those on the no. 36 sieve. Fines were discarded, the residue further crushed and sieved. Retained grains were dried at 120°C for three hours and stored in closed sample bottles in a dessicator over calcium chloride. Prior to use, grains were washed with carbon tetrachloride to remove any grease or dust, rinsed with ether and dried at 120°C for three hours.

7.2.4. Glass Electrode Preparation

Simple unscreened glass electrodes of the type described in Chapter 3 and illustrated in Figure 3.1 were prepared by blowing bulbs of about 10 mm diameter and 0.05 - 0.2 mm wall on stem glass, of 6 mm diameter and 0.7 mm wall, using an air-gas jet.

Although the author was not particularly skilled in glass-blowing techniques and totally new to working with soft glasses and fabricating glass electrodes, it was quite apparent that some of the glasses were more difficult to handle than others. These necessitated higher working temperature, or had a tendency to form bubbles, presumably entrapped air. Some developed inhomogeneities within the membrane, others readily devitrified. The aim during fabrication was to work the glass as quickly as possible at as low a temperature as practical.

After air-chilling, the better-looking electrode blanks were partly filled with 0.1m hydrochloric acid and assemblies completed with electrolytic silver, silver chloride electrodes as detailed in Chapter 3. Electrodes were conditioned and stored in deionized water, usually for three to four weeks prior to use. Membranes of glass N6 disintegrated after about ten days storage, and consequently electrodes of this glass were tested after four days conditioning. Electrodes fabricated from glass L3 disintegrated within two days, accordingly, further study of this composition was abandoned (preparative details of the electrodes are presented in Table 7.3).

7.3 EXPERIMENTAL PROCEDURE; ELECTRODE RESPONSE

Time-potential responses of the electrodes were determined against Pt-hydrogen gas electrodes by transfers from and to 0.1m hydrochloric acid and a series of test solutions in the manner described in Chapter 4. Test solutions used were

Table 7.3
Details of Glass Electrode Preparation

Glass no.	Composition wt %	Comparative working properties	Conditioning effect
N1	20-8-72	difficult, bubbles	
N2	22-6-72	fair, striation	
N3	22-6-72	fairly good, lot of heat	
N4	25-10-65	very good, few bubbles	
N5	25-5-70	soft, good, bubbles	
N6	30-5-65	fair, inhomogeneities	disintegrates
N7	20-5-75	very good	
N8	15-10-75	good, few bubbles	
N9	15-15-70	very good	
N10	20-10-70	very good	
L1	17.5-5-77.5	fair, bubbles, inhomogeneities	
L2	15-10-75	fair, bubbles, inhomogeneities	devitrify and disintegrate
L3	20-5-75	fair	
L4	10-15-75	fair, inhomogeneities	
L5	12.5-10-77.5	difficult, inhomogeneities	
L6	15-5-80	good	

5m hydrochloric acid, 0.01m borax and 0.1m and 1m sodium hydroxide.

0.1m hydrochloric acid was retained as the standard transfer solution in which the glass electrodes are regarded to be error free. This is certainly a reasonable assumption for commercial electrodes [3,5] and the results of this study suggest the same is true for the compositions examined.

The test solutions were chosen as relevant error data has been reported in one or more of these solutions for some electrodes of the glass compositions used.

Prior to use, the electrode stems were dried and coated with paraffin wax to suppress potential electrical leakage.

7.4 EXPERIMENTAL PROCEDURE; DURABILITY STUDY

7.4.1 Glass-leaching Unit

The leaching apparatus illustrated in Figure 7.2 is a modification of that used by Rana and Douglas[44] and is essentially a Soxhlet extraction assembly.

A unit comprised a 500 ml fused silica boiling flask provided with a sample extraction tube seated in a heating-mantle. Mounted on the flask was a glass tube, within which a fused silica syphon-crucible of 8.5 ml capacity was placed. Fitted on this extraction section was a wide-bore glass tube into which was sealed a spiral tube, through which refluxed water dropped onto the sample. A by-pass across the two sections of the tube permitted steam to pass upwards into the condenser tubes mounted above. Glassware was of 'Pyrex' and connections were standard ground-glass joints with PTFE sleeves. The assembly was wrapped in thermal insulating tape.

On boiling the water in the flask, steam passed via the by-pass into the condensers. Refluxed water entered the spiral and dropped into the syphon that filled and emptied on a 3.25 minute cycle. The design of the unit was such that the refluxed water and sample, both bathed in steam, were very nearly at the boiling-point, not less than 99.5°C. Products of leaching collected in the boiling flask.

7.4.2 Sample-leaching Procedure

Before commencing experimental runs, the apparatus was thoroughly cleansed. Unit sections were cleaned overnight in 20% hydrochloric acid, washed with deionized water and assembled. 250 ml of deionized water was placed in the flask, and the heater switched on. The assembly was run with refluxing water for two hours, cooled and emptied. This refluxing procedure was repeated six times. Between leaching runs, the assembly was rinsed six times with deionized water and a blank run of six hours carried out. Through a window in the insulation, syphoning was noted to commence about half-an-hour after switching on the heating mantle.

In leaching experiments 0.5 g glass grain samples wrapped in 44 mesh silver gauze, were introduced into the syphon about thirty minutes after syphoning commenced by removing the upper section and inserting. Analysis samples of the reaction products collected in the flask were taken with a 10ml borosilicate glass syringe through a stainless-steel needle sealed into the sampling tube. Samples were immediately transferred to stoppered polythene bottles for sodium and calcium analysis.

The duration of each experimental run was about 22 hours and reaction products were sampled approximately 1, 3, 5, 10 and 22 hours following introduction of the glass sample into the syphon.

7.5 CHEMICAL ANALYSIS OF EXTRACTS

Samples of the extraction products were analyzed for either sodium or lithium and calcium. As fused silica boiling-flasks were used and the pH of the contents continuously increased during a leaching run, any determination of silica would be misleading.

7.5.1 Sodium and Lithium Analysis

Sodium and lithium were analyzed directly using a Pye-Unicam SP900 flame-photometer. For sodium, the peak maximum at 589 nm was selected and for lithium that at 670.8 nm. A frosted glass filter and small slit-widths were found necessary for good results. An air-acetylene flame with gas pressures of 28 and 14 psig respectively was used.

No serious problems were encountered but it was essential to run standards frequently between samples to allow for the continual slight drift arising from thermal effects on the optical bench arrangement during operation.

Calibration solutions were prepared from 'AnalaR' grade sodium and lithium carbonates and minimum volumes of dilute hydrochloric acid, made up to volume with deionized water using grade 'A' borosilicate glassware and stored in polythene bottles.

Plots of both sodium and lithium were virtually linear up to 20 mg dm^{-3}. Interference from calcium was negligible up to 5 mg dm^{-3} and could be ignored, in agreement with the report of Williams and Adams[157]. Volume corrections were made to the analytical results. No allowance was applied for evaporative loss as this was determined to be no greater than 1% over a leaching run. Analytical accuracy was estimated to be about 5%.

7.5.2 Calcium Analysis

Attempts to use flame photometry at the peak maximum at 622 nm were abandoned by reason of severe interference from the high level of sodium in the soda-glass extracts. The waveband peak at 422 nm was too insensitive.

A very sensitive and highly selective spectrophotometric method using

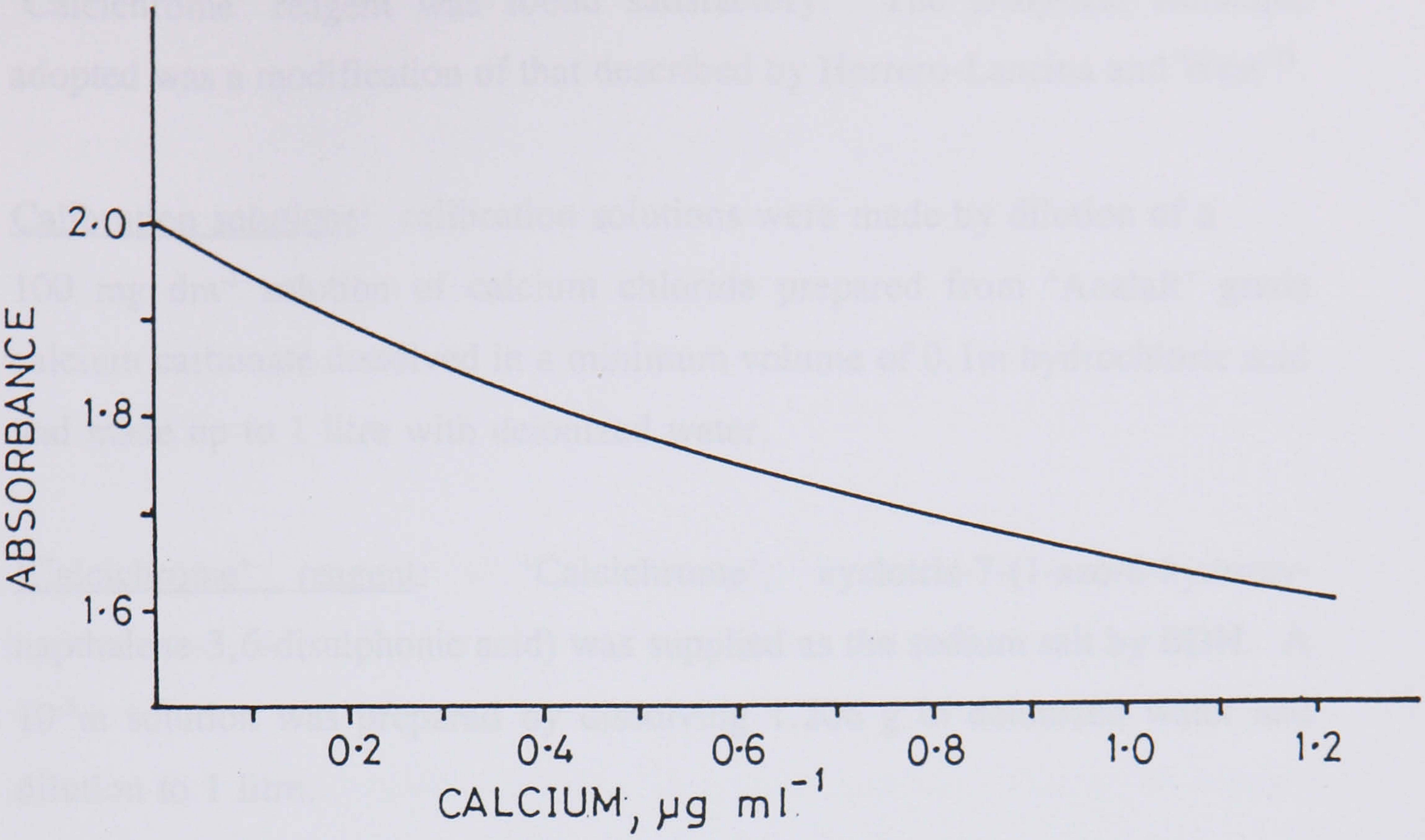


FIG 7·3 TYPICAL Ca CALIBRATION CURVE.

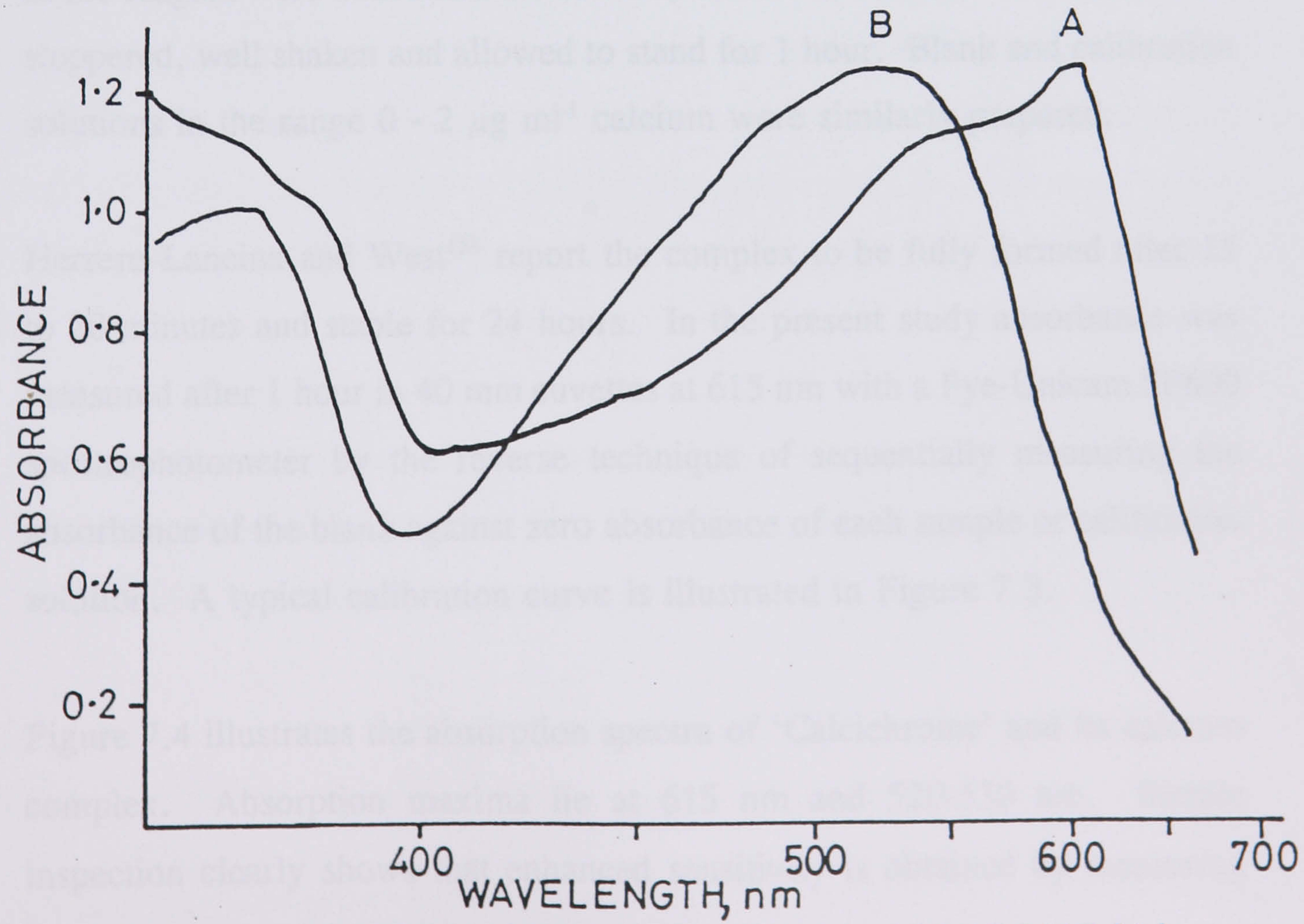


FIG 7·4 ABSORPTION SPECTRA OF CALCICHROME (A) AND Ca-CALCICHROME COMPLEX B (AFTER HERRERO-LANCINA AND WEST (158))

'Calcichrome' reagent was found satisfactory. The analytical technique adopted was a modification of that described by Herrero-Lancina and West[158].

Calibration solutions: calibration solutions were made by dilution of a 100 mg dm^{-3} solution of calcium chloride prepared from 'AnalaR' grade calcium carbonate dissolved in a minimum volume of 0.1m hydrochloric acid and made up to 1 litre with deionized water.

'Calcichrome' reagent: 'Calcichrome', cyclotris-7-(1-azo-8-hydroxy-napthalene-3,6-disulphonic acid) was supplied as the sodium salt by BDH. A 10^{-3}m solution was prepared by dissolving 1.206 g in deionized water and dilution to 1 litre.

pH12 buffer solution: prepared by adding, (a) 3.002 g glycine and 2.34 g sodium chloride dissolved in 500 ml water to, (b) 500 ml of 1.5×10^{-1}m sodium hydroxide. 'AnalaR' grade reagents were used.

Procedure: Aliquots ranging from 1 to 6 ml of extract were pipetted into 100 ml borosilicate volumetric flasks, 10 ml of the buffer solution and 2 ml of the reagent were added and the contents diluted to 100 ml. The flasks were stoppered, well shaken and allowed to stand for 1 hour. Blank and calibration solutions in the range 0 - 2 μg ml^{-1} calcium were similarly prepared.

Herrero-Lancina and West[158] report the complex to be fully formed after 15 to 20 minutes and stable for 24 hours. In the present study absorbance was measured after 1 hour in 40 mm cuvettes at 615 nm with a Pye-Unicam SP600 spectrophotometer by the reverse technique of sequentially measuring the absorbance of the blank against zero absorbance of each sample or calibration solution. A typical calibration curve is illustrated in Figure 7.3.

Figure 7.4 illustrates the absorption spectra of 'Calcichrome' and its calcium complex. Absorption maxima lie at 615 nm and 520-530 nm. Simple inspection clearly shows that enhanced sensitivity is obtained by measuring decrease of the reagent, hence this reverse measurement technique was used.

Improved calibration linearity was obtained by decreasing the reagent concentration by 40% of that recommended by Herrero-Lancina and West[158]. Analytical accuracy was estimated to be about 5%.

7.6 RESULTS

Time-potential data for the soda-based electrodes are illustrated in Figures 7.5 to 7.8 and for the lithia-based in Figures 7.9 to 7.12. Final error results are collated in Tables 7.4 and 7.5 respectively together with the electrode resistances and their emfs in 0.1m hydrochloric acid against the Pt-hydrogen gas electrode. For the soda-based electrodes Table 7.4 also includes the 1 h hygroscopicities for glasses of the sample compositions determined by Hubbard, Cleek and Rynders[148].

Electrodes prepared from glasses N9 (15-15-70) and L4 (10-15-75) were not tested as their extremely high resistances precluded electrochemical measurements. The rapid disintegration of electrodes of glass L3 (20-5-75) prevented any useful testing of this composition.

Alkali extraction results for the soda-based glasses are plotted in Figure 7.13 and for the lithia-based in Figure 7.14. Lime-extraction for both series of glasses are illustrated in Figure 7.15. For ease of display, leaching results are plotted as 'weight per cent component extracted' rather than the more common 'weight per gram glass extracted'.

Results are presented in both units in Table 7.6 for the soda-based glasses and in Table 7.7 for the lithia-based glasses. Extraction ratios of soda:lime and lithia:lime are given in Tables 7.8 and 7.9 respectively.

Glass L4 was omitted from the leaching experiments. Calcium analysis samples of N6 and L1 extracts were not done.

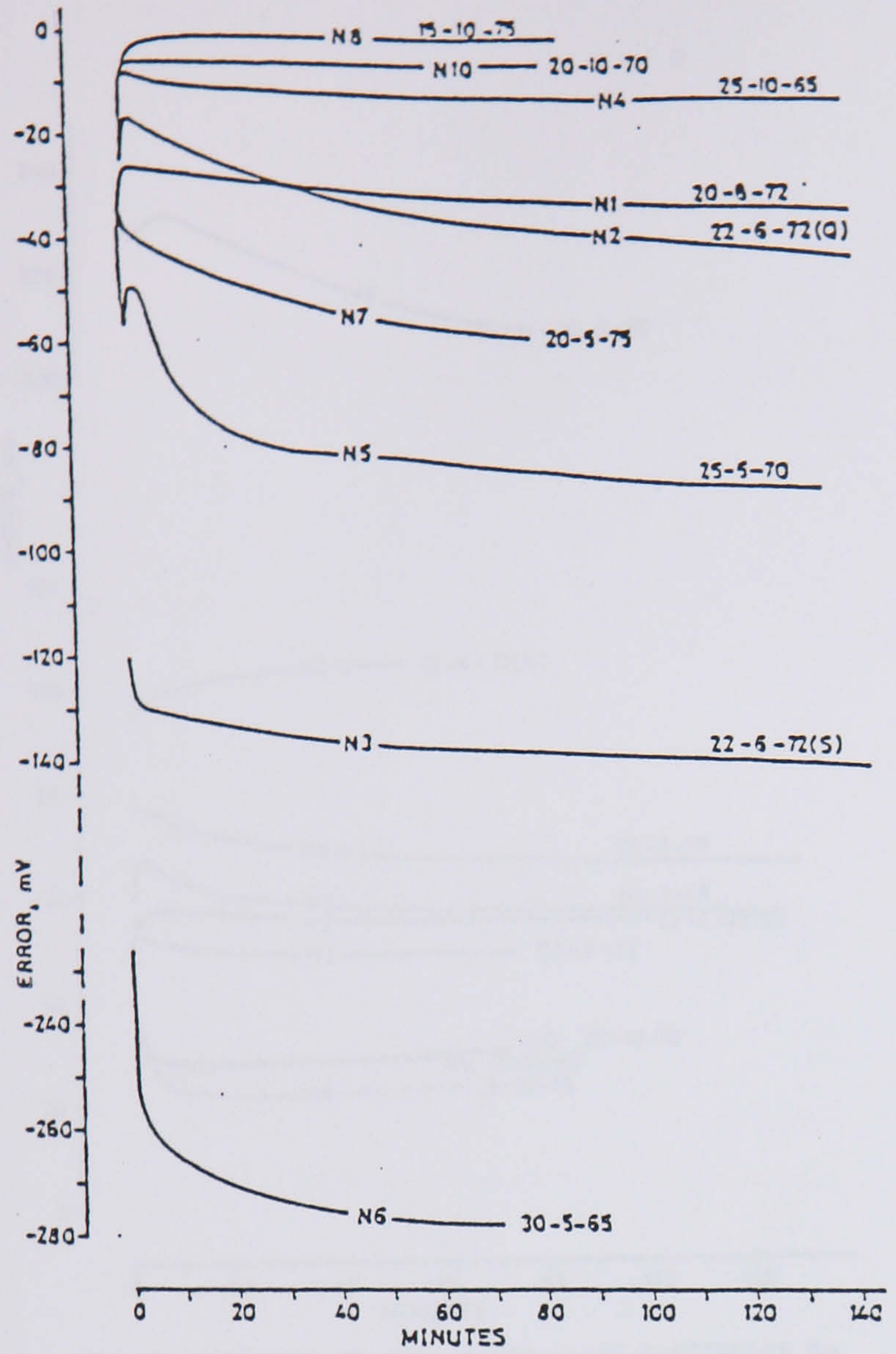


FIG 7.5A RESPONSE OF SODA-BASED GLASS ELECTRODES ON TRANSFER FROM 0·1m HCl INTO 5m HCl.

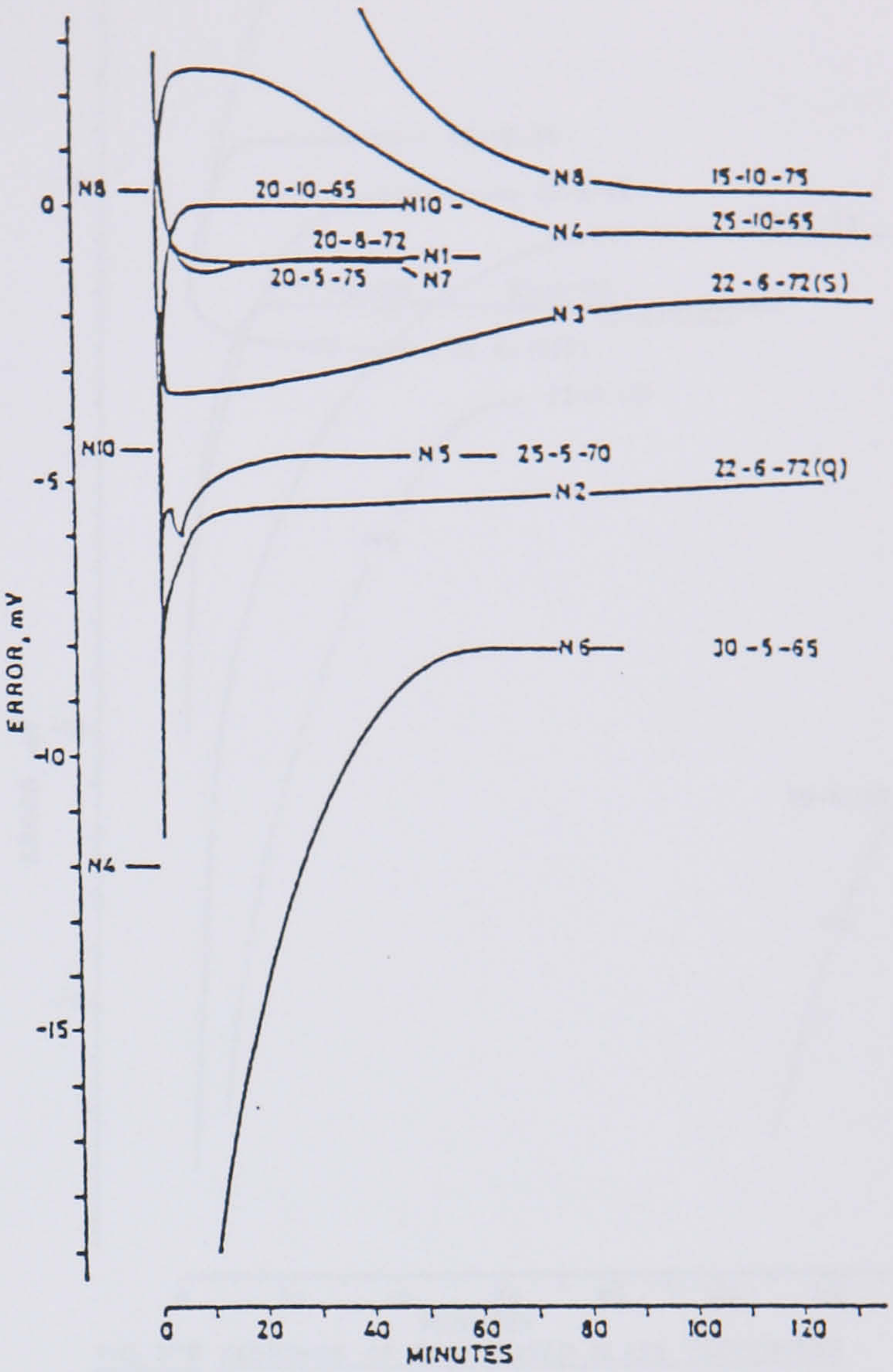


FIG. 7·5B RESPONSE OF SODA-BASED GLASS ELECTRODES ON TRANSFER FROM 5m HCl INTO 0·1m HCl.

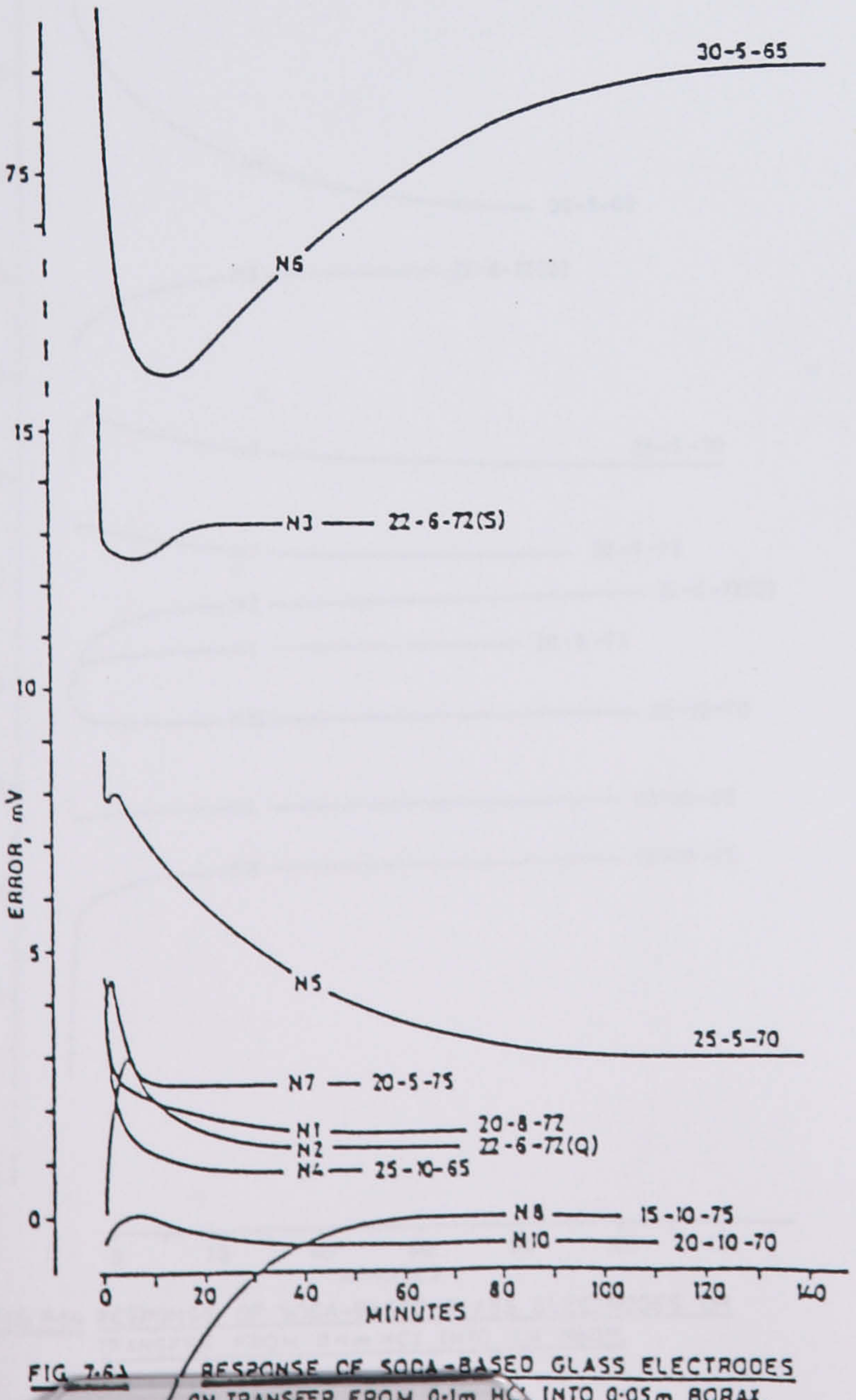


FIG. 7·6A RESPONSE OF SODA-BASED GLASS ELECTRODES ON TRANSFER FROM 0·1m HCl INTO 0·05m BORAX.

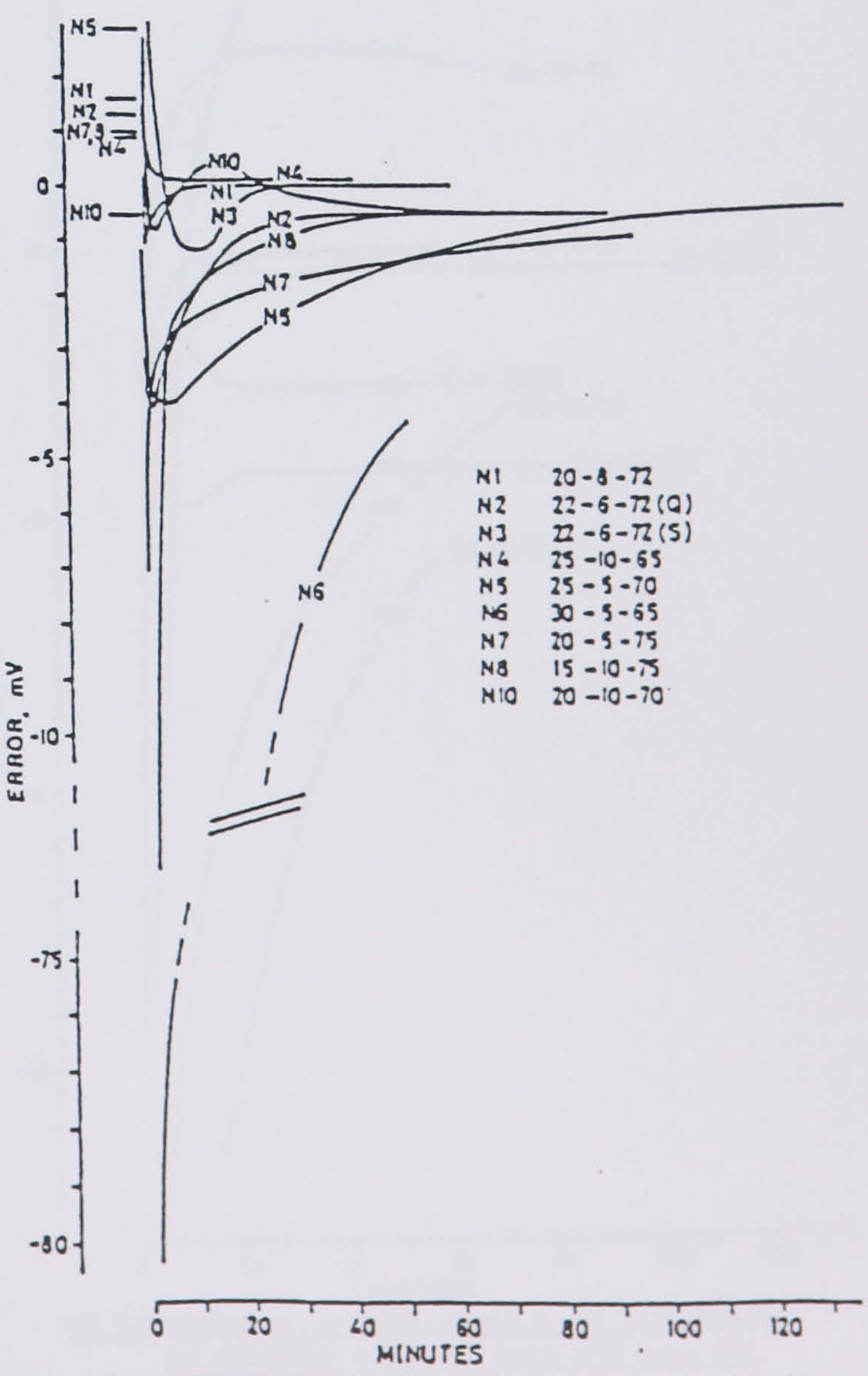


FIG. 7·6B RESPONSE OF SODA-BASED GLASS ELECTRODES ON TRANSFER FROM 0·05m BORAX INTO 0·1m HCl.

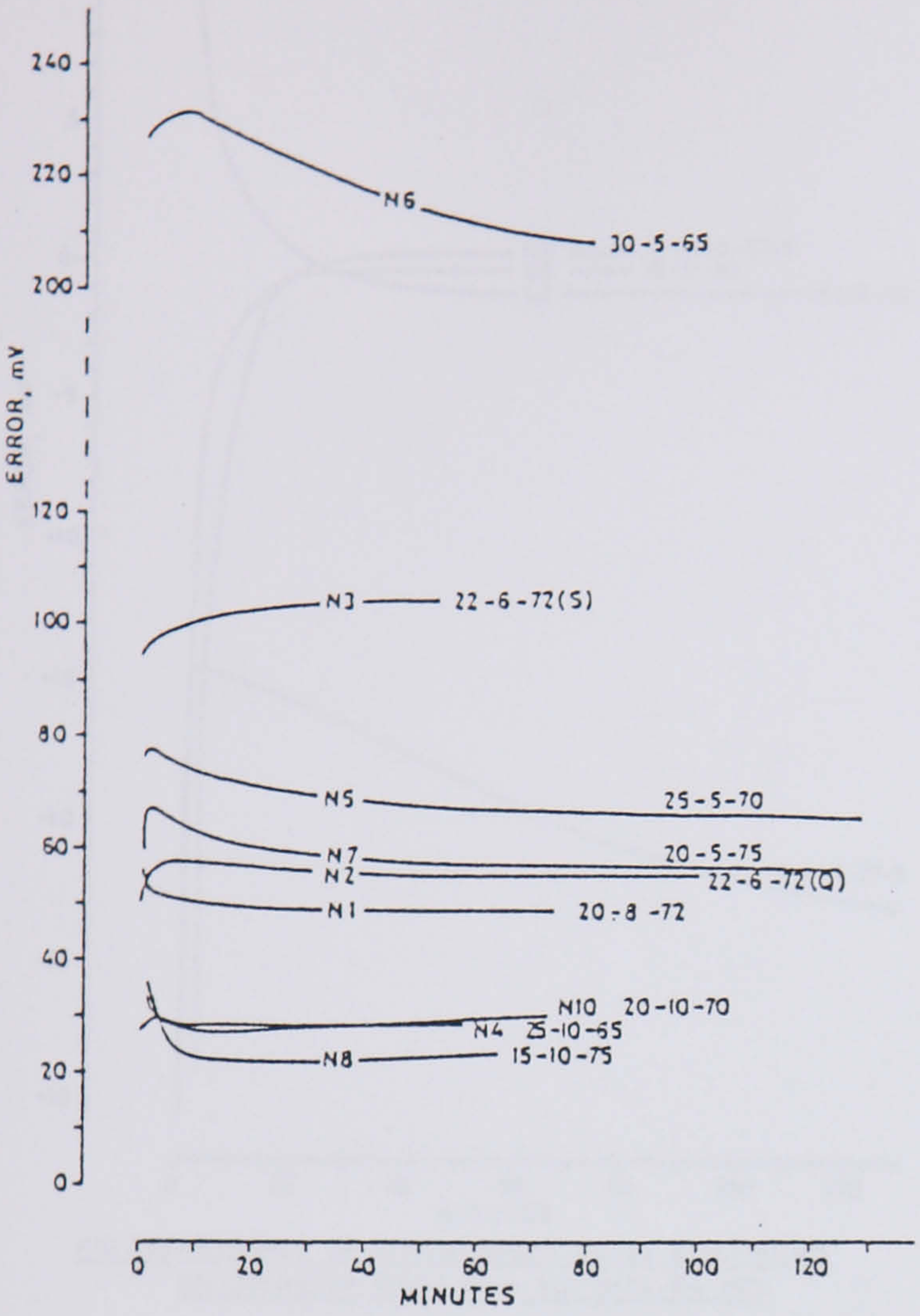


FIG. 7·7A RESPONSE OF SODA BASED GLASS ELECTRODES ON TRANSFER FROM 0·1m HCl INTO 0·1m NaOH.

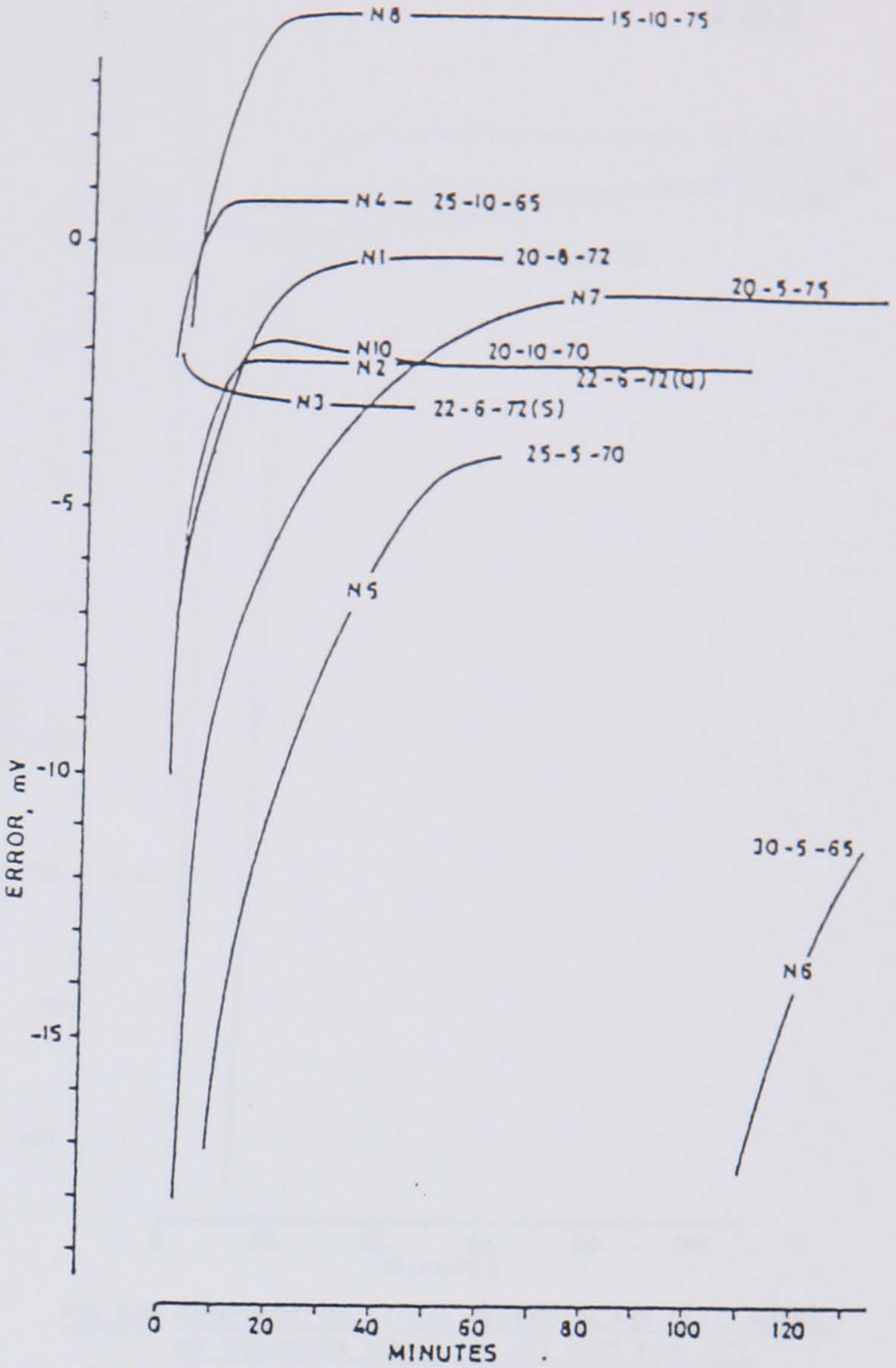


FIG. 7·7B RESPONSE OF SODA-BASED GLASS ELECTRODES ON TRANSFER FROM 0·1m NaOH INTO 0·1m HCl.

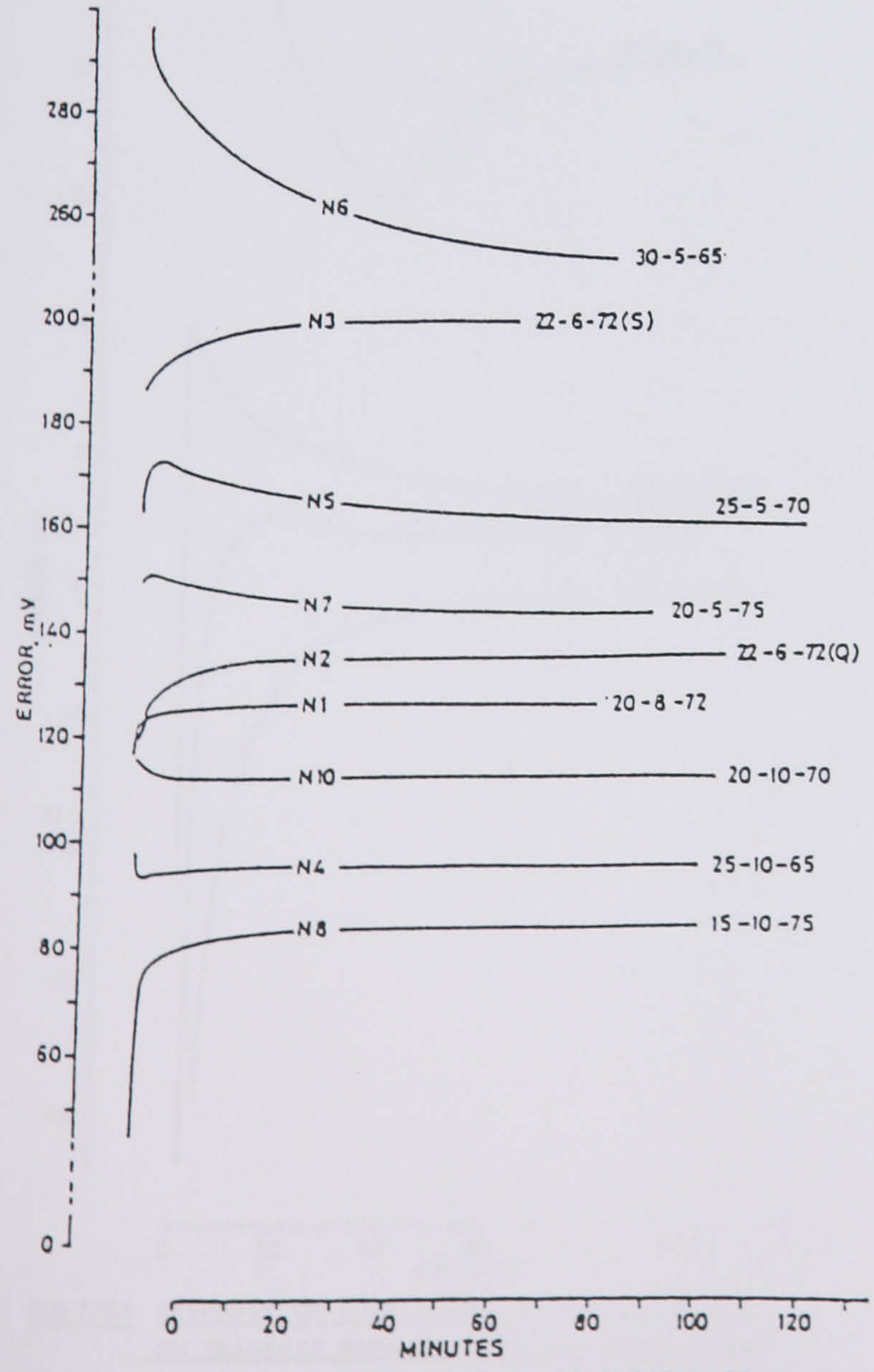


FIG 7·8A RESPONSE OF SODA-BASED GLASS ELECTRODES ON TRANSFER FROM 0·1m HCl INTO 1M NaOH.

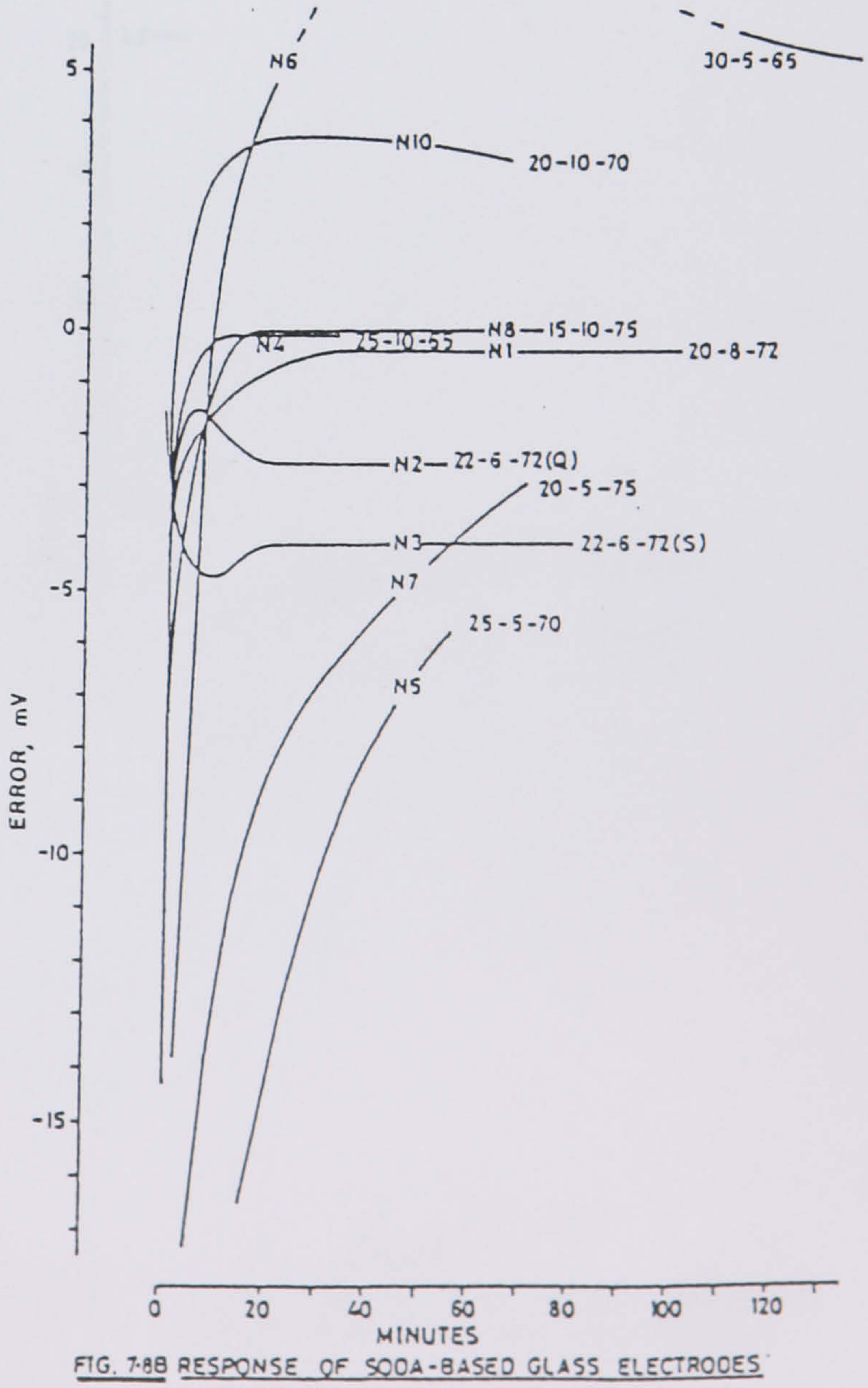


FIG. 7·8B RESPONSE OF SODA-BASED GLASS ELECTRODES ON TRANSFER FROM 1m NaOH INTO 0·1m HCl.

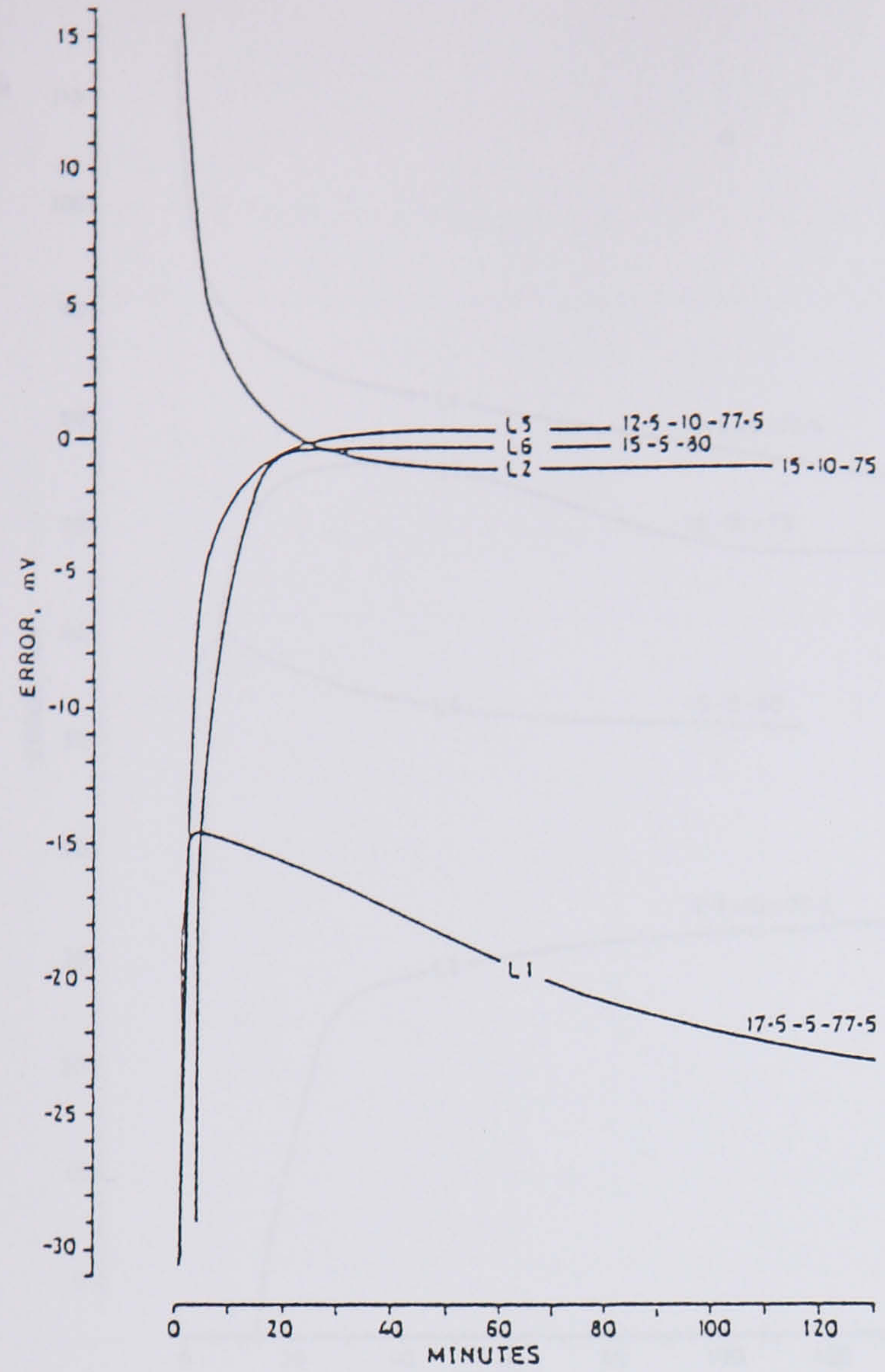


FIG 7·9A RESPONSE OF LITHIA-BASED GLASS ELECTRODES ON TRANSFER FROM 0·1m HCl INTO 5m HCl.

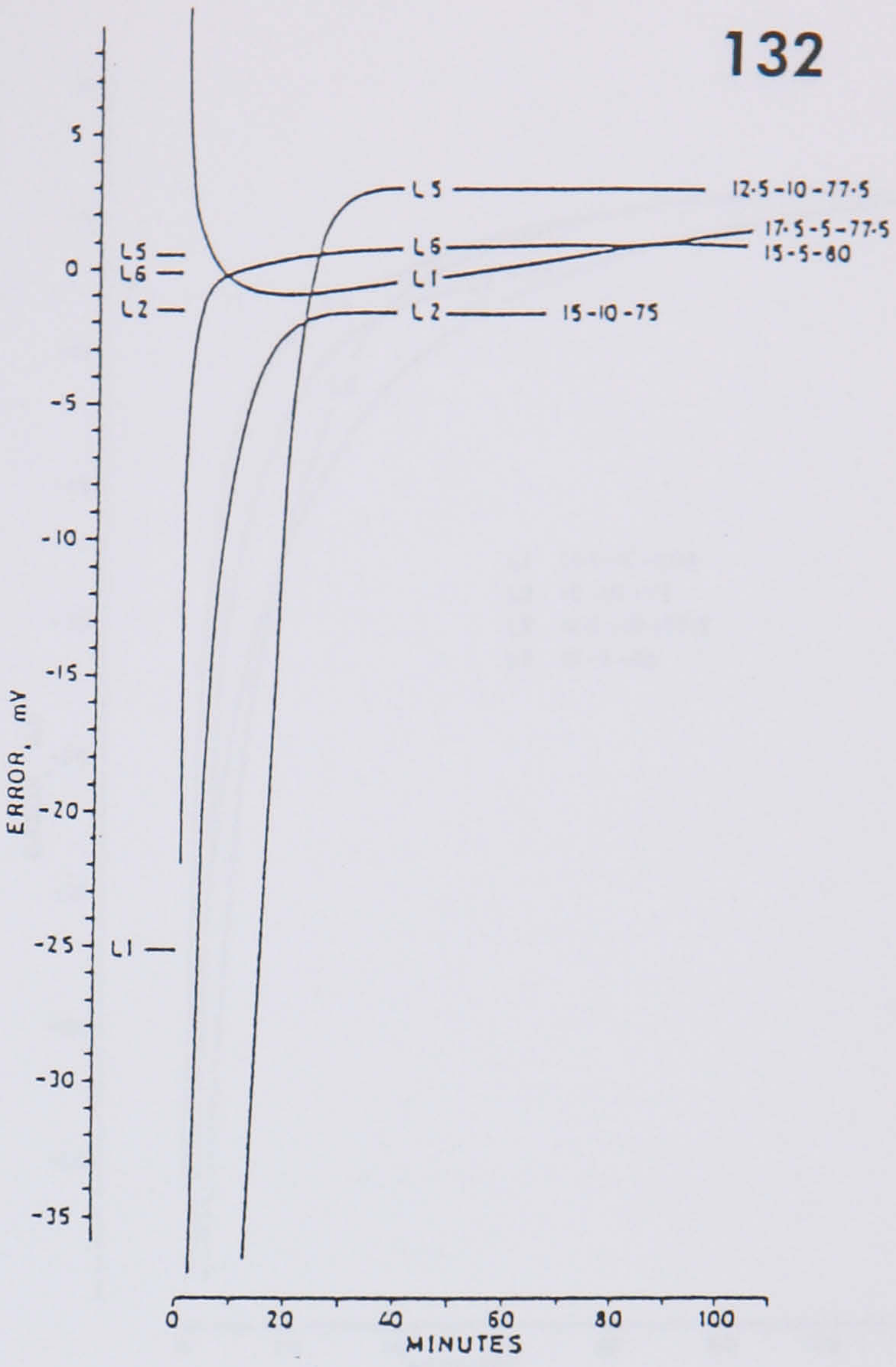


FIG. 7·9B RESPONSE OF LITHIA-BASED GLASS ELECTRODES ON TRANSFER FROM 5m HCl INTO 0·1m HCl.

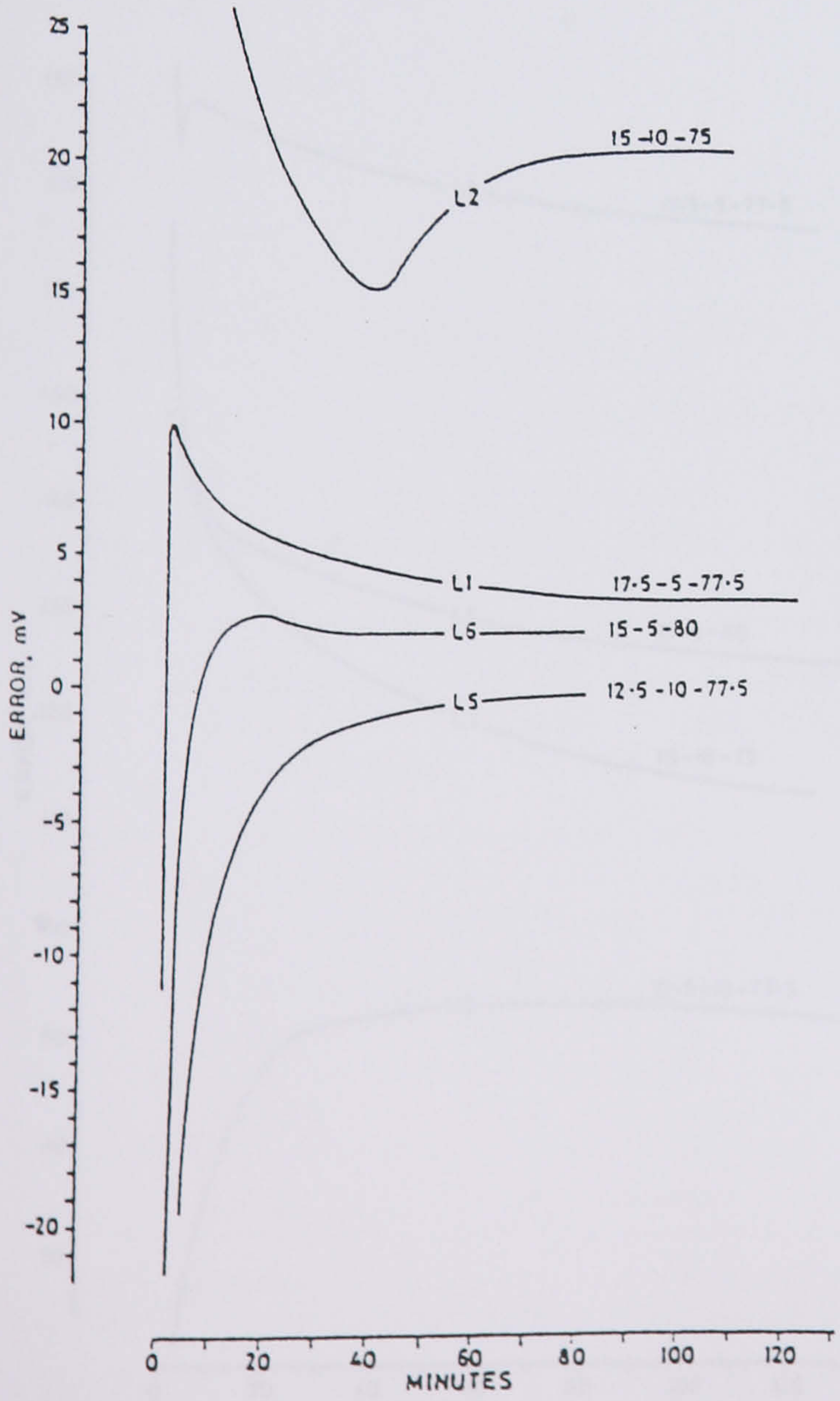


FIG. 7·10A RESPONSE OF LITHIA-BASED GLASS ELECTRODES ON TRANSFER FROM 0·1m HCl INTO 0·05m BORAX.

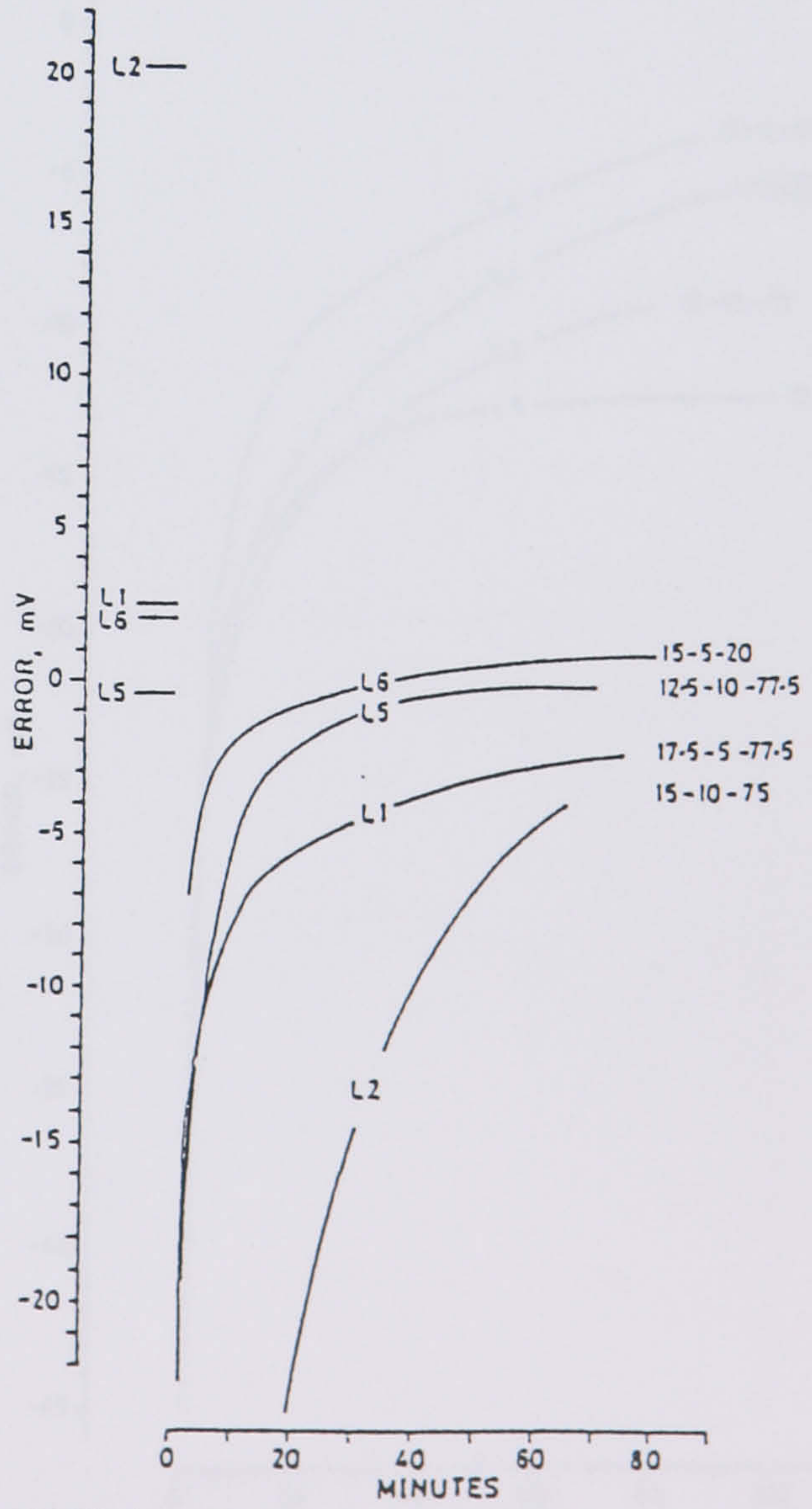


FIG. 7·10B RESPONSE OF LITHIA-BASED GLASS ELECTRODES ON TRANSFER FROM 0·05m BORAX INTO 0·1m HCl.

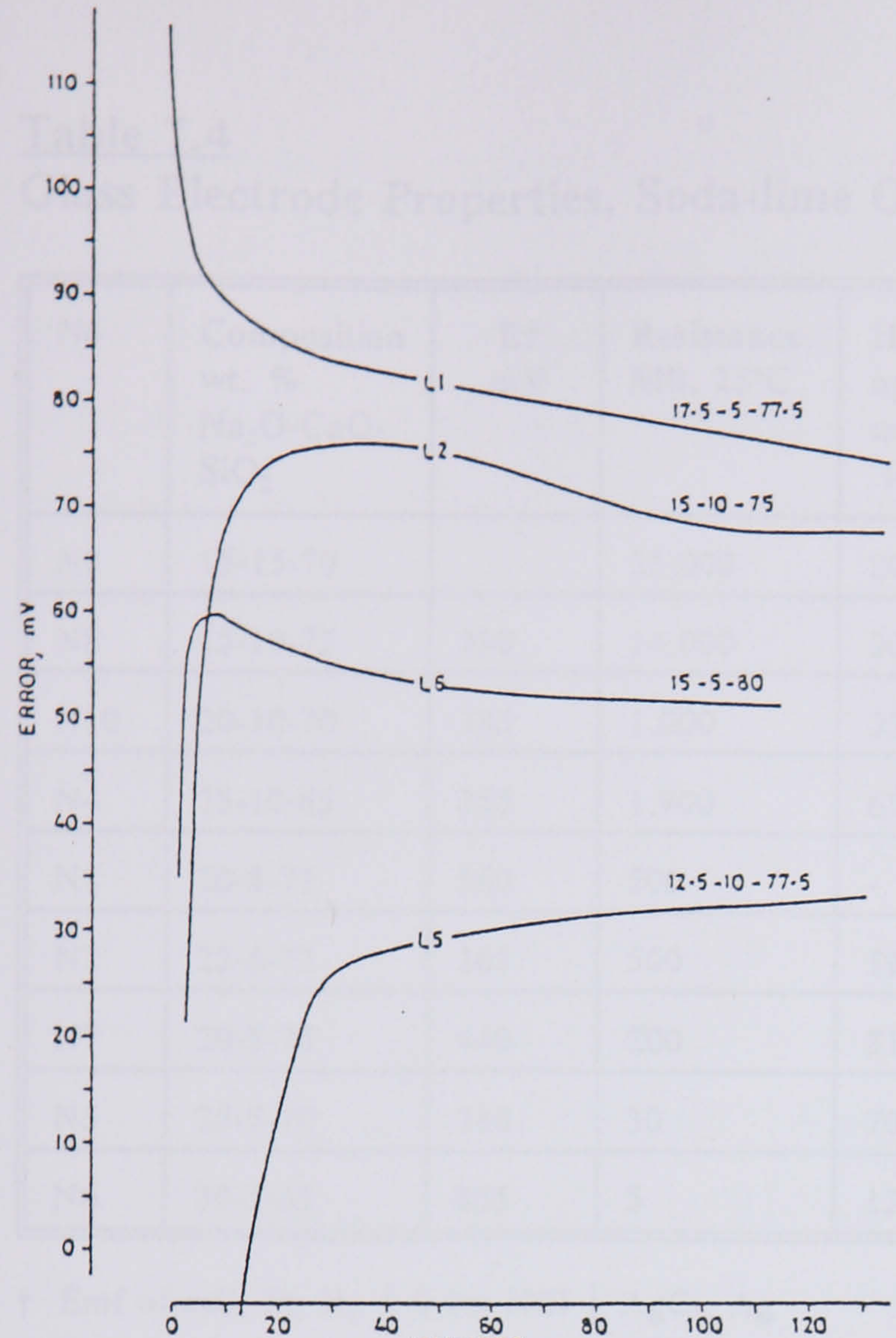


FIG. 7·11A RESPONSE OF LITHIA-BASED GLASS ELECTRODES ON TRANSFER FROM 0·1m HCl INTO 0·1m NaOH.

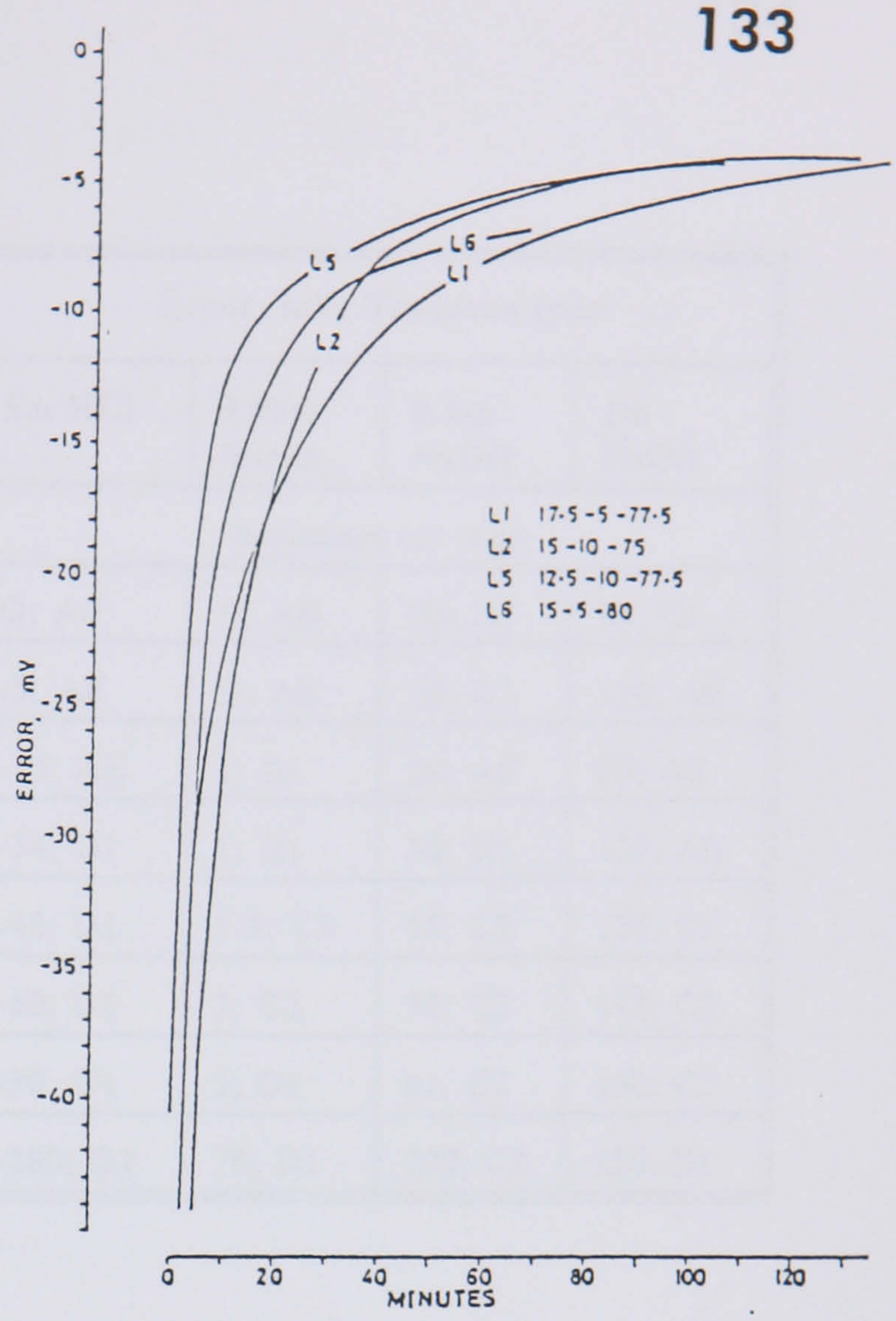


FIG. 7·11B RESPONSE OF LITHIA-BASED GLASS ELECTRODES ON TRANSFER FROM 0·1m NaOH INTO 0·1m HCl.

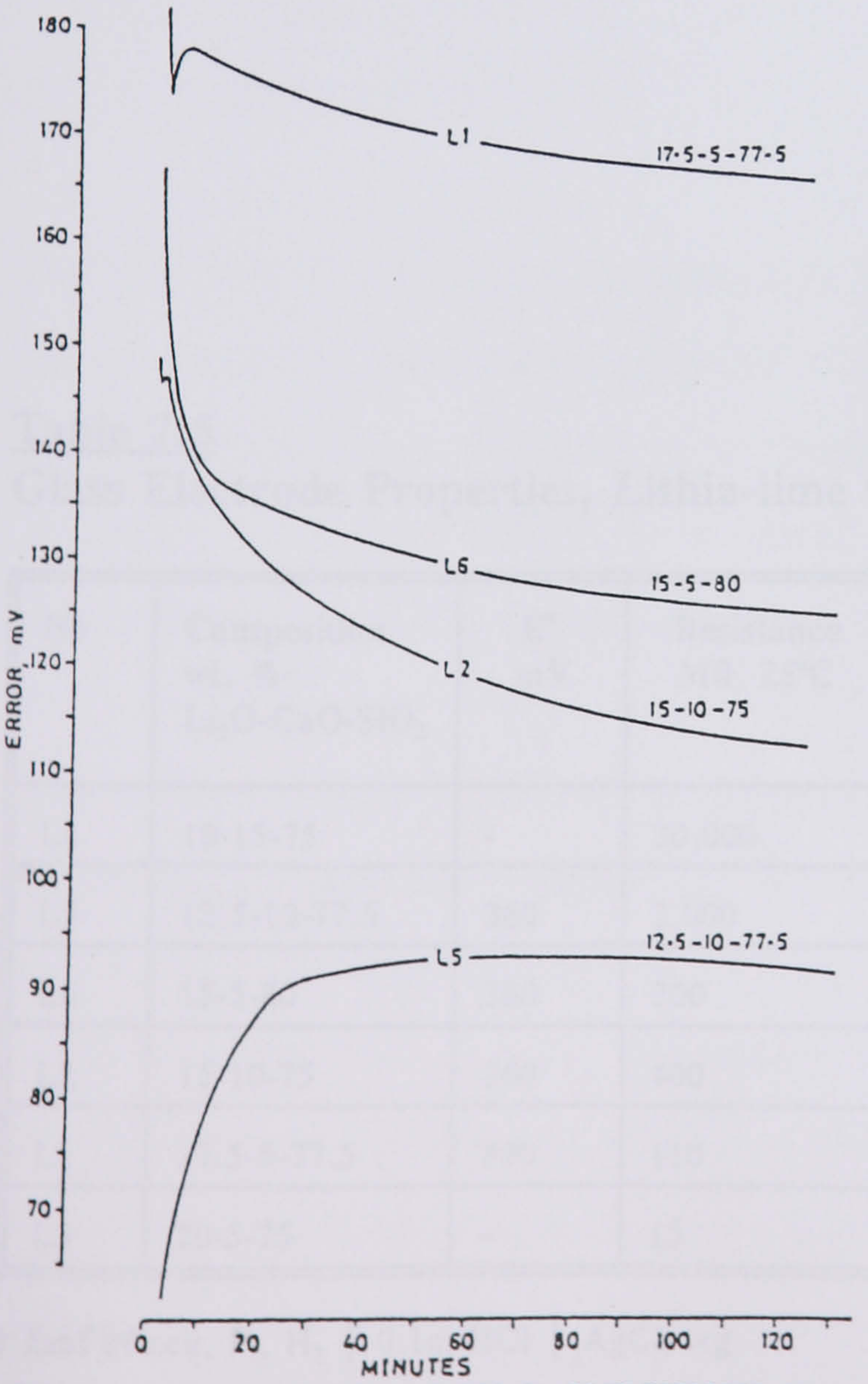


FIG. 7·12A RESPONSE OF LITHIA-BASED GLASS ELECTRODES ON TRANSFER FROM 0·1m HCl INTO 1m NaOH.

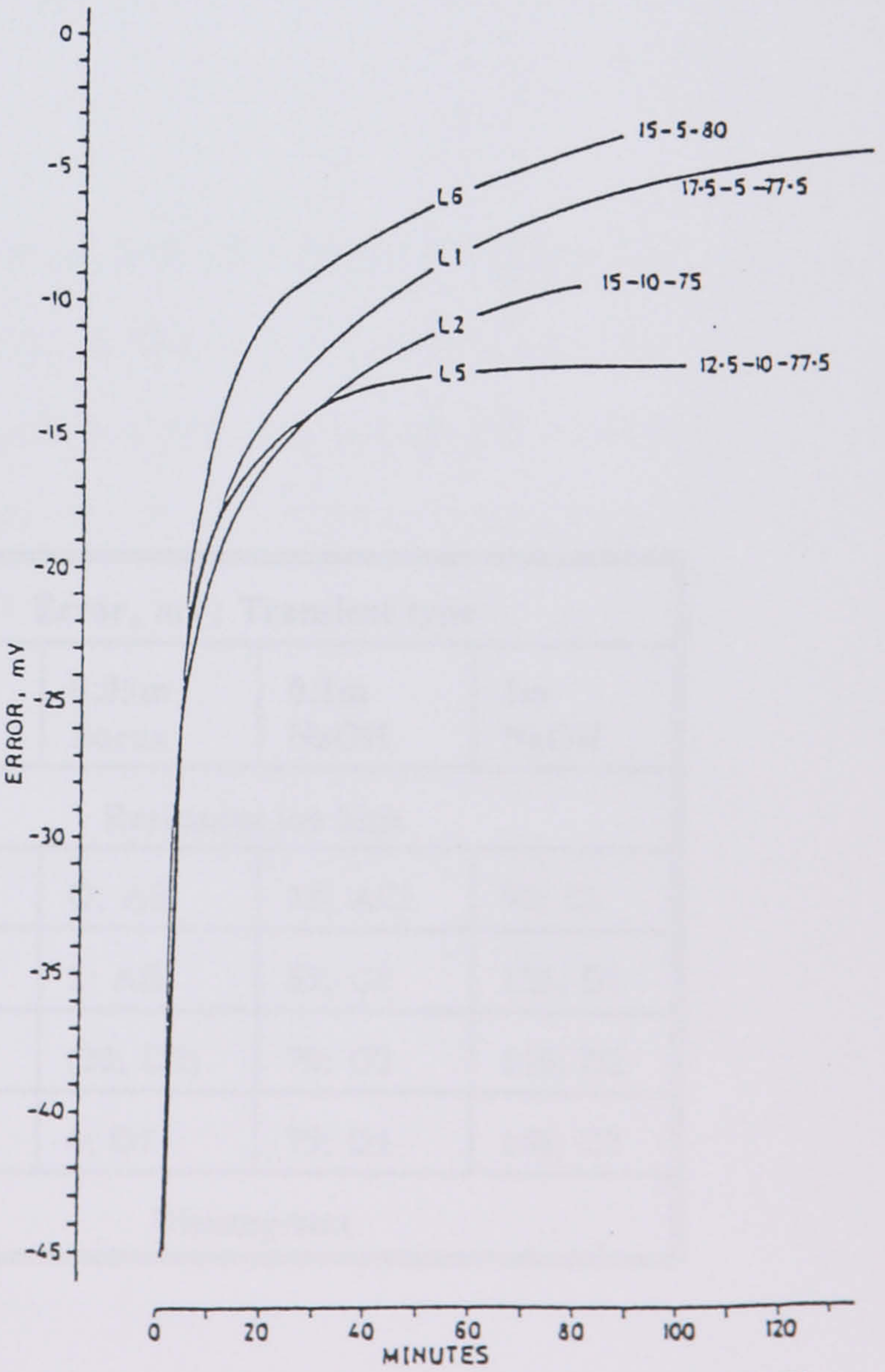


FIG. 7·12B RESPONSE OF LITHIA-BASED GLASS ELECTRODES ON TRANSFER FROM 1m NaOH INTO 0·1m HCl.

Table 7.4
Glass Electrode Properties, Soda-lime Glasses

No	Composition wt. % Na_2O-CaO-SiO_2	E† mV	Resistance MΩ, 25°C	Hygroscopicity mg. cm^{-3} Ref 148	Error, mV; Transient type			
					5m HCl	0.05m Borax	0.1m NaOH	1m NaOH
N9	15-15-70		25,000	20	Resistance too high			
N8	15-10-75	390	14,000	30	0; AB	0; AB	20; D2	85; C1
N10	20-10-70	385	1,000	35	-5; AE	0; AB	25: D2	110; AE
N4	25-10-65	365	1,900	67	-13; AE	1; D1	29; AE	95; AE
N1	20-8-72	360	500	-	-34; D1	1; D1	50; D1	125; AE
N2	22-6-72	365	500	59	-42; D1	1.5; C2	55; C2	135; C1
N7	20-5-75	440	200	51	-60; D1	2; C2	56; C2	145; C2
N5	25-5-70	380	30	70	-90; D1	3; D1	61; C2	160; C2
N6	30-5-65	825	5	137	-280; D1	78; D1	200; C2	250; D1

† Emf of cell, Pt, H_2 | 0.1m HCl | AgCl, Ag

Table 7.5
Glass Electrode Properties, Lithia-lime Glasses

No	Composition wt. % Li_2O-CaO-SiO_2	E† mV	Resistance MΩ, 25°C	Error, mV; Transient type			
				5m HCl	0.05m Borax	0.1m NaOH	1m NaOH
L4	10-15-75	-	30,000	Resistance too high			
L5	12.5-10-77.5	360	2,000	0; AB	0; AB	35; AC1	90; C1
L6	15-5-80	360	200	0; AB	2: AE	55; C2	125; D1
L2	15-10-75	360	400	0; AB	(20; D2)	70; C2	110; D2
L1	17.5-5-77.5	390	110	-23; D2	4; D1	75; D1	165; C2
L3	20-5-75	-	15	Disintegrates			

† Emf of cell, Pt, H_2 | 0.1m HCl | AgCl, Ag

Potential-time and leaching results for glass N3 are presented in Figures 7.5 to 7.8 and Figures 7.13 and 7.15 respectively, to illustrate its anomalous properties. The glass was probably adulterated during fusion, an opinion based on the observed working properties of the glass noted whilst blowing the electrode bulbs, as well as on these results. The glass is of the same composition as glass N2 (22-6-72) and differs only in the variety of silica used 'Spectrosil'(S) rather than Indian quartz (Q). It is virtually inconceivable that the 'Spectrosil' was contaminated, nevertheless, the possibility cannot be discounted as this is the only glass for which it was used. It is, of course, possible that the formulation was incorrectly prepared but this is regarded as unlikely. The composition is that of Corning 015 and comparison of the response of electrode N3 with the reported properties of Corning 015, e.g. the response in borax buffer solution of electrode 23 presented in Table 5.12, depicts its deviant behaviour, whereas that of glass N2 is in good agreement. The durability of glass N3 is significantly poorer than would be expected from its composition by comparison with glass N2 and other glasses examined, as is readily apparent in Figure 7.13. On these various grounds, glass N3 is regarded to be corrupted and in consequence dismissed from further consideration.

7.7 DISCUSSION

For the soda-based glasses the electrode error response data collected in Figure 7.4 are presented in the general order of increasing error in the test solutions. As the electrode resistances decrease in substantially the same sequence, glass N9 which possessed the highest resistivity is placed at the head of the list, although testing of electrodes of this glass composition was impractical.

Inspection of Table 7.4 shows a distinct relationship between glass composition and electrode performance. Electrodes of glasses containing between 15 and 25% soda and 5 and 10% lime display in 0.05m borax solution zero, or quite modest errors of up to no more than 3 mV. The errors increase with both increasing soda and/or decreasing lime content. As alluded to earlier, the resistivity of glass N9 (15-15-70) is too high for it to be useful as an electrode glass, at least at ambient temperature. Glass N6 (30-5-65) too is unsatisfactory for electrode use, exhibiting very large errors, e.g. an 80 mV positive error between 0.1m hydrochloric acid and 0.05m borax, as well as its rather rapid disintegration on storage in water.

Electrode performance in the test solutions is in good agreement with published data. Manov[112] reported the error of Corning 015 electrodes, of the same nominal composition as glass N2 (22-6-72), in 0.05m borax to be 3.5 mV, about twice the 1.5 mV error shown by electrode N2. Kelm[159], however, has disclosed that commercial batches of Corning 015 were occasionally contaminated by impurities from the fusion pots resulting in inferior glass electrodes. For the same electrode composition, MacInnes and Dole[13] reported a stable 32 mV error in 0.1m sodium hydroxide solution, some 25 mV lower than the error illustrated in Figure 7.7A for electrode N2. They had examined the reponse characteristics of a series of soda-lime glasses of composition Na_2O 20-24; CaO 4-8; SiO_2 70-74 and concluded the composition 22-6-72 to be superior to all others in attaining the lowest error in 0.1M sodium hydroxide. They reported a greater error with the Hughes[11] composition 20-8-72, whereas in this study electrode N1 of that composition displayed marginally smaller errors in all test solutions. For the other glasses studied, their paper shows errors that increase with both increasing soda and/or decreasing lime content.

An error of 180 mV was reported by Cary and Baxter[19] for the Corning 015 electrode composition in 1M sodium hydroxide solution, some 45 mV greater than the error shown by electrode N2 of the same nominal composition illustrated in Figure 7.5A.

Errors varying between -40 and -120 mV were observed 30 minutes after transfer into 5m hydrochloric acid for commercial Corning 015 electrodes by Caudle[3], rather greater than the 30 minute error of - 25 mV of electrode N2 shown in Figure 7.5, but he indicated the error response in strong hydrochloric acid solutions was dependent on age and past usage.

There is some variance with the electrode responses reported by Shul'ts *et al.*[160] for soda-lime glasses of comparable, but not identical compositions.

Their electrode 20.6 - 4.7 - 74.8 is reported to be error-free between pH -1 and pH 9.5, whereas in this work the similar electrode N7 (20-5-75) exhibits an error of - 60 mV in 5m hydrochloric acid, pH < 0 and a small error of 2 mV in 0.05m borax, pH 9.18 on transfers from 0.1m hydrochloric acid. Otherwise agreement with the response of the other glass compositions they studied is good.

As apparent in this study, their data show both increasing error and decreasing resistivity with increasing soda and/or decreasing lime content.

Hubbard, Cleek and Rynders[148] compared the hygroscopicities of a wide range of soda and soda-lime compositions with their electrode responses and concluded that only those soda-lime glasses absorbing between approximately 30 and 75 mg cm^{-3} h^{-1} water developed a satisfactory pH response between about pH 2-12. Glasses with higher hygroscopicities exhibited errors and low durabilities; those with lower hygroscopicities were highly durable and displayed no noticeable surface swelling in buffer solutions between about pH2-9 at 80°C. These highly durable glasses were reported not to develop the theoretical response, however, electrodes of these compositions possess high resistances and they suspected that the input impedance of their instrumentation was too low. Such glasses may, nevertheless, be suitable for use at elevated temperatures as has recently been demonstrated by Kritsunov and MacDonald[161] for 'Pyrex', a highly durable glass quite without a pH function at ambient temperature[162], in dilute sulphuric acid solutions between 200° and 250°C, in which its pH function was Nernstian.

The hygroscopicities determined by Hubbard *et al.*[148] are tabulated in Table 7.4 alongside the electrode response data of this study for some of their soda-lime compositions, and demonstrate agreement with their general conclusions. Soda extraction results illustrated in Figure 7.13 and summarized in Table 7.6 are, neglecting data for glass N9, in accord with the hygroscopicity data of Hubbard *et al.*[148] in that the rate of soda extraction rises with increasing water absorption and is directly related to increasing electrode response error. Although the hygroscopicity of glass N9 is low, soda extraction appears comparatively high. This is, however, consistent with the results of Rana and Douglas[44].

No simple correlation of the lime extraction results presented in Figure 7.15 and Table 7.6 with glass composition, hygroscopicity or electrode response is apparent.

A distinct relationship is evident between the electrode response error and the weight ratio of soda:lime extracted for the glass compositions collected in Table 7.8. For the low hygroscopicity glass N9 (15-15-70) the extract ratio increases over the 22 hour leaching period approaching that of the weight ratio of the glass. Rana and Douglas[44] have shown that the silica:lime ratio of leached extract of soda-lime glasses is constant at the same ratio as that of the glass, indicating that lime passes into solution as the surface silicate structure is destroyed. The examination by Lengyel and Dobos[38] for the distribution of calcium in the surface layers, developed in water at 40°C, for the relatively low durability soda-lime glass, 28.75-3.75-67.5(28-4-68 mol %), was in agreement with the conclusions of Rana and Douglas[44]. Covington and Flynn[163], however, have established, by an ion-beam sputtering-spectroscopic study of the gel layers developed by soda-lime (15-5-70 mol%) and lithia-lime (20-5-75 mol %) glasses, that the surface layer is calcium depleted, indicating that calcium is leached into solution by an ion-exchange mechanism. It would appear that for glass N9 soda is extracted solely with dissolution of the silaceous surface and suggesting that the glass grains are initially surface-alkali deficient.

Soda:lime ratios for the other glasses are seen to be substantially constant during the 5 to 22 hour leaching, and for glasses N2 (22-6-72), N7 (20-5-75) and N5 (25-5-70) considerably higher than the glass ratio, signifying diffusion of sodium ions from the bulk glass to the surface and its solution at a more rapid rate than the dissolution of the surface layers. This behaviour is in marked contrast to the extraction ratios of glasses N8 (15-10-75), N10 (20-10-70), N4 (25-10-65) and N1 (20-8-72) for which soda:lime extraction ratios are only slighly higher than the glass ratios. As suggested for glass N9 (15-15-70), the increasing ratio for glass N4 during the progress of leaching may be due to an initial alkali deficient layer, but the lime extraction data for this glass shown in Figure 7.15 do, perhaps, appear suspect.

Inspection of Figure 7.13 and Table 7.6 show that for the better electrode compositions studied, which not surprisingly include the Corning 015 formulation,

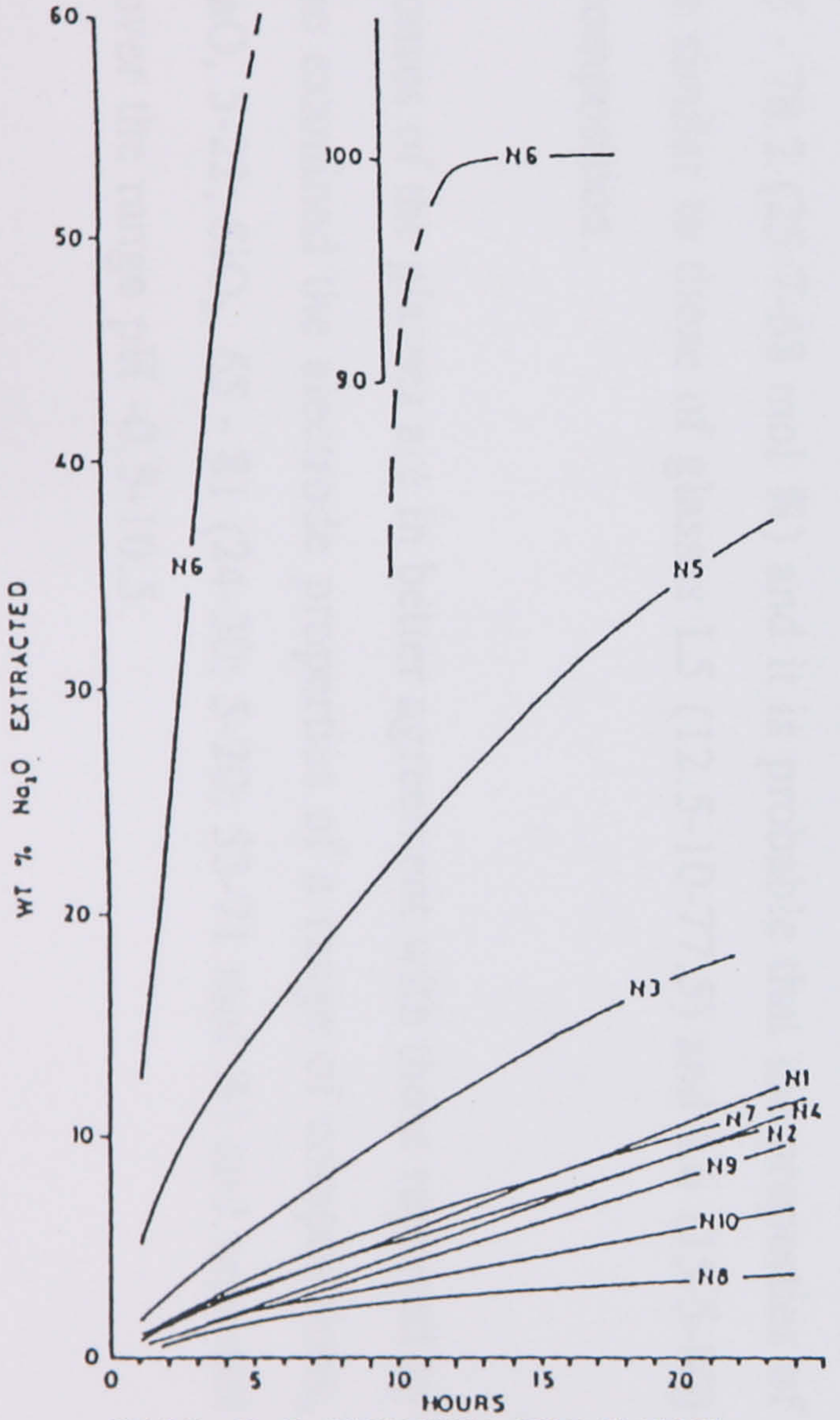


FIG. 7.13 Na$_2$O EXTRACTION FROM GLASSES

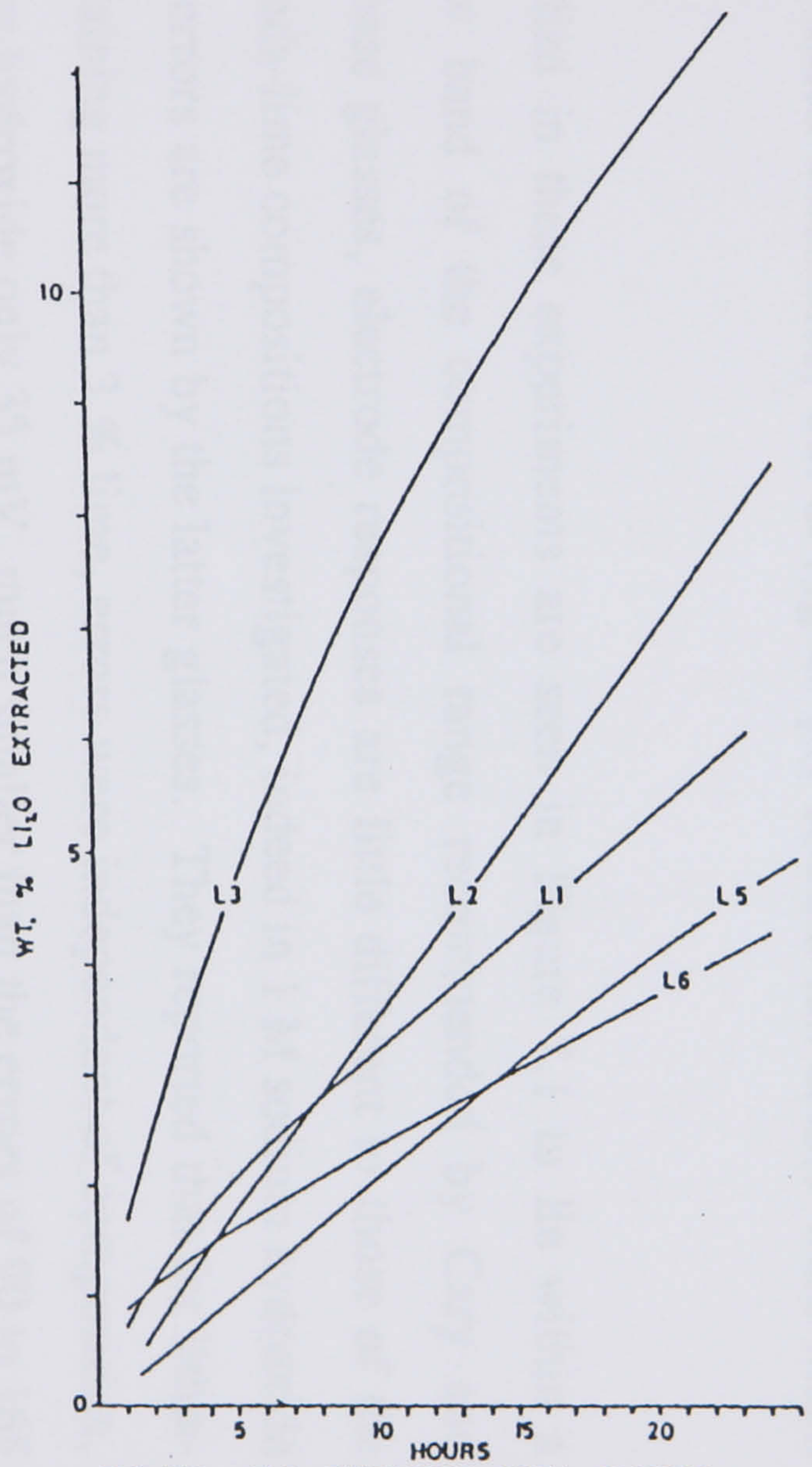


FIG. 7.14 Li$_2$O EXTRACTION FROM GLASSES

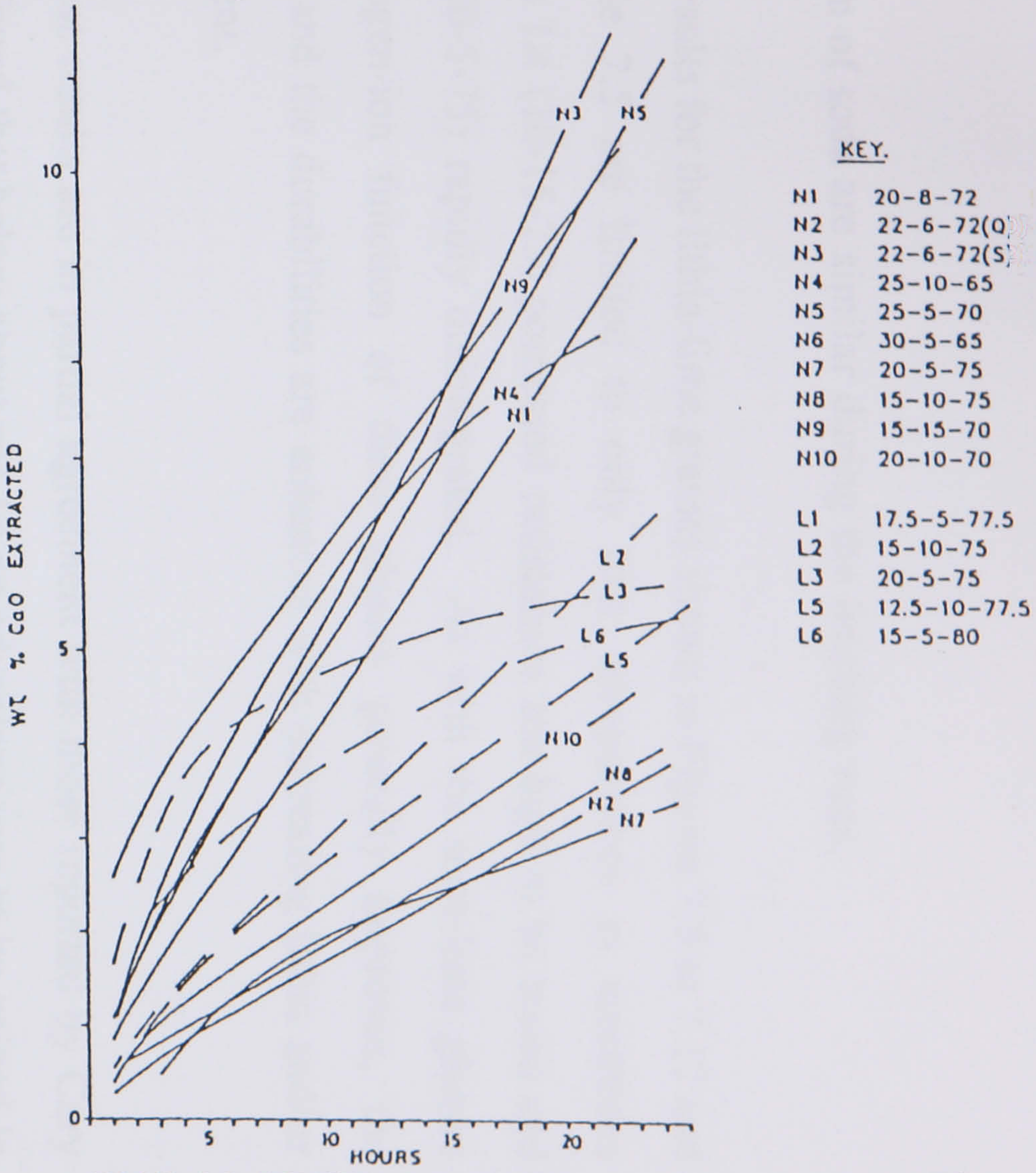


FIG. 7.15 CaO EXTRACTION FROM GLASSES.

the rates of extraction of soda are similar during the leaching runs.

Electrode response results for the lithia-lime glasses shown in Figures 7.9 to 7.12 and summarised in Table 7.5 are limited to only four compositions as electrodes fabricated from glass L4 (10-15-75) possessed resistances too high to be tested and those of glass L3 (20-5-75) rapidly disintegrated. As with the soda-lime glasses discussed the hydrogen-ion function of these glasses generally improves, the resistivities increase and the durabilities are enhanced with decreasing lithia and/or increasing lime content.

The electrode response results are in partial agreement with those reported by Cary and Baxter[19]. They found that below about pH 10 no advantage was to be gained in using lithia-lime based electrodes, but at higher pH sodium ion errors were much reduced.

The glasses studied in these experiments are seen in Figure 7.1 to lie within a relatively narrow band of the compositional range recommended by Cary and Baxter[19]. For these glasses, electrode responses are little different to those of the majority of the soda-lime compositions investigated, indeed in 1 M sodium hydroxide solution smaller errors are shown by the latter glasses. They reported that for lithia-lime glasses containing more than 3 % lime, errors were independent of composition, and in 1M sodium hydroxide only 35 mV, much smaller than the errors of 90 to 165 mV displayed by the glasses studied. Cary and Baxter's preferred composition is stated as 14.3 - 7.5 - 78.2 (25-7-68 mol %) and it is probable that the properties of this glass would be similar to those of glasses L5 (12.5-10-77.5) and L6 (15-5-80) which bracket its composition.

Hydrogen-ion responses of the glasses are in better agreement with those reported by Shul'ts *et al.*[164] who examined the electrode properties of a range of compositions, Li_2O, 13.5 - 18; CaO, 5-22; SiO_2, 65 - 81 (24-30; 5-20; 53-71 mol %) and reported them to be useful over the range pH -0.5-10.5.

Little other data for simple lithia-lime glasses have been reported. The major work

Table 7.6
Soda and Lime Extraction

No	Composition wt. % Na_2O-CaO-SiO_2	Na_2O Extraction, hours						CaO Extraction, hours					
		wt. %			mg/g			wt. %			mg/g		
		5	10	22	5	10	22	5	10	22	5	10	22
N9	15-15-70	2.1	4.1	9.0	3.2	6.2	13.5	4.4	6.0	10.1	6.5	9.0	15.2
N8	15-10-75	1.6	2.5	3.6	2.5	3.8	5.4	1.2	1.9	3.8	1.2	1.9	3.8
N10	20-10-70	2.1	3.4	6.3	4.2	6.7	12.5	1.4	2.3	4.5	1.4	2.3	4.5
N4	25-10-65	2.3	4.8	10.3	5.6	11.9	25.6	3.5	5.6	8.4	3.5	5.6	8.4
N1	20-8-72	3.0	5.5	11.5	6.0	11.0	23.0	2.4	4.3	8.9	1.9	3.4	7.1
N2	22-6-72	3.3	5.3	10.0	7.2	11.6	22.0	1.0	1.7	3.5	0.6	1.0	2.1
N7	20-5-75	3.8	6.3	10.8	7.5	12.5	21.5	1.1	2.0	3.2	0.5	1.0	1.6
N5	25-5-70	14.5	23	36	36	56	90	3.1	5.0	10.3	1.6	2.5	5.1
N6	30-5-65	54	33	100	162	244	300	-	-	-	-	-	-

Table 7.7
Lithia and Lime Extraction

No	Composition wt. % Li_2O-CaO-SiO_2	Li_2O Extraction, hours						CaO Extraction, hours					
		wt. %			mg/g			wt. %			mg/g		
		5	10	22	5	10	22	5	10	22	5	10	22
L4	10-15-75	-	-	-	-	-	-	-	-	-	-	-	-
L5	12.5-10-77.5	1.5	2.1	4.5	1.8	2.6	5.6	1.7	2.8	5.0	1.7	2.8	5.0
L6	15-5-80	1.9	2.4	4.0	2.8	3.5	6.0	2.9	3.8	5.2	1.5	1.9	2.6
L2	15-10-75	2.5	3.5	7.7	3.8	5.3	11.5	1.8	3.0	6.0	1.8	3.0	6.0
L1	17.5-5-77.5	2.6	3.2	5.8	4.6	5.6	10.2	-	-	-	-	-	-
L3	20-5-75	3.0	7.6	12.1	6.0	15.1	24	3.9	4.8	5.5	2.0	2.4	2.8

Table 7.8
Extraction Ratios, Soda-lime Glasses

No	Ratio Na_2O: CaO	Extraction ratio Na_2O: CaO, hours					
		wt. %			wt.		
N9	1	0.5	0.7	0.9	0.5	0.7	0.9
N8	1.5	1.4	1.3	1.0	2.1	2.0	1.4
N10	2	1.5	1.5	1.4	3.0	2.9	2.8
N4	2.5	0.4	0.9	1.2	1.6	2.1	3.1
N1	2.5	1.3	1.3	1.3	3.1	3.3	3.3
N2	3.7	3.3	3.1	2.9	11.9	11.3	10.5
N7	4	3.6	3.1	3.4	14.2	12.5	13.4
N5	5	4.7	4.6	3.5	23	23	17.7
N6	6	-	-	-	-	-	-

Table 7.9
Extraction Ratios, Lithia-lime Glasses

No	Ratio Li_2O: CaO	Extraction ratio Li_2O: CaO, hours					
		wt. %			wt.		
		5	10	22	5	10	22
L4	0.67	-	-	-	-	-	-
L5	1.25	0.9	0.8	0.9	1.1	0.9	1.1
L6	3	0.6	0.6	0.8	1.9	1.9	2.3
L2	1.5	1.4	1.2	1.3	2.1	1.8	1.9
L1	3.5	-	-	-	-	-	-
L3	4	0.8	1.6	2.2	3.1	6.3	8.8

of Perley[165], upon which all modern pH glass compositions are based, deals primarily with the substitution of lanthanum oxide for alkaline-earth oxides and the introduction of cesium or rubidium oxides to reduce alkali-ion errors. He[166] reported an error of 18 mV at pH 13 at a concentration of 2M sodium ion for an electrode of composition 13 - 15- 72 (22.9 - 14.1 - 63 mol %) that is consistent with the pattern of errors shown in Table 7.5. MacInnes and Dole[13] reported an electrode of composition 22-6-72 (36.1-5.2-58.7 mol %) to exhibit initially a low error, unstated, presumably in 0.1M sodium hydroxide, that rapidly devitrified, behaviour consistent with the rapid disintegration in water of electrode L3 (20-5-75) with a lower lithia content.

Sokolov and Passynsky[18] claimed a glass of composition 10-10-80 (18.1 - 9.7 - 72.2 mol %) to be essentially error-free in 0.1M sodium hydroxide, however, Gabbard and Dole[167] were unable to fabricate satisfactory electrodes from this high resistance glass.

It is of interest to note that such was the reputation of Dole at the time that a decade elapsed before lithia-based electrodes were widely available and some twenty-five years passed before the Corning 015 electrode was finally superseded by modern full-range lithia-based electrodes.

Results for the leaching of lithia from the glasses follow a similar pattern to those of soda from the soda-lime glasses, the rate of alkali extraction rising with increasing lithia and/or decreasing lime content. Electrode errors increase and resistances decrease in like manner. No discernible connection of lime extraction with glass composition or electrode properties is apparent for the few glasses studied.

Although lime extraction results for glasses seem perhaps doubtful, the lithia:lime ratios collated in Table 7.9 appear significant. During leaching, the ratios for compositions L2, L5 and L6, which exhibit excellent pH response between pH < 0 and pH 9.18, are substantially constant. The more durable glasses L5 and L6 exhibit extraction ratios slightly lower than the glass ratios, that for glass L2 being marginally higher, suggesting the maintenance of surface layers of constant thickness. Such is not the case for glass L3 for which the extraction ratio increases with time, an indication of progressive growth of the surface layer and penetration by water with consequent extraction of alkali from the bulk glass, demonstrated by the rapid disintegration of this glass that precluded its testing as electrodes.

7.8 CONCLUSIONS

Durability studies with water at 100°C by analysis of the extraction of alkali alone do not appear to provide a practical means of screening a family of simple alkali-lime glasses for potential pH glass electrode compositions.

The technique will identify, on a qualitative basis, those glasses that disintegrate rapidly and are of too low a durability for electrode application. It will also identify the more durable glasses that may have application at elevated temperatures, but possess resistivities too high for use at ambient temperature.

No correlation with electrode properties and lime extraction is apparent. There is, however, indication that a meaningful correlation exists between electrode properties and the alkali oxide:lime or alkali oxide:silica extract ratios.

For soda-lime glasses it is doubtful whether or not such studies would provide a better means of classification than the hygroscopicity tests devised by Hubbard and his co-workers[148]. Their technique has the advantage that it is relatively simple to execute and may be applied at the electrode test temperature, whereas durability studies with water are practical only at temperatures above about 50°C and below 100°C necessitating operation under partial vacuum. Arguably, in the absence of water-absorption data, similar comments would also be applicable to lithia-lime compositions.

CHAPTER EIGHT

DISCUSSION AND CONCLUSIONS

8.1 INTRODUCTION

Three distinct aspects of the performance of the glass electrode have been examined,

(i) the nature of the small errors displayed by commercial electrodes in aqueous buffer solutions between about pH 1-9.2,

(ii) the effect of varying the nature of the internal filling of the electrode on its response in aqueous and partially aqueous acid and buffer solutions, and

(iii) the relationship of the durabilities to electrochemical properties for soda-lime and lithia-lime glass compositions.

The experimental results have been presented in Chapters 5-7.

8.2 THE RESPONSE ERRORS IN AQUEOUS BUFFER SOLUTIONS

That commercial glass electrodes exhibit small, positive errors in aqueous buffer solutions is unambiguously demonstrated by the experimental work described in Chapter 5. Errors are apparent for all types of electrode tested in buffer solutions above pH 2.5. They are independent of both the pH and total ionic strength of a buffer solution, are a function of the buffer composition and its molality, and increase with decreasing buffer concentration. For a particular electrode, the magnitude of the error displayed is dependent on the membrane glass composition and its past use. The errors are shown to be independent of the nature of the cation, other than for glasses which exhibit an alkaline error, e.g. the Jena 9000 electrode tested. They cannot be ascribed to the presence of added chloride to the buffer solutions, or to carry over of absorbed hydrochloric acid from the previous solution, although the latter effect may contribute, in part, to the overall error shown. The results imply that the 0.025 equimolal phosphate solution is too dilute for use as a standard pH buffer solution for glass electrodes, and that the same comment may also apply for the 0.05 m phthalate buffer solution, the Reference Value Standard for the BS pH scale[98], where errors may exceed 0.002 in pH.

Errors displayed by commercial glass electrodes in standard buffer solutions, tabulated in Tables 5.8 and 5.9 are in agreement with those reported by Caudle[3] and reproduced in Table 5.1. The errors observed in TRIS-hydrochloric acid buffer solutions also confirm those observed by Caudle[3] and illustrated in Figure 5.1, which reveal not only increasing error with decreasing buffer concentration, but also increasing error as the buffer capacity is reduced at a particular ionic strength.

Results to a precision of 0.1 mV, for cells without liquid junction, determined by Serjeant and Warner[168] for the transfer of glass electrodes between 0.02 m hydrochloric acid solution and a series of equimolal phosphate buffer solutions, of 5×10^{-2} - 5×10^{-4} m concentration with added salt, are qualitatively in agreement with this present study. Where comparison is possible, their errors are somewhat less than those of this work. Their attempts to determine errors for 10^{-4} m equimolal phosphate solutions were abandoned as a stable glass electrode cell emf could not be obtained. Below concentrations of 0.02 equimolal phosphates, they were unable to obtain linear plots of$(pa_H\gamma_{Cl})^\circ$. As in this work, stable potentials were established within 10-15 minutes, equilibration time increasing with decreasing buffer concentration. Response transients observed are implied to be either A + B/E or C_1, with C_2 transients exhibited. Glass electrode potentials, once established, were stable for the duration of the electrode run, 3 h, in all solutions. It is, perhaps, of interest to note that the glass electrodes used, EIL 1070 series, were from one of the author's commercial pH glass compositions.

With respect to the response of glass electrodes in phosphate buffer solutions, a rather odd comment was recorded by Distèche and Dubuisson[62]: - 'better results .... than with phosphate buffers, because the latter, prepared from crystallized sodium and potassium salts, always contains grease which deposits on the membrane'. The statement seems dubious, and effect of grease was not considered, in this work, to be a contributory factor in the electrode response.

Poor reproducibility of glass electrode potentials in phosphate solutions of 10^{-4} m was also reported more recently by other workers. Gamble[169] concluded that the hydrogen-ion function of the glass electrode in dilute, weakly buffered solutions between pH 6 and pH 8 is unsatisfactory.

Small positive transients for the glass electrode were found by Kennedy[170] for the addition of small aliquots of different divalent cation salt solutions to an unbuffered 10^{-3} m potassium chloride 10^{-4} m calcium sulphate test solution at pH 5.4. Injection of small aliquots of the divalent salt solutions at the same pH into a flowing stream of the sample produced transients of 2-15 mV that dissipated over 5-30 minutes depending on the nature of the cation. Smaller transients of 1-5 mV, dissipating over 30-60 s were obtained if the salt solutions were added to stirred test solutions. Smaller effects were obtained when the sample solution was adjusted to pH 4.5. The reverse effect, i.e. transients to higher pH, were obtained when aliquots of the test solution were added to divalent cation salt solutions.

Kennedy[170] proposed, by analogy with theories for the absorption of ions on to silicate and metal oxide surfaces[171], that for the glass electrode, hydrogen ions are exchanged at highly selective reaction sites within the surface gel-layer, establishing the surface potential, and metal ions are exchanged at less selective sites at the gel-layer-solution interface. The positive errors arise from the absorption into the gel-layer of the released hydrogen ions, giving rise to an apparent fall in pH. As hydrogen ions diffuse from the gel-layer into the solution, the potential will drift until equilibrium is re-established, the rate being increased by stirring. The explanation accounts for the phenomena and is in accord with the phase boundary potential theory.

A recent study has been made by Davison and Harbinson[172] of the time response of glass electrodes for the pH determination of lake waters, dilute salt, and 5 x 10^{-4} m equimolal phosphate buffer solutions. A flow technique was employed where a stream of either 10^{-4} m hydrochloric acid or dilute phosphate buffer solutions was replaced with injected samples of an acid lake water (pH 5.6), NIST and dilute equimolal phosphate buffer solutions and distilled water; the glass electrode response was rapid and equilibria were established in about one minute. For neutral natural and artificial lake waters and 10^{-3} - 10^{-4} m solutions of simple salts of, e.g., KCl,

KNO_3, $KHCO_3$, $CaCl_2$, NaCl, the glass electrode response was very slow, equilibration requiring about 10 minutes to become established. Similar effects were obtained for static conditions, and for different types of glass electrode.

For the weak electrolyte solutions, the slow response of the glass electrode is associated with poor buffer capacity and is independent of ionic strength, observations which are consistent with the experimental results of the present work, reported in Chapter 5. The fast response of the glass electrode shown in distilled water led them to conclude that the transient effect is primarily related to low cation concentration and that buffer capacity and ionic strength are only minor factors. The exponential shape of the time response curves for injected salt solutions indicated a diffusion controlled process. They obtained reasonably linear plots of log $((E_\infty - E_t)/E_\infty)$ against $\sqrt{t}$ for the majority of their results. This linearization equation adopted had been reported by Rechnitz and Kugler[173] for alkali-cation responsive glass electrodes in rapidly changing systems, and demonstrated diffusion to be the rate controlling step for the potential determining mechanism, in agreement with Eisenman's[174] observations that the uptake of cations at the glass electrode surface is diffusion controlled.

Small errors exhibited by the glass electrode for standard buffer solutions, observed by Baucke *et al.*[175], are comparable to those reported in the present and other studies[176]. The similarity of these errors obtained with different glass membrane compositions for buffer solutions in the pH range for which positive and negative glass electrode errors can be discounted, led Baucke[61] to suggest that sub-Nernstian response is an intrinsic property of glass electrodes and that in the intermediate range pH 3 to 10 they exhibit electromotive efficiencies, α, of 0.9970 to 0.9980. He has explained the errors on the basis of a dissociation mechanistic approach to the response of the glass electrode and ascribes the effect to the variation of the activities of siloxy; $\equiv$Si-O$^-$, and silanol, $\equiv$Si-OH groups at the interfacial gel-layer with changing pH, and which determine the phase boundary potential. The dissociation mechanism of the glass electrode response has been discussed in Chapter 2. The results of this present study, although in qualitative agreement with Baucke's[61] data, do not corroborate his hypothesis for which α should be constant and independent of solution pH. Values for $\propto$ of the present work, 0.9966 to 0.9989 (see Chapter 5), are marginally wider than those he reported, and both his results and those of this study show $\propto$ to be a minimum in the neutral pH phosphate buffer solutions. He further proposes that $\propto$ is independent of pH electrode glass composition, which is at variance with the core of his argument that the sub-Nernstian response is a function of the gel-layer siloxy and silanol group activities.

For the study, the time response characteristics, comprehensively recorded in Appendix B, are mostly of B and E type transients with occasional examples of C and D types exhibited, generally for the lower buffer concentrations. For the lithia based glass electrodes, the initial random A transient, thought to be electrical in nature[3,4], is common.

The various forms of the time response curves exhibited preclude an overall linearization relationship. Transient types B and E, linear with time, are commonly displayed, and the initial A transient, if considered present, must be identified and ignored. The transient C_1 and D_1 features suggest exponential relationships, but the C_2 and D_2 response features possess turning points which preclude simple treatment. For the C_1 and D_1 transients exhibited, the small changes for glass electrode potentials with time, compared to the measurement discrimination, render attempts to linearize by, e.g. the relationship proposed by Rechnitz and Kugler[173], illusory. Inspection of Figures 5.2-5.5 amply illustrates the difficulties presented.

The response of glass electrodes to a pH change was generally fast; often potential stability has been established before the first reading was recorded. Equilibration times lengthened with increasing pH and decreasing buffer capacity of the test solutions. Transfers into the acid standard solutions were usually more rapid. The more sluggish C and D responses shown for the lower buffer capacity test solutions and for older glass electrodes, suggest a diffusion process. Conflicting processes are implied for C_2 and D_2 transients, possibly the initial rapidly changing portion of the responses prior to the turning points are electrical in origin. Buck[5] has suggested that C_1 transients may be D_2 transients with the initial feature extinguished by the time the first potentials are recorded, and similarly that D_1 features are rapid response forms of C_2 transients.

The results are in accord with the phase boundary potential theory and the diffusion controlled cation exchange processes at the electrode surface demonstrated by Eisenman[174]. The dissociation mechanism equilibria hypothesis of Baucke[61] qualitatively accounts for the hydrogen-ion function errors observed, and also the proton release mechanism suggested by Kennedy[170] and the establishment of new equilibria with surface exchange sites for fresh cations proposed by Davison and Harbinson[172].

8.3 THE EFFECT OF VARYING THE NATURE OF THE INTERNAL FILLING SOLUTION OF THE GLASS ELECTRODE

Reports in the literature, e.g., those of Badoz-Lambling *et al.*,[6], and Juillard[132], that markedly improved time response and smaller, or insignificant errors are obtained in partially and non-aqueous media for glass electrodes with internal filling solutions of, and conditioned in, the same solvent media have not been substantiated.

8.3.1 The Effect for Aqueous Buffer Solutions

Corning 'Triple-purpose' and Pye 'Combi' glass electrodes with internal filling solutions of aqueous, deuterium oxide, 50 wt. % dioxan, 20, 60 and 80 wt. % ethanol-water solutions of 0.1 m hydrochloric acid, aqueous acetate buffer or mercury were transferred through a series of NIST buffer solutions containing 0.1 m potassium chloride.

For both types of glass electrode, the results are similar. Response characteristics for the aqueous, deuterium oxide and mercury filled Corning electrodes are virtually identical and stable potentials were quickly established. Those for the aqueous acid and mercury filled electrodes are marginally more rapid. Transient types A + B/E are generally exhibited, with occasional examples shown of D type transients. The response of the 60% ethanol-water filled electrode is comparable for all solution transfers except to and from the calcium hydroxide buffer solution. On transfer to this solution the glass electrode promptly develops a linear positive potential drift of about 1.5 mV/h and subsequent transfer into 0.1 m hydrochloric acid results in the relatively slow establishment of a steady potential, perhaps the result of absorbed calcium-ions, as these are known to participate in the ion-exchange equilibrium in the gel-layer[163].

For the Pye electrodes, the responses of mercury, aqueous, and 50% dioxan-water mixture filled electrodes are comparable. Steady or slow, linear drifting potentials, exhibiting generally D_1 transient features, are established within 20-30 minutes in all solutions. The performance of the 20% ethanol-water filled electrode is analogous, except for the much slower response shown, for the transfer into the calcium hydroxide buffer solution. The 60% ethanol-water mixture filled electrode, however, exhibits a more markedly slow response for all transfers with drifting potentials and significantly larger errors, reducing with time. An electrode with an 80% ethanol-water filling was found impractical to test because of the rapidly changing potential displayed.

No reports of the use of glass electrodes, with partially or non-aqueous fillings, in aqueous solutions have been traced in the literature, other than for those with mercury fillings. Mercury filled electrodes were used by Thompson[135] and Bréant and Georges[134] for acid-base titrimetry, the latter noting that stable potentials were immediately established for a pH change. Hubbard *et al.*[148] determined the hydrogen-ion functions of the glasses used for their hygroscopicity - pH response studies with this type of electrode.

The high positive potentials observed for the partially aqueous-filled electrodes reflect the negative potentials established at the inner glass membrane surface. For ethanol-water mixture solutions, Beck and Wynne-Jones[1] have shown that for mixtures below about 75% ethanol content the negative drift exhibited by glass electrodes in these solutions, on extrapolation to the instant of transfer from aqueous to ethanolic solutions, suggests zero error, and that the subsequent time-dependent error is simply a change of asymmetry potential resulting from water exchange at the glass surface. The effect was shown by Burns[177], to be less for lithia than for soda-based glass electrodes, and to be smaller for methanolic than for ethanolic solutions. For hydrochloric acid solutions in these media, errors exhibited were greater than for sulphuric acid solutions. The difference of the potentials shown for a glass electrode in aqueous and non-aqueous solutions of 0.1 m hydrochloric acid was termed the 'specific effect' by Shul'ts and Ivanovskaya[33, 35]. 'Specific effects' for potentials in acetic acid, DMF and various alcohol solvent media were measured for electrodes of various soda and lithia glass compositions. Stable potentials were established by the more useful glass compositions in these media within 1-2 days for lithia glasses and 1-7 days for soda glass compositions by electrodes that were initially fully water conditioned. The magnitude of the effect was a function of the glass composition and the nature of the solvent. Specific effects of -300 mV for commercial lithia-based glass electrodes in acetonitrile solutions were reported by Farinato and Tomkins[178].

Shul'ts and Ivanovskaya[33, 35] proposed, in agreement with Beck and Wynne-Jones[1], that the negative potentials arise as the result of either replacement of water in, or dehydration of, the solvated surface layer by the solvent. Either process will similarly affect the energy states of ions and surface sites in the gel layer as the lower dielectric constant within the layer will reduce the dissociation constants for the silanol surface site equilibria and alter ion mobilities. The effect for soda glasses would be greater than for lithia glasses, as the hydrated gel-layers for the latter are thinner[50,179]. They concluded that for the media studied, the specific effect of the solvent decreases with increasing water content, i.e. increasing dielectric constant.

Inspection of the results for this series of experiments, collected in Table 6.10, shows the potential of the 60% ethanol filled Pye electrode to be about 85 mV greater than that for the similarly filled Corning electrode, in agreement with the Ivanovskaya and Shul'ts [35] data for Li_2O-BaO and Li_2O-La_2O_3 glasses which correspond, respectively, to the Pye and Corning compositions detailed in Table 6.1. The potential shift, however, for the 50%

dioxan filled Pye electrode is about 85 mV less than that exhibited for the 60% ethanol filled Pye electrode; the solvent media dielectric constants are respectively approximately 34 and 44[180] and are thus unlikely to account for the results[33, 35].

The response aberrations shown for these electrodes indicate that they are dependent on the glass composition, the nature and concentration of the organic component, and the pH of the test solution. They are initially apparent at high pH and, as the organic component is increased, anomalous behaviour is developed at lower pH values. The effect is greater for the less electrochemically efficient Pye glass electrodes which exhibit larger errors than comparably filled Corning electrodes.

8.3.2 The Effect for Partially-aqueous Solutions

The response characteristics exhibited by yellow Corning glass electrodes, with aqueous, 50% and 95% methanol-water mixture internal filling solutions conditioned in the three solvent media, were determined for transfers between acid and buffer solution in the methanolic media. The results are illustrated in Figures 6.6-6.12 and collected in Tables 6.11 and 6.12.

The performance of 'white' Corning glass electrodes, with aqueous and 95% DMF-water mixture internal filling solutions conditioned in water and 95% DMF, for transfers between 95% DMF acid and buffer solutions and aqueous acid solutions is depicted in Figures 6.13 - 6.16 and the results presented in Table 6.13. Transfers to and from aqueous hydrochloric acid solutions were included in the experimental runs as, other than the report of Ivanovskaya and Shul'ts[35] for the 'specific effect' in DMF solutions, there is no information for electrode transfer between aqueous and DMF solutions.

Methanol, a hydroxylic solvent, was selected as it is considered by Folman and Yates[181] to be absorbed at silanol surface sites. Haugaard[37] had demonstrated that ethanol is absorbed at glass surfaces and Lowen and

Broge[182] have concluded from spectroscopic studies that alcohols esterify the silanol surface sites. DMF was chosen, as being a non-hydroxylic solvent it is unlikely to solvate the glass surface.

The performance of the electrodes in either methanol-water or 95% DMF-water mixture solutions does not support the contention of Bacarella *et al.*[128] that, for precise measurements in partially and non-aqueous media, glass electrodes, with aqueous fillings, must be conditioned and stored in solvents of exactly the same composition as the test solutions. Neither do they corroborate the reports of, e.g. Badoz-Lambling[6], Juillard[132] and Douhéret[129] that stable potentials with lower errors or correct response are obtained for glass electrodes conditioned in, and with internal filling solutions of the same solvent media as the test solutions. Juillard[183] subsequently reported that for DMF solutions the response of aqueous and DMF filled electrodes was similar, but that equilibration was more rapidly attained with the DMF-filled electrode. Demange-Guerin[184] also noted that DMF filled electrodes could be used without prior conditioning in DMF, whereas aqueous-filled electrodes required 15 days soaking in the solvent. Results, in poor agreement with other work, were reported by Ritchie and Megerle[131] from data obtained in DMF solutions with DMF-filled electrodes, from which the hydrated surface layer had been removed by etching prior to introducing the non-aqueous solution. They ascribed the discrepancies to impure solvent.

Virtually all reports concerning the use of non-aqueous solvent filled and/or conditioned glass electrodes refer to their use either for general acid-base titrations or for the titrimetric determination of acid dissociation constants in non-aqueous media employing cells both with [6,131] and without[128] liquid-junctions. Without exception, the authors claim more rapid equilibration is obtained for glass electrodes filled with mercury or the same solvent medium as the test-solution than for aqueous-filled electrodes.

Results for transfers between 95% methanol solutions show the 50% methanol-filled and conditioned electrode C5 to be superior on the basis of stable B/E type transients established within 10 minutes of transfer. The B/E response is preceded by an initial C-type transient which extrapolates to zero error at the moment of transfer and for most solutions is never greater than about 1 mV. The 50% filled, 95% conditioned electrode C8 exhibits more sluggishly established E type responses which drift positively in buffer solutions and are stable in acid solutions in which they exhibit negative errors. The aqueous filled electrodes C1 and C7, conditioned in water and 95% methanol respectively, exhibit C or F type responses for which the initial transient features, of about 10 minutes duration, extrapolate to zero error. It is probable that the results shown for the 95% methanol-filled electrodes C6 and C9, conditioned in 50% and 95% methanol are flawed. The magnitude of the errors displayed between acid solutions and between acid and buffer solutions suggests partial electrical leakage, probably at the junction-box. For the transfer experiments between 50% methanol solutions the best performance, on the basis of A + B or C type transients, is exhibited by the 50% methanol-filled, water conditioned electrode C2. Responses displayed for aqueous-filled, water and 95% methanol conditioned electrodes C1 and C7 and for the 50% methanol filled, 50% and 95% methanol conditioned electrodes C5 and C8 are similar. These electrodes exhibit F type response for all transfers. Of the 95% methanol filled electrodes, the 95% methanol conditioned electrode C9 establishes steady or linearly drifting potentials rapidly, but exhibits errors in acid solutions. Acid errors are shown only in the stronger 0.1 m hydrochloric acid for the 50% methanol conditioned electrode C6, which displays similar response characteristics. The response of the water conditioned electrode C3 is a very sluggish.

With the exclusion of the probably flawed results for the 95% methanol-filled electrodes in 95% methanol solutions discussed earlier, it is apparent that, regardless of filling and conditioning regimes adopted, all electrodes tested can be satisfactorily used for general acid-base titrimetry in 50% and 95% methanol-water mixture solutions. On the criteria of either B or F type transients, the responses shown for aqueous and 50% methanol-filled electrodes, conditioned in all three solvent media, suggest support for the instantaneous potential concept and can be used for precise measurement by the procedure described by Covington and Prue[2]. The 50% methanol filled, 95% methanol conditioned electrode C8, which exhibits an error response in acid solutions, is an exception. Errors exhibited for the 95% methanol filled, 50% and 95% methanol conditioned electrodes and the sluggish drifting response shown for the water-conditioned electrode, preclude their use for precise potentiometry in 50% methanol solutions.

The performance shown for transfers between 95% DMF solutions and between aqueous acid and 95% DMF solutions by the aqueous and 95% DMF filled and alternatively conditioned electrodes is markedly different to the comparable study described for the two series for methanol-water mixtures previously described. The stable E-type and small error response for the aqueous filled and conditioned electrode C11 is rapidly established for the same transfer sequence, and is reproducible to within about 1 mV. Immersion in 0.095 m hydrochloric acid in 95% DMF solution degrades this electrode's performance for subsequent transfers. The effect is removed by prolonged soaking in water, indicating that it arises from the absorption of acid within the gel-layer. The responses shown for the other electrodes are poor. Errors are displayed for both 95% DMF solutions and rapidly negatively drifting potentials are shown in the aqueous acid solutions for the 95% DMF filled, water conditioned electrode C12. Stable but irreproducible potentials are initially rapidly established for the 95% DMF filled and conditioned electrode C14 in 95% DMF solutions. Prolonged exposure to acid solutions slows the response and subsequent immersion in the aqueous acid solutions results in slowly established drifting potentials. The performance for the aqueous filled, 95% DMF conditioned electrode C13 is more random. Results for this initial study of the performance of glass electrodes in 95% DMF-water mixture solutions demonstrate that only the aqueous filled and conditioned electrode C11 is useful. They indicate that the glass electrode may not be a satisfactory hydrogen-ion sensor for precise measurements in DMF-rich mixtures with water.

This initial scanning study of the effect of alternative glass electrode filling and conditioning regimes has not confirmed reports that for measurements in non-aqueous media, improved response times and lower errors are obtained for electrodes with internal fillings of, and conditioned in the same solvent medium as, the test solution[129,131]. Results show, however, that alternative fillings and conditioning can affect the electrode response. Many of the reports advocating the use of such electrodes have discussed their application in anhydrous solvent media, whereas for this work aqueous-organic solvent mixtures were used. The distinction may be significant, especially perhaps, for solutions in aprotic solvent media. Juillard[132] has noted that for DMF solutions, DMF filled electrodes presumably conditioned with DMF, exhibited steady and reproducible potentials which were rapidly established and that an aqueous filled electrode exhibited limited reversibility, but that correct response for this electrode was obtained on the addition of 2% methanol, a hydroxylic solvent. Nevertheless, he later stated[183] that for these solutions, the only difference shown for the two electrode fillings was more rapid equilibration for the DMF-filled electrode.

For the methanol-water mixture study the performance for most electrodes was an instantaneous error-free response on transfer between solutions. These electrodes establish B/E type behaviour or exhibit E type transient responses that imply the existence of two linear competing reactions, for which the first positive, rapidly changing, feature can be extrapolated to zero error at the moment of transfer. The second feature, a negative drifting potential suggests, in agreement with the conclusions of Beck and Wynne-Jones[1], a changing asymmetry potential that can be ascribed to solvent exchange at the electrode surface. Contact with 0.1 m hydrochloric acid solutions for the aqueous conditioned electrodes magnifies the initial positive transient feature for the following transfer to a buffer solution. The exaggerated feature subsequently drifts to more negative potentials as the absorbed acid diffuses into the test solution. Schwabe *et al.*[31] have demonstrated by radiotracer measurements, for aqueous solutions, that hydrochloric acid is absorbed at the glass surface and is subsequently slowly removed on prolonged soaking in water. Burns[177] has shown that small errors are developed for glass electrodes transferred from aqueous to 99.9% and pure methanol solutions of 0.01 m hydrochloric acid, which are slowly removed by soaking in aqueous solutions. Acid errors are rapidly established for most of the 95% methanol filled electrodes. For these electrodes there was no subsequent drift to more negative potentials following transfer from acid to buffer solutions. The errors were apparently real.

Csákvári *et al.*[50] found that on conditioning soda-glass electrodes for two weeks at 40°C in water or ethanol, the surface layer developed for the ethanol conditioned electrode was much thinner than that of the water conditioned electrode. This observation was supported by Wikby,[185] who demonstrated that the development of the surface layer was inhibited by isopropanol. Further studies with Karlberg[186] showed that isopropanol was not absorbed at the gel-layer and concluded that a hydrated surface layer was progressively dehydrated by the solvent. Whether or not a solvent diffuses into the gel-layer, as has been previously discussed for methanol,[181,182] or simply dehydrates the surface-layer, the results, as Ivanovskaya and Shul'ts[35] have reported for the origin of the 'specific effect', is the lowering of the dielectric constant in the surface layer. The effects are the lowering of the dissociation constants of the weakly acidic silanol groups and ion mobilities within the gel-layers. These effects will be greater for the more organic solvent rich mixtures. Karlberg[187] has reported that the sluggish response developed for a water conditioned electrode on prolonged use in isopropanol is the result of dehydration of the outer volume of the gel-layer and that rapid response is restored by partially etching the surface, removing the dehydrated portion. He recommends that for use in non-aqueous solvents, glass electrodes should be either conditioned and stored in water, or water conditioned electrodes etched, stored in the test solution medium, when further hydration will cease, and prior to use, soaked in water for a few minutes. His results corroborate Mattock's[188] opinion that surface hydration of the glass membrane is necessary to develop a reproducible hydrogen-ion function for the glass electrode in partially and non-aqueous media.

8.3.3 Conclusions

The hypothesis of Dole[7], the foundation of theories of the glass electrode response, is that the inner and outer potentials of the glass electrode are independently established. On this tenet, differences in the response characteristics shown, for nominally identical glass electrodes in the same test solutions, arise solely as a result of their differing external glass-solution interfaces determined by alternative conditioning solvent media. The nature of the internal filling of the electrodes is inconsequential. The response shown for a glass electrode in partially or non-aqueous media would be subject to ion-exchange equilibria determined by the dissociation constants for the silanol exchange sites and ion mobilities dependent on the local dielectric constant, in accordance with the phase boundary potential theory. A changing asymmetry potential may be displayed as a consequence of dehydration or solvent exchange with the test solution.

The responses shown for some of the electrode transfer experiments in partially aqueous media in this work can be generally described on the basis of this argument. The often larger errors observed for 95% methanol conditioned electrodes exhibited in the methanol-water solutions can be ascribed to the glass-surface-solution reactions. For these media, the dielectric constants are, water 78.3[85], 50% methanol 56.3[88], and 95% methanol 35.5[89]. Small errors exhibited for a water conditioned electrode and the larger errors presented for the 95% DMF conditioned electrodes for transfers in 95% DMF and aqueous acid solutions are similarly explained. The dielectric constant for this solvent medium is 40.6[189].

It would be attractive to conclude from this study of the performance of glass electrodes in aqueous and partially-aqueous solvents, that the response was the result of the conditioning medium and the solvent medium of the test solutions. Such a neat explanation is not tenable for all observations however, e.g. the 95% DMF filled aqueous conditioned electrode exhibits large errors and drifting potentials and errors are displayed for the ethanol-water mixture filled electrodes in aqueous buffer solutions.

The results conflict with the long accepted hypothesis of Dole[7] that the inner and outer potentials of the glass electrode are developed independently, which led to Haugaard[36,37] to propose the three layer model for the glass electrode and to demonstrate that electrical conduction through glass was solely by alkali ions. Tritium tracer electrolysis experiments by Schwabe and Dahms[190] confirmed that hydrogen-ions are not transported through the glass membrane. On this well-founded basis, it is unthinkable to contemplate the passage of hydrogen ions across the glass membrane as Badoz-Lambling *et al.*[6] appear to propose. The results do not indicate either the existence of liquid-junction potentials at cracked glass membranes or response degradation due to electrical insulation loss. Further detailed study is necessary before these observations may be satisfactorily explained.

8.4 THE DURABILITY - pH RESPONSE RELATIONSHIP FOR SODA-LIME AND LITHIA-LIME GLASSES

The study was undertaken to ascertain if there is a quantitative relationship between the durability and pH response for soda-lime and lithia-lime glasses. Results of this examination, presented and comprehensively discussed in Chapter 7, are summarized in this section.

Glasses were prepared from compositions reported to provide promising pH response functions. The hydrogen-ion functions for the glasses were determined over the range, approximately pH -1 to 14. Electrical resistances of the glass electrodes were measured. Durabilities of the glasses were determined by leaching glass grains in fresh water for about 24 h and analyzing periodically, the products of the leached extract for sodium, or lithium, and calcium.

Glass electrodes of compositions 15-25 wt. % Na_2O : 5-10 wt. % CaO and, 12.5-17.5 wt. % Li_2O : 5-10 % CaO, exhibit modest errors between about pH 1-9.2. For both series of glass compositions, electrode errors increase and electrical resistances decrease with increasing alkali and/or decreasing lime content.

Electrode errors increase with decreasing durabilities of the glasses, i.e. increasing rate of alkali extraction. No discernable direct relationship with lime extraction is apparent.

The most useful correlation for glass durability and electrode response is the ratio of the alkali oxide:lime in the leaching extract. Glasses with extraction ratios comparable to the composition ratio and remaining substantially constant throughout the leaching process, indicative of the maintenance of hydrated surface layers of constant depth, are suitable for general purpose electrode compositions. Those glasses with extraction ratios lower than the composition ratio, and increasing with time towards it, provide electrode compositions with high resistance and low errors at pH extremes, that may find application for high temperature use. The glasses with higher extract ratios than the composition ratio exhibit low durabilities. These compositions are unsuitable for electrode fabrication.

Where results are comparable, they are in reasonable agreement with reports in the literature.

Related to the work presented, a theoretical model for the corrosion, or ageing, of glass electrodes in aqueous solutions has recently been published by Morf[191]. The hypothesis provides a kinetic foundation from which it is possible to predict the pH and temperature dependent corrosion for a chosen glass composition.

The nature of the hydrated gel-layer has been characterized in terms of the concentrations and fluxes, in the perpendicular plane to the surface, of the interdiffusing hydrogen and metal ions and the rate of the accompanying degradation of the silicate structural network.

The thickness δ, and the hydrogen-ion content n_H, of the gel-layer are shown to be inversely proportional to the rate of network corrosion a, i.e.,

$$\delta = D_H/a \qquad 1$$

$$\text{and, } n_H = Ac_T\, y_{1/2} \qquad 2$$

where D_H is the diffusion coefficient of the hydrogen-ion, A the surface area, c_T is the total concentration of hydrogen c_H, and metal c_M ions, and $y_{1/2}$ is the depth within the gel-layer where $c_H=c_M$.

To ascertain a, Morf has assumed the network corrosion model adopted by Grambow[192] for estimating the rate of corrosion of high-durability glasses, which provided data in good agreement with experimental results for these glasses and amorphous silica. The model supposes simultaneous dissolution of all glass components at a uniform rate. Components are considered as compositional mole fractions of amorphous silica, alkali and alkali-earth metasilicates and metal oxides. The rate equation for glass dissolution,

$$a=a_o\exp(-\Delta G_R/RT) \qquad 3$$

where a_o is the standard rate for ΔG_R=zero at a given temperature, and ΔG_R the free energy change, which is calculated from the sum of the individual free energies ΔG_k. Standard free energy changes ΔG°_k are obtained from the equilibrium constants K_k, for the dissolution reactions. The component free energy changes ΔG_k are,

$$\Delta G_k \approx \Delta G^\circ_k + \nu \times 2.303RTpH \qquad 4$$

$$\approx \Delta G^\circ_k + \nu' \times 2.303RT(pK_w\text{-}pH) \qquad 5$$

where ν and ν' are the stoichiometric quantities of hydrogen and hydroxyl ions for the dissolution reactions. Rates are referenced to an empirical relationship in temperature for the standard free energy change for the dissolution of amorphous silica.

Corrosion rates calculated for simple lithia-silica glasses in leaching solutions at pH 7, at different temperatures, were in good agreement with experimental results[193].

In principle, the hypothesis allows the effect of varying or different oxide additions to a glass composition on the corrosion rate, and consequently, the nature of the gel-layer, for solutions of different pH values and temperatures, to be assessed. Calculations for the corrosion rates of alkali oxide-aluminosilicate, ion-selective glass compositions were in general agreement with their known corrosion behaviour at pH 2, pH 7 and pH 12. For alkali oxide-silica pH electrode compositions, calculated rates at pH 2 were very much greater than expected[194].

The discrepancies of the corrosion model adopted by Morf, originally devised for high silica, low alkali, high durability compositions, are that it does not take into account the alkali-deficient profiles of the gel-layers of moderate silica, high alkali, pH glass compositions, identified and characterized by, e.g. Bach and Baucke[49] and Wikby[48]. For these moderately durable glasses, within the hydrated gel layer, the high resistance film originally identified by Buck[45], is a high activation energy barrier to ion transport, and effectively controls the corrosion of the silicate network[59,179]. It is possible that for high durability glasses, such as 'Pyrex', which do not display a pH response or absorb water[148] under normal conditions[67,161], corrosion by simultaneous component dissolution is a reasonable assumption.

The hypothesis proposed by Morf provides the promise of a powerful additional tool for simulating the effects on corrosion rates and resistances at fixed pH for the screening of, e.g., pH glass composition variation. The model may be applicable only for neutral and alkaline solution simulation, but this is not necessarily a barrier to its potential usefulness. Testing of the theory against experimental data is necessary to assess its application and sensitivity. Regrettably, it is inapplicable to the results obtained for the glass durability studies, where the pH does not remain constant, presented in Chapter 7.

8.5 SUMMARY OF CONCLUSIONS AND RECOMMENDATIONS FOR PRECISE MEASUREMENTS WITH GLASS ELECTRODES

1. In aqueous buffer solutions, small but significant errors are apparent for all glass electrodes tested. Errors are independent of pH, but are dependent on the

buffer composition and its molality, increasing markedly with decreasing buffer strength. They are independent of the nature of the cation (Na^+, K^+ or NMe_4^+), the presence of chloride and total ionic strength. The magnitude of the error for a particular electrode is dependent on the glass composition and its past use.

The results do not corroborate Baucke's[61] hypothesis that the electromotive efficiency of a glass electrode is a constant less than 1, independent of both solution pH and glass composition.

Errors of 0.003 - 0.005 in pH noted in the equimolal 0.025 m mixed phosphates buffer solution imply its unsuitability as a primary standard for use with glass electrodes. The results also indicate that the 0.05 m potassium hydrogen phthalate solution also is probably unsatisfactory for high precision measurements with the glass electrode, but further work is necessary to confirm this.

For precise pH measurements, glass electrodes should be stored, between use, in deionized water or a mildly acidic solution. High molality buffer solutions should be used to calibrate pH measurement cells.

2. The study has shown that in partially-aqueous solvent solutions, the time responses and errors of nominally similar glass electrodes are affected by changing the aqueous internal filling solution to a partially-aqueous one, and by alternative conditioning.

The results do not substantiate the reports[128,129] of improved time response and negligible or zero error, for glass electrodes with internal fillings of, and conditioned in, the solvent media in which they are used.

Further work is necessary to clarify the nature of the effects of partially and non-aqueous solvent solutions at the glass-solution interface.

3. For a series of soda-lime and lithia-lime glass compositions, electrical resistances decrease and glass electrode errors, for the range pH 1-9.2, increase with increasing alkali oxide and/or decreasing lime content. Electrode errors increase with decreasing glass durability, i.e. with increasing rate of alkali extraction. No apparent direct relationship with lime extraction is discernible. There is a meaningful correlation between the electrode response and the alkali oxide:lime ratio of the leached extract. Glasses with extraction ratios comparable to the composition ratio throughout the leaching process are suitable general purpose pH glass compositions. The relationship, however, is probably not sufficiently sensitive to provide a useful means of screening glasses for their suitability as potential pH glass compositions.

APPENDIX A

RECORD OF GLASS ELECTRODES USED IN AQUEOUS BUFFER SOLUTIONS

Electrodes were conditioned and stored in distilled water.

Other than for numbers 1, 3 and 24, membranes were of 10 mm diameter bulb format.

R, resistance at 25 °C

E†, emf at 25 °C of the cell

Pt, H_2 | 0.1m HCl | glass electrode

No. 1
GFH 33
Electronic Instruments Limited, Richmond, England.
0-11 pH, 0-50 °C, 12mm diameter, flat-head.
Li_2O, BaO, UO_2
Inner, Ag,AgCl | 0.1m HCl
E†, 400 mV
R, 500 MΩ
Introduced, 29.6.65
Prior use, HCl solutions July 1965

No. 3
242C
Radiometer AB, Copenhagen, Denmark.
0-12 pH, 10-60 °C, 20 mm diameter, flat-head.
Li_2O based
Inner, Ag,AgCl | citrate, Cl^-
E†, 617 mV
R, 170 MΩ
Introduced 29.6.65
Prior use, HCl solutions July 1965, buffer solutions July 1965

No. 4
GHS 33
Electronic Instruments Limited, Richmond, England.
0-14 pH, 0-140 °C
Li_2O, Cs_2O, CaO, BaO, La_2O_3, CeO_2, TiO_2
Inner, Ag | AgCl | 0.1m HCl
E†, 378 mV
R, 510 MΩ
Introduced 24.8.60
Prior use, acid and buffer solutions December 1960-May 1962

No. 6
476020 blank
Self-assembled
Specification, see No. 10
Inner, Ag, AgCl | 0.1m HCl
E†, 359 mV
R, 170 MΩ
Introduced 8.7.66

No. 10
476020 ('Triple Purpose')
Corning Glassworks, Medfield, Mass., USA.
0-14 pH, -5-110 °C.
Li_2O, Cs_2O, La_2O_3, Ta_2O_5, UO_2
Inner, Ag,AgCl | phosphates, Cl^-
E†, 664 mV
R, 300 MΩ
Introduced 8.7.66

No. 19
476020 ('Triple Purpose')
Specification, see No. 10
E†, 680 mV
R, 250 MΩ
Introduced, 16.5.66
Prior use, Buffer Solutions May-December 1966

No. 22
HA 9401
Jena Glaswerk, Mainz, Germany
1-14 pH, 0-70 °C
Li_2O, Cs_2O, CaO
Inner, Ag,AgCl | acetate, Cl^-
E†, 490 Mv
R, 500 MΩ
Introduced 20.11.65
Prior use, buffer solutions November 1965-September 1966

No. 23
GG33
Electronic Instruments Limited, Richmond, England.
1-10 pH, 10-45 °C.
MacInnes-Dole (Corning 015) composition, Na_2O, CaO
Inner, Ag,AgCl | 0.1m HCl
E†, 404 mV
R, 120 MΩ
Introduced 20.7.64
Prior use, buffer solutions, July 1964-August 1966

No. 24
N9000
Jena Glaswerk, Mainz, Germany.
Na_2O based
Inner, Ag | AgCl | 0.1m HCl 30mm bulb, unscreened
E†, 334 mV
R, < 1 MΩ
Prior use, intermittent use in acid and buffer solutions within the Department for some years.

No. 25 202C
Specification, see No. 3.
E†, 625 mV
R, 165 MΩ
Introduced March 1967

No. 26 467020 ('Triple Purpose')
Specification, see No. 10.
E†, 679 mV
Introduced, March 1967

No. 27 GG33
Specification, see No. 23
E†, 410 mV
R, 75 MΩ
Introduced March 1967

No. 28 GG33
Specification see No. 23
E†, 407 mV
R, 140 MΩ
Introduced July 1967

No. 29 U530050-15C
Sargent-Jena, Chicago, Ill., USA.
1-14 pH, -10-70 °C
Li_2O based
Inner, Ag, AgCl | phosphates, Cl^-
E†, 632 mV
R, 230 MΩ
Prior use in D_20 solutions, Epiphany Term 1966

No. 30 202B
Radiometer AB, Copenhagen, Denmark.
0-14 pH, 20-60 °C
Li_2O based
Inner, Ag,AgCl | citrate, Cl^-
E†, 611 mV
R, 400 MΩ
Prior use in D_20 solutions, Epiphany Term 1966.

No. 31 E2, 41263
Beckman Inc., Fullerton, Calif., USA.
0-14 pH, 15-80 °C
Li_2O, BaO
Inner, Ag, AgCl | phosphates, Cl^-
E†, 565 mV
R, 220 MΩ
Prior use in D_20 solutions, Epiphany Term 1966

No. 32 HTA 530056-10
Sargent-Jena, Chicago, Ill., USA.
1-14 pH, 20-120 °C
Li_2O based
E†, 581 mV
R, 555 MΩ
Prior use in D_20 solutions, Epiphany Term 1966

APPENDIX B

RECORD OF GLASS ELECTRODE POTENTIAL TIME DATA OF TRANSFERS IN AQUEOUS BUFFER SOLUTIONS

		Page Number
HCl	Tetroxalate + KCl series	174
HCl	Glycine + KCl series	176
HCl	Phthalate + KCl series	179
HCl	Phosphate + KCl series	183
HCl	TRIS + KCl series	188
HCl	TRIS + Me_4NCl series	192
HCl	Borax + KCl series	196
HCl	Mixed + KCl series	198
H_2SO_4	Phosphate + KCl series	202
H_2SO_4	Phosphate series	205
H_2SO_4	Phthalate series	207
H_2SO_4	Phthalate + KCl + $KClO_4$ series	209
H_2SO_4	Phosphate + KCl + $KClO_4$ series	211

Record of Transfers in Aqueous Buffer Solutions

Run	Acid	Buffer Series	Added Salt	Electrode Number																Date
				1	3	4	6	19	22	23	24	25	26	27	28	29	30	31	32	
1	HCl	phosphate	KCl		x		x	x												12.01.67
2	HCl	borax	KCl		x		x	x												18.01.67
3	HCl	TRIS	KCl		x		x	x												19.01.67
4	HCl	tetroxalate	KCl		x		x	x												25.01.67
6	HCl	glycine	KCl		x		x	x												30.01.67
7	HCl	glycine	KCl	x		x			x	x										31.01.67
8	HCl	glycine	KCl								x									01.02.67
9	HCl	TRIS	KCl		x		x	x			x									02.02.67
10	HCl	TRIS	KCl	x		x			x	x										03.02.67
11	HCl	phosphate	KCl		x		x	x			x									07.02.67
12	HCl	phosphate	KCl	x		x			x	x										08.02.67
13	HCl	TRIS	$(CH_3)_4NCl$		x		x	x			x									14.02.67
14	HCl	TRIS	$(CH_3)_4NCl$	x	x	x			x	x										15.02.67
15	HCl	phthalate	KCl		x	x		x			x									21.02.67
16	HCl	phthalate	KCl	x		x			x	x										22.02.67
17	H_2SO_4	phosphate	KCl	x				x												16.03.67
18	H_2SO_4	phosphate	KCl		x				x	x	x									17.03.67
29	HCl	phthalate	KCl											x					x	02.05.67
30	HCl	phthalate	KCl		x				x								x	x		03.05.67
31	HCl	phthalate	KCl	x				x				x				x				04.05.67
32	HCl	phosphate	KCl	x				x				x								09.05.67
33	HCl	phosphate	KCl						x									x		10.05.67
34	HCl	phosphate	KCl		x					x				x		x			x	11.05.67
35	HCl	phosphate	KCl			x							x							12.05.67
36	HCl	mixed	KCl	x	x	x			x											16.05.67
37	HCl	mixed	KCl						x											17.05.67
38	HCl	mixed	KCl							x		x	x	x		x	x	x	x	18.05.67
39	HCl	mixed	KCl				x	x			x									19.05.67
41	H_2SO_4	phosphate	none		x										x					02.08.67
42	H_2SO_4	phthalate	none		x					x					x					03.08.67
43	H_2SO_4	phosphate	none							x					x					04.08.67
44	H_2SO_4	phthalate	KCl, $KClO_4$		x					x					x					21.08.67
45	H_2SO_4	phosphate	KCl, $KClO_4$		x					x					x					01.09.67

TETROXALATE BUFFER SERIES

Transfers between 0.1m HCl and

1. 0.1m K tetroxalate + 0.1m KCl
2. 0.05m K tetroxalate + 0.1m KCl
3. 0.01m K tetroxalate + 0.1m KCl

Electrodes: 3, 6, 19

Run: 4

Transfers from 0.1m HCl into Buffer 1

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
3	4	0.7	0.2	0	0	0	-	0	0	0	-	-	0	AB
6	4	-0.1	0	0	0	-	-	-	-	-	0	0	0	B
19	4	-1.1	-0.5	-0.1	0	-	-	-	0	0	-	-	0	AB

Transfers from Buffer 1 into 0.1m HCl

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
3	4	0.5	0.1	0	0	0	-	-	-	0	0	-	0	AB
6	4	-0.3	-0.1	-0.05	0	0	-	-	0	0	-	-	0	AB
19	4	-0.1	-0.1	0	-	-	-	-	-	0	0	-	0	B

Transfers from 0.1m HCl into Buffer 2

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
3	4	0.4	0.1	0	-	-	-	0.1	0.1	-	-	-	0.1	AB
6	4	0	0	0	0	-	-	-	0	0	-	-	0	B
19	4	-0.5	-0.2	-0.1	0	0	-	-	0	0	-	-	0	AB

Transfers from Buffer 2 into 0.1m HCl

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
3	4	-0.3	-0.25	-0.2	-0.1	0	0	-	-	-	0	-	0	AB
6	4	-0.6	-0.1	0	-	-	-	-	0	0	-	-	0	AB
19	4	-0.4	-0.2	-0.1	-	-	-	-	0	0	-	-	0	AB

Transfers from 0.1m HCl into Buffer 3

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
3	4	0	-0.2	-0.15	-0.1	-	-	0	0	-	-	-	0	AB
6	4	-0.3	-0.1	0	0	-	0	0	0	-	-	-	0	AB
19	4	-0.2	-0.1	-0.05	-	-	-	-	0.2	0.2	0.2	-	0.2	AE

Transfers from Buffer 3 into 0.1m HCl

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
3	4	-0.4	-0.2	-0.05	-	-	-	-	0.1	0.1	-	-	0.1	AB
6	4	-0.4	0	0	0	-	-	0	0	-	-	-	0	AB
19	4	-0.5	-0.2	0	0	0	-	-	0.1	0.1	-	-	0.1	AB

GLYCINE BUFFER SERIES

Transfers between 0.1 m HCl and

1. 0.2m glycine + 0.1m HCl
2. 0.1m glycine + 0.05m HCl + 0.05m KCl
3. 0.02m glycine + 0.01m HCl + 0.09m KCl

Electrodes: 1, 3, 4, 6, 19, 22, 23, 24.

Runs: 6, 7, 8

Transfers from 0.1m HCl into Buffer 1

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
1	7	-1.0	-0.5	-0.2	-0.1	-	-	0	0	-	-	-	0	AB
3	6	-0.2	-0.1	-0.1	0	-	-	0	-	-	-	-	0	AB
6	6	0	0.1	0.1	0.1	-	0	0	-	-	-	-	0	B
4	7	0.9	0.4	0.1	-0.1	-	-	-	0.2	-	0.3	0.4	0	AB
19	6	-0.2	-0.1	0	0	-	-	0	0	-	-	-	0	AB
22	7	0.2	0.1	2.0	1	-	-	0.2	0.2	-	-	-	0.2	E
23	7	-0.3	0	0.2	0.4	0.4	-	-	-	-	-	-	0.4	AB
24	8	0.3	0.2	0.1	0.1	0.1	0.1	-	-	-	-	-	0.1	AB

Transfers from Buffer 1 into 0.1m HCl

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
1	7	0.5	0.3	0.05	0	0	0	0	0	-	-	-	0	AB
3	6	-1.5	-0.6	-0.3	-0.1	-	-	-0.1	-0.1	-	-	-	-0.1	AB
6	6	0	0	0	0	0	-	0	0	0	-	-	0	B
19	6	-0.6	-0.3	-0.1	0	0	-	-	-	0	0	-	0	AB
22	7	-0.6	-0.1	-	0.05	-	-	-	-0.1	-0.1	-0.1	-	-0.1	AB
24	8	0.1	0	0	-0.1	-0.1	-0.1	-0.1	-	-	-	-	-0.1	AB

Transfers from 0.1m HCl into Buffer 2

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
1	7	-1.1	-0.4	-0.1	0	0.1	0.1	-	-	0.1	0.1	-	0.1	AB
3	6	-1.1	-0.6	-0.3	-0.1	0	-	-	-	0	0	-	0	AB
4	7	0.6	0.3	0.15	0	-	-	0.2	0.25	0.3	-	-	0	AB
6	6	0.1	0.2	0.2	0.1	0	0	-	-	0	0	0	0	AB
19	6	-0.4	-0.3	-0.1	-	-0.05	-	-0.05	-	-	-	-0.2	0	AB
22	7	0.1	0	0.1	0.1	-	-	-	0.2	0.2	0.2	-	0.2	AE
23	7	0.6	0.6	0.6	0.6	-	-	0.3	0.8	-	-	-	0.8	D2
24	8	0.1	0.1	0.1	0.1	0.1	-	-	0.1	0.1	-	-	0.1	B

Transfers from Buffer 2 into 0.1m HCl

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
1	7	-0.4	-0.2	-0.1	-0.1	-	-	-0.1	-0.1	-	-	-	-0.1	AB
3	6	0.1	0	0	0	-	-	-	0.05	0.05	-	-	0	B
4	7	-	0	0	0	-	-	-	0	0	-	-	0	B
6	6	-0.2	-0.1	0	0	0	0	-	-	-	-	-	0	AB
19	6	0.2	0.1	0	0	-	-	-	-	0	0	0	0	AB
22	7	-0.5	-0.3	-0.2	-0.1	-0.1	-	0	0	-	-	-	0	AB
23	7	-0.5	-0.6	-0.7	-0.7	-0.8	-0.8	-	-	-	-	-	-0.8	AE
24	8	0.1	0	-0.1	-0.1	-	-	-	-0.1	-0.1	-	-	-0.1	B

Transfers from 0.1m HCl into Buffer 3

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
1	7	1.5	1.0	0.5	0.3	0.2	-	-	-	0.1	0.1	-	0.1	AB
3	6	-0.6	-0.3	-0.1	0	0.1	0.1	-	-	-	-	-	0.1	AB
4	7	1.0	0.9	0.7	0.3	0.2	0.2	-	-	-	-	-	0.2	AE
6	6	0.6	0.5	0.4	0.1	0	0	0	-	-	-	-	0	AB
19	6	-0.1	-0.5	0	0.1	0.1	0.1	0.1	-	-	-	-	0.1	B
22	7	-0.3	0.5	0.6	0.3	0.2	0.2	0.2	-	-	-	-	0.2	AE
23	7	-0.6	0.5	0.8	0.9	0.9	0.9	0.9	0.9	-	-	-	0.9	AE
24	8	0.4	0.3	0.2	0.2	0.2	0.2	0.2	-	-	-	-	0.2	AE

Transfers from Buffer 3 into 0.1m HCl

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
1	7	0.5	0.2	0	-0.1	-0.1	-0.1	-	-	-	-	-	-0.1	AB
3	6	0.2	0.05	0	0	-	-	-	0	0	-	-	0	AB
4	7	-1.2	-1.0	-0.9	-0.7	-0.55	-0.4	-0.2	0.1	-	-	-	0	AB
6	6	0.2	0	0	0	0	0	-	-	-	-	-	0	AB
19	6	-0.2	-0.15	-0.05	0	-	-	-	-	-	0	0	0	AB
22	7	-0.2	-0.2	-0.1	-0.1	-	-	-0.05	-0.05	-	0	0	0	AB
23	7	-0.6	-0.7	-	-	-0.9	-0.9	-	-0.9	-	-	-	-0.9	AE
24	8	-0.1	-0.2	-0.2	-0.2	-	-	-	-	-	-0.2	-0.2	-0.2	E

PHTHALATE BUFFER SERIES

Transfers between 0.1 m HCl and

1. 0.1m KH phthalate + 0.1m KCl
2. 0.05m KH phthalate + 0.1m KCl
3. 0.01m KH phthalate + 0.1m KCl

Electrodes:	1, 3, 4, 6, 19, 22, 23, 24, 25, 27, 29, 30, 31, 32.
Runs:	15, 16, 29, 30, 31

Transfers from 0.1m HCl into Buffer 1

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
1	16	-1.3	-0.5	-0.2	0.05	0	0	0	0	0	-	-	0	AB
1	31	4.0	1.5	0.7	0.3	0.1	-	-	0	0	-	-	0	AB
3	15	0.5	0	-0.1	0	0	0	-	-	-	-	-	0	B
3	30	-	-0.3	-0.15	0.1	0.1	0.1	0.1	-	-	-	-	0.1	AB
4	16	0.3	0.2	0.1	-	-	-	-	-	-	0.3	0.3	0.3	D2
6	15	1.0	0.5	0.4	0.2	0.1	0.1	0.1	0.1	-	-	-	0.1	AB
19	31	-1.0	-0.3	0	0.1	0.1	-	0.1	0.1	-	-	-	0.1	AB
22	16	0.3	0.3	0.3	0.2	-	-	0.1	0.1	0.1	-	-	0.1	AB
22	30	0.1	0.2	0.2	0.1	0.1	-	-	-	0.1	0.1	0.1	0.1	B
23	16	0.1	0.3	0.4	-	-	-	0.4	0.4	-	-	-	0.4	AE
23	31	0.5	0.4	0.4	-	-	0.5	0.5	0.5	-	-	-	0.5	E
24	15	0.4	0.3	0.2	0.1	-	-	0	0	0	-	-	0	AB
25	31	-0.3	-0.1	0	0.1	-	-	-	-	-	-	-	0.1	AB
27	29	0.3	0.2	0.1	-	-	-	-	-	0.1	0.1	0.1	0.1	AB
29	31	3.2	2.1	1.7	1.0	-	-	-	0.5	0.4	0.4	0.4	0.4	D1
30	30	-0.1	0	0.1	0.1	-	0.1	0.1	0.1	-	-	-	0.1	B
31	30	-0.8	-0.5	-0.15	-	-	-	0.1	-	-	0.1	0.1	0.1	AB
32	29	0.4	0.2	0.1	-	-	-	-	-	0.1	0.1	0.1	0.1	AB
32	29	0.1	0.1	0.1	0.1	-	-	-	-	-	0.2	0.2	0.2	E

Transfers from Buffer 1 into 0.1m HCl

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
1	16	-0.9	-0.4	-0.1	0	-	-	-	-	0	0	0	0	AB
1	31	-0.6	-0.3	-0.15	-	-	-	0.1	0.1	0.1	-	-	0.1	AB
3	15	0.5	0.2	0.1	0.1	-	-	-	-	-	0.1	0.1	0.1	AB
3	30	-0.2	-0.3	-0.2	-	-	-	-	-	0	0	-	0	AB
4	16	-1.1	-1.0	-0.9	-0.7	-	-	-	-	-0.3	-0.3	-0.3	-0.3	D1
6	15	0.1	0	0	-0.1	-0.1	-0.1	-	-	-	-	-	-0.1	B
19	31	-1.5	-0.8	-0.3	-0.1	-	-	-0.1	-0.1	-0.1	-	-	-0.1	AB
22	16	0.1	0	0	0	-	-	0	0	-	-	-	0	B
22	30	0.2	0.1	0	-0.1	-0.1	-	-	-0.1	-0.1	-	-	-0.1	AB
23	16	-0.5	-0.6	-0.6	-0.6	-	-	-	-0.7	-	-0.8	-	-0.8	AE
23	31	-0.8	-0.7	-0.6	-	-	-	-0.5	-0.5	-0.5	-	-	-0.5	AE
24	15	0.5	0.4	-	-	-	-	-	-	-	0.1	0.1	0.1	AB
25	31	-0.3	-0.2	-0.2	-0.1	-	-	-	-0.1	-0.1	-	-	-0.1	AB
27	29	-1.1	-0.8	-0.5	-	-	-	-	-0.2	-0.2	-	-	-0.2	AE
29	31	-1.2	-	-	-	-	-0.4	-0.4	-0.4	-	-	-	-0.4	AE
30	30	-1.0	-0.5	-0.3	-0.2	-	-	-	-	-	-	-	-	-
31	30	-1.8	-0.8	-0.4	-0.2	-	-	-0.1	-0.1	-	-	-	-0.1	AB
32	29	-0.3	-0.2	-0.1	0	0	-	0	0	-	-	-	0	AB
32	29	0	0	0	-	-	-	-	-0.1	-0.1	-	-	-0.1	B

Transfers from 0.1m HCl into Buffer 2														
No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
1	16	0.9	0.5	0.4	0.4	-	-	0	0	0	-	-	0	AB
3	15	0.1	0.05	0	0.1	-	-	-	0.1	0.1	-	-	0.1	AB
3	30	-1.3	-0.6	-0.1	0.1	-	0.2	0.2	0.2	0.1	-	-	0.2	AE
4	16	0.3	0.6	0.4	0.15	-0.1	-0.2	-0.2	-0.2	-	-	-	-0.2	D1
6	15	0.7	1.1	1.1	0.5	0.3	0.2	0.1	0.1	-	-	-	0.1	C1
19	15	-0.2	-0.1	0	0	-	-	-	0	0	-	-	0	AB
19	31	-1.4	-0.5	-0.1	0.1	-	-	-	0.1	0.1	-	-	0.1	AB
22	16	0.5	0.4	0.4	0.3	-	-	0	0	0	-	-	0	AB
22	30	0.3	0.4	0.3	0.2	0.1	-	-	-	0.1	0.1	0.1	0.1	AB
23	16	0.9	0.3	0.3	0.3	-	-	0.3	0.3	-	-	-	0.3	E
23	31	0.2	0.4	0.6	-	-	-	0.7	0.7	-	-	-	0.7	AE
24	15	0.4	0.3	0.2	0.2	0.1	0.1	-	0.1	-	-	-	0.1	AB
25	31	-0.5	-0.2	0	0.1	-	-	0.1	0.1	-	-	-	0.1	AB
27	29	0.5	0.3	0.2	0.1	-	-	-	-	-	0.1	0.1	0.1	AB
29	31	3.3	2.3	1.4	1.0	0.7	-	-	0.32	0.3	-	-	0.3	D1
30	30	-1.0	-	-	-	-	0	0	-	-	-	-	0	AB
31	30	-1.0	-0.4	-	-	-	-	0.3	0.3	-	-	-	0.3	AE
32	29	0.6	0.2	0.1	0	-	-	0	0	0	-	-	0	AB

Transfers from Buffer 2 into 0.1m HCl														
No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
1	16	1.0	0.3	0	-0.15	-	-	-	-	-	0	0	0	AB
3	15	0.1	-0.1	-0.1	-0.1	0	-	0	0	0	-	-	0	B
3	30	-0.2	-0.3	-0.3	-	-	-	-	-0.2	-0.2	-0.2	-	-0.2	E
4	16	-1.0	-1.1	-0.9	-	-	-	-	-0.2	-0.2	-	-	-0.2	AE
6	15	0	-0.1	-0.1	-0.1	-	-	-0.1	-0.1	-	-	-	-0.1	B
19	15	-0.2	-0.2	-0.05	0	-	-	0	0	-	-	-	0	AB
22	16	-0.05	-0.15	-0.1	-0.1	0	-	-	-	0	0	-	0	B
22	30	-0.4	-0.2	-0.1	-	-	-	-	0	0	-	-	0	AB
23	16	-0.5	-0.6	-0.65	-0.65	-	-	-0.7	-0.7	-	-	-	-0.7	AE
23	31	-2.0	-1.2	-0.9	-0.7	-	-	-	-0.8	-0.8	-	-	-0.8	AE
24	15	0	-0.1	-0.1	-	-	-	-	-	-0.1	-0.1	-	-0.1	B
25	31	-0.3	-0.3	-0.2	-0.2	-	-	-	-0.2	-0.2	-	-	-0.2	E
27	24	-0.9	-0.3	-0.5	-0.3	-0.25	-0.2	-0.2	-0.15	-0.15	-	-	-0.15	AE
29	31	-1.5	-1.0	-0.7	-0.5	-	-	-	-0.1	-0.1	-	-	-0.1	D1
30	30	-0.5	-0.4	-0.3	-0.2	-	-0.2	-0.2	-	-	-	-	-0.2	AE
31	30	-1.6	-0.7	-	-	-	-	-0.3	-0.3	-	-	-	-0.3	AE
32	29	-0.2	-0.2	-0.2	-0.1	-0.1	-	-	-0.1	-0.1	-	-	-0.1	AB

Transfers from 0.1m HCl into Buffer 3

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
1	16	-1.5	0	1.1	1.5	-	-	-	-	0.3	0.3	0.3	0.3	AE
3	15	0	0	0	0	-	-	-	0	0	-	-	0	B
3	30	0.3	0.6	0.5	0.5	-	-	0.5	0.5	-	-	-	0.5	AE
4	16	1.7	1.4	1.1	0.3	-	-	-	0.8	1.0	1.1	1.1	1.1	D2
6	15	5.0	4.7	4.0	2.3	-	1.1	0.3	0.5	0.5	0.5	-	0.5	D1
19	15	0.1	0.1	0.1	0	-	0	-	0	0	-	-	0	B
19	31	0.4	0.5	-	-	-	-	0.4	0.4	-	-	-	0.4	E
22	16	0.2	0.6	0.3	-	-	-	0.6	0.6	-	-	-	0.6	AE
22	30	0.3	0.6	-	-	0.5	0.5	-	-	-	-	-	0.5	AE
23	16	1.1	1.1	1.1	1.1	-	-	1.2	1.2	-	-	-	1.2	E
23	31	-	-	-	-	-	-	-	-	1.2	1.2	1.2	1.2	E
24	15	2.8	1.6	0.8	0.4	0.3	0.3	-	-	-	-	-	0.3	D1
25	31	0.2	0.4	0.5	0.45	0.4	0.4	-	-	-	-	-	0.4	AE
27	29	0.9	0.7	0.6	0.5	-	-	-	-	-	0.3	0.3	0.3	AE
29	31	4.5	-	-	-	0.9	0.8	-	-	-	0.6	0.6	0.6	D1
30	30	-0.7	0	0.2	-	-	0.3	0.3	-	-	-	-	0.3	AE
31	30	-0.4	0.1	0.3	-	-	0.4	0.4	-	-	-	-	0.4	AE
32	29	1.0	0.8	0.6	0.4	0.4	-	-	-	-	0.4	0.4	0.4	AE

Transfers from Buffer 3 into 0.1m HCl

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
1	16	-	1.6	-0.1	-0.3	-	-	-	-	-0.2	-0.2	-	-0.2	AE
3	30	-	-	-	-0.4	-0.4	-0.4	-0.4	-	-	-	-	-0.4	E
4	16	-1.3	-1.4	-1.2	-1.1	-	-	-	-0.7	-0.7	-0.7	-0.7	-0.7	D1
6	15	-0.5	-0.5	-0.4	-	-	-	-	-0.5	-0.5	-	-	-0.5	E
19	31	-1.0	-0.7	-0.6	-	-0.5	-	-	-0.4	-0.4	-	-	-0.4	AE
22	16	-0.5	-0.5	-	-	-	-	-0.5	-0.5	-	-0.5	-	-0.5	E
22	30	0.4	-0.2	-0.4	-0.5	-	-	-	-0.5	-0.5	-	-	-0.5	AE
23	16	-0.9	-1.1	-1.1	-1.1	-	-	-1.1	-1.1	-	-	-	-1.1	AE
23	31	-0.5	-0.8	-1.0	-1.1	-	-	-	-	-1.2	-1.2	-1.2	-1.2	AE
24	15	-0.1	-0.2	-0.25	-0.3	-0.3	-0.3	-0.3	-	-	-	-	-0.3	AE
25	31	-0.6	-0.5	-0.5	-0.4	-	-	-0.4	-0.4	-	-	-	-0.4	AE
27	29	-1.1	-0.9	-0.6	-0.4	-	-0.4	-0.4	-	-	-	-	-0.4	AE
29	31	-1.1	-0.9	-	-	-	-0.6	-0.6	-0.6	-	-	-	-0.6	AE
30	30	-2.0	-1.0	-0.7	-0.6	-0.5	-0.5	-0.5	-	-	-	-	-0.5	AE
31	30	-1.1	-0.8	-0.6	-	-0.4	-	-0.4	-0.4	-	-	-	-0.4	AE
32	29	-0.1	-0.2	-0.2	-0.3	-	-	-	-	-0.3	-0.3	-0.3	-0.3	AE

PHOSPHATE BUFFER SERIES

Transfers between 0.1 m HCl and

1. 0.05m Na_2HPO_4 + 0.05m KH_2PO_4 + 0.1m KCl
2. 0.025m Na_2HPO_4 + 0.025m KH_2PO_4 + 0.1m KCl
3. 0.0125m Na_2HPO_4 + 0.0125m KH_2PO_4 + 0.1m KCl
4. 0.0025m Na_2HPO_4 + 0.0025m KH_2PO_4 + 0.1m KCl

Electrodes: 1, 3, 4, 6, 19, 22, 23, 24, 25, 26, 27, 29, 31, 32.

Runs: 1, 11, 12, 32, 33, 34, 35.

Transfers from 0.1m HCl into Buffer 1

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
1	32	-1.5	-0.6	0.1	0.3	-	-	-	0.4	0.4	0.4	-	0.4	AE
3	34	1.6	0.4	0.2	0.1	0.1	0.1	0.1	-	-	-	-	0.1	AB
4	35	1.0	0.6	0.4	-	-	-	-	-	1.6	1.6	1.6	1.6	D2
19	32	-0.5	0	0.2	0.2	-	-	-	-	0.4	0.4	0.4	0.4	AE
										(100-150 mins)				
22	33	0.2	-0.4	-0.1	-	-	-	-	0.3	0.3	0.3	0.3	0.3	AE
23	34	0.5	0.5	0.5	-	-	-	-	-	-	0.6	0.6	0.6	B
25	32	-1.0	-0.3	0	-	-	-	-	0.1	0.1	0.1	-	0.1	AB
26	35	>4	3.3	2.5	2.5	2.0	-	-	-	1.3	1.3	1.3	1.3	D1
27	34	1.0	0.5	0.3	0.2	0.2	0.2	-	-	0.2	0.2	0.2	0.2	AE
										(80-100 mins)				
29	34	>13	10.0	3.5	2.3	-	-	-	-	0.5	0.5	0.5	0.5	D1
31	33	3.5	1.7	0.7	0.2	-	-	-	-	0.2	0.2	0.2	0.2	AE
										(90-100 mins)				
32	34	2.7	2.0	1.2	0.5	-	-	-	-	-	0.2	0.2	0.2	AE

Transfers from Buffer 1 into 0.1m HCl

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
1	32	-1.8	-1.3	-0.9	-0.6	-0.5	-0.3	-0.3	-0.3	-	-	-	-0.3	AE
3	34	1.5	0.6	0.2	0	-	-	-	-	0	0	0	0	AB
4	35	-6.0	-5.9	-6.3	-	-	-	-	-	-2.0	-2.0	-2.0	-2.0	D1
19	32.	-0.1	-0.15	-0.2	-	-	-	-0.2	-0.2	-	-	-	-0.2	E
22	33	0.3	0	-	-	-	-	-	-	-0.3	-0.3	-0.3	-0.3	AE
23	34	-1.5	-0.9	-0.7	-0.5	-	-	-	-0.5	-0.5	-	-	-0.5	AE
25	32	-0.3	-0.2	-0.2	-	-	-	-0.2	-0.2	-0.2	-	-	-0.2	E
26	35	-1.3	-1.5	-1.5	-1.5	-	-1.5	-1.5	-	-	-	-	-1.5	AE
27	34	0.2	-0.1	-0.1	-0.2	-0.2	-	-	-0.2	-0.2	-0.2	-	-0.2	AE
29	34	-2.2	-1.3	-0.9	-0.7	-	-	-	-	-0.5	-0.5	-0.5	-0.5	AE
31	33	0.2	0	-0.1	-	-	-	-	-	-0.2	-0.2	-0.2	-0.2	AE
32	34	0.1	0	-0.1	-0.15	-	-	-	-0.2	-0.2	-0.2	-	-0.2	AE

Transfers from 0.1m HCl into Buffer 2														
No	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
1	12	1.0	0.5	0.5	0.4	0.3	0.3	0.2	0.2	0.2	-	-	0.2	D1
1	32	-0.5	0	0.3	0.4	0.4	-	-	-	0.3	0.3	0.3	0.3	AE
3	1	-2.0	-0.4	0.1	0.2	0.2	0.2	0.2	0.2	-	-	-	0.2	AE
3	1	0.6	0.2	0.2	0.2	0.2	0.2	0.2	0.2	-	-	-	0.2	AE
3	11	-0.2	0.1	0.2	0.3	0.3	0.3	-	-	0.3	0.3	-	0.3	AE
3	34	-0.2	-0.1	0	0.1	0.1	-	0.1	0.1	-	-	-	0.1	AB
4	12	1.0	0.3	0.5	0.2	-	-	-	-	0.5	0.5	0.5	0.5	D2
4	35	1.2	0.9	0.7	-	-	0.4	0.4	-	-	-	-	0.4	AE
6	1	1.0	0.7	0.6	0.5	0.5	0.5	0.5	-	-	-	-	0.5	AE
6	11	1.3	1.1	1.0	0.3	-	-	0.5	0.5	-	-	-	0.5	AE
19	1	1.5	-	0.2	0.2	0.2	0.2	-	-	-	-	-	0.2	AE
19	11	-2.0	-0.6	0.2	0.3	0.3	-	0.3	0.3	-	-	-	0.3	AE
19	32	0.2	0.3	0.3	0.3	-	-	-	0.2	0.2	-	-	0.2	E
22	12	0.3	0.4	0.4	0.3	0.3	0.3	0.3	-	-	-	-	0.3	AE
22	33	-	-0.1	-	-	-	-	-	-	0.3	0.3	0.3	0.3	AE
23	12	0.5	0.6	0.6	0.6	-	0.7	-	0.7	0.7	-	-	0.7	E
23	34	0	0.6	-	-	-	-	-	0.4	0.4	0.4	-	0.4	AE
24	11	3.3	2.6	2.2	1.7	-	-	1.3	1.3	-	-	-	1.3	D1
25	32	-0.8	-0.3	0	0.1	-	-	-	0.3	0.3	-	-	0.3	AE
26	35	2.6	2.5	2.4	2.2	2.1	-	-	1.5	1.5	-	-	1.5	D1
27	34	0.3	0.4	0.4	0.4	-	-	0.4	0.4	-	-	-	0.4	AE
29	34	-	>7	5.5	3.1	2.0	-	-	-	-	0.4	0.4	0.4	D1
31	33	-	-	-	-	-	-	-	-	0.3	0.3	0.3	0.3	AE
32	34	-	-	-	-	-	-	0.3	0.3	0.3	-	-	0.3	AE

Transfers from Buffer 2 into 0.1m HCl														
No	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
1	12	2.0	-	-	-	-	-	-0.2	-0.2	-0.2	0.1	-	-0.2	AE
1	32	-1.2	-	-	-	-	-	-	-	-	-0.5	-0.5	-0.5	AE
3	1	>3	0.5	0	-0.2	-0.3	-0.3	-	-	-	-	-	-0.3	AE
3	1	1.0	0	-0.1	-0.2	-0.2	-0.2	-0.2	-0.2	-	-	-	-0.2	AE
3	11	-	-	-	-	-	-	-0.1	-0.1	-0.1	-0.1	-	-0.1	AB
3	34	0.5	0	-0.1	-0.1	-	-	-0.1	-0.1	-0.1	-	-	-0.1	AB
4	12	-0.6	-1.0	-1.1	-	-	-	-	-	-0.6	-0.6	-0.6	-0.6	AE
4	35	-1.2	-1.3	-1.3	-	-1.1	-	-	-	-	-	-	-	-
6	1	0.1	-0.4	-0.4	-0.4	-0.4	-0.4	-0.4	-	-	-	-	-0.4	AE
6	11	-1.8	-0.8	-0.5	-0.4	-0.4	-0.4	-0.4	-	-	-	-	-0.4	AE
19	1	0.4	-0.1	-0.2	-0.2	-0.2	-0.2	-0.2	-0.2	-0.2	-0.2	-	-0.2	AE
19	11	1.0	0	-0.2	-0.2	-	-	-	-	-	-0.2	-0.2	-0.2	AE
19	32	-0.6	-	-	-0.2	-0.2	-0.2	-	-	-	-	-	-0.2	AE
22	12	-0.3	-0.3	-	-	-0.3	-	-0.4	-0.4	-0.4	-	-	-0.4	E
22	33	0.2	-	-	-	-	-	-	-0.3	-0.3	-0.3	-	-0.3	AE
23	12	-0.7	-0.7	-0.7	00.7	-0.7	-0.7	-0.7	-	-	-	-	-0.7	E
23	34	-2.3	-	-	-	-	-	-0.6	-0.6	-0.6	-	-	-0.6	AE
24	11	-1.4	-1.4	-1.4	-1.3	-1.3	-1.3	-	-	-	-	-	-1.3	E
25	32	-0.5	-0.3	-0.3	-0.3	-	-	-0.3	-0.3	-	-	-	-0.3	AE
25	35	-1.2	-1.5	-1.7	-1.7	-1.7	-	-	-1.7	-1.7	-	-	-1.7	AE
27	34	-0.2	-0.3	-0.4	-0.4	-	-	-	-	-	-0.3	-0.3	-0.3	E
29	34	-0.9	-0.8	-0.7	-0.6	-0.5	-0.5	-	-	-0.5	-0.5	-	-0.5	AE
31	33	-0.6	-0.5	-0.3	-0.2	-0.2	-	-	-	-	-0.2	-0.2	-0.2	AE
32	34	-0.1	-0.3	-0.2	-0.1	-0.1	-	-	-0.3	-0.3	-0.3	-	-0.3	AE

Transfers from 0.1m HCl into Buffer 3

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
1	12	1.1	0.9	0.7	-	-	0.8	-	0.5	0.3	0.3	0.3	0.3	D1
3	1	-1.3	-0.6	0.1	0.2	0.2	-	-	-	-	0.3	0.3	0.3	AE
3	11	0.4	0.4	0.4	0.3	0.3	-	-	0.3	0.3	0.3	-	0.3	E
4	12	1.1	0.9	0.8	0.5	0.3	0.4	0.5	0.7	1.0	1.0	1.0	1.0	D2
6	1	1.5	1.4	1.5	1.4	1.0	0.9	-	0.6	0.6	0.6	-	0.6	D2
6	11	1.1	0.9	0.8	0.8	-	-	0.7	0.7	-	-	-	0.7	AE
19	1	-	1.1	0.6	0.2	-	-	-	0.2	0.2	0.2	-	0.2	AE
19	11	1.2	0.7	0.6	0.4	0.4	-	-	0.4	0.4	-	-	0.4	AE
22	12	1.0	0.5	0.4	-	-	-	0.4	0.4	-	-	-	0.4	AE
23	12	1.5	1.0	0.9	0.8	-	-	0.9	0.9	-	-	-	0.9	AE
24	11	2.5	2.1	1.8	1.5	1.4	1.4	1.4	-	-	-	-	1.4	AE

Transfers from Buffer 3 into 0.1m HCl

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
1	12	3.5	1.0	-0.2	-0.5	-0.5	-	-0.4	-0.4	-	-	-	-0.4	AE
3	1	1.0	-0.2	-0.3	-0.3	-0.3	-	-	-	-	-	-	-0.3	AE
3	11	-0.1	-0.3	-0.3	-0.3	-	-	-0.3	-0.3	-0.3	-	-	-0.3	AE
											(60-100 mins)			
4	12	-1.0	-1.2	-1.2	-1.1	-	-1.3	-1.1	-	-0.8	-0.7	-0.5	-0.5	D2
6	1	-0.7	-0.7	-0.7	-0.7	-0.7	-	-	-	-0.7	-0.7	-0.7	-0.7	E
6	11	-0.8	-0.7	-0.6	-0.6	-0.6	-0.7	-0.7	-0.7	-	-	-	-0.7	E
19	1	0.5	-0.4	-0.3	-0.3	-0.3	-	-	-0.3	-0.3	-	-	-0.3	AE
19	11	0	-0.4	-0.4	-	-0.4	-0.4	-	-	-0.4	-	-	-0.4	AE
22	12	-0.4	-0.3	-0.3	-0.3	-	-	-	-0.3	-0.3	-0.3	-	-0.3	E
23	12	-1.0	-0.9	-0.9	-0.9	-0.9	-	-	-0.9	-0.9	-	-	-0.9	E
24	11	-1.6	-1.5	-1.5	-1.4	-1.4	-	-	-1.4	-1.4	-	-	-1.4	AE

Transfers from 0.1m HCl into Buffer 4

No	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
1	12	0	1.6	2.3	2.8	2.4	-	-	-	1.7	1.7	1.7	1.7	AC2
1	32	1.3	1.2	1.4	-	-	-	0.6	0.6	-	-	-	0.6	D2
3	1	-0.5	0.2	0.4	-	-	-	-	0.5	0.5	-	-	0.5	AE
3	11	-0.2	0.3	1.0	1.2	-	-	-	1.1	1.1	1.1	-	1.1	AE
3	34	0.5	0.3	0.9	1.0	-	-	-	-	1.0	1.0	1.0	1.0	AE
4	12	6.0	4.7	3.5	2.9	2.5	2.2	2.0	1.9	1.9	1.9	1.9	1.9	D1
4	35	3.0	2.9	-	-	1.3	1.3	1.3	-	-	-	-	1.3	AE
6	1	3.2	5.0	4.5	3.0	2.2	2.0	1.9	1.3	1.3	1.3	-	1.3	C2
6	1	4.2	5.5	5.0	3.5	2.4	2.0	1.7	1.2	1.0	1.0	1.0	1.0	C2
6	11	3.3	3.6	6.5	5.0	3.2	2.6	-	1.7	1.7	-	-	1.7	C2
19	1	-	2.5	1.5	1.0	-	-	-	-	-	0.6	0.6	0.6	D1
19	11	2.3	2.0	1.7	1.4	1.3	-	-	1.1	1.1	1.1	-	1.1	D1
19	32	1.0	1.1	1.1	0.9	-	0.9	0.9	0.9	-	-	-	0.9	E
22	12	2.0	2.2	-	-	2.1	2.0	2.0	2.0	-	-	-	2.0	AE
22	33	1.6	2.0	1.3	1.5	-	-	1.4	1.4	-	-	-	1.4	AE
23	12	1.0	1.3	1.9	-	-	2.0	2.0	-	-	-	-	2.0	AE
23	34	2.3	2.4	2.1	-	-	1.7	1.7	-	-	-	-	1.7	D1
24	11	>20	>13	>8	4.0	3.2	3.0	2.3	2.8	-	-	-	2.8	D1
25	32	-0.2	-0.3	-0.4	-0.5	-0.5	-	-	-	0.7	0.7	0.7	0.7	D2
26	35	2.1	3.9	4.2	3.7	-	-	-	-	2.7	2.6	2.6	2.6	D2
27	34	2.0	1.8	1.6	1.5	-	-	-	-	-	1.3	1.3	1.3	D1
29	34	-	-	>8	4.5	3.3	-	-	-	-	1.9	1.9	1.9	D1
31	33	1.1	0.9	0.8	0.8	0.7	0.7	0.7	-	-	-	-	0.7	AE
32	34	5.0	4.0	3.0	2.1	-	-	1.2	1.2	-	-	-	1.2	D1

Transfers from Buffer 4 into 0.1m HCl

No	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
1	12	-	-2.3	-2.2	-2.0	-	-1.8	-1.8	-	-	-1.7	-1.7	-1.7	D1
1	32	0	-0.7	-0.8	-0.9	-	-	-	-0.6	-	-0.6	-0.6	-0.6	D1
3	1	0.7	-0.2	-0.5	-0.5	-	-	-0.5	-0.5	-	-	-	-0.5	AE
3	11	0	-0.9	-1.1	-1.1	-	-	-	-1.1	-1.1	-	-	-1.1	AE
3	34	-	-	-1.2	-1.1	-1.0	-1.0	-	-	-1.0	-1.0	-	-1.0	AE
4	12	-2.5	-2.6	-2.5	-2.5	-2.4	-2.5	-2.4	-	-	-2.0	-2.0	-2.0	D2
6	1	-1.3	-1.3	-1.3	-1.8	-1.3	-1.3	-1.3	-	-	-	-	-1.8	E
6	1	-0.8	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-	-	-	-	-1.0	AE
6	11	-1.8	-1.7	-1.7	-1.7	-	-	-1.7	-1.7	-	-	-	-1.7	E
19	1	-1.3	-0.9	-0.6	-0.6	-0.7	-	-	-0.7	-0.7	-	-	-0.7	AE
19	11	-3.0	-2.0	-1.4	-1.2	-1.2	-	-	-	-1.2	-1.2	-	-1.2	AE
19	32	-2.5	-1.8	-1.3	-1.2	-1.2	-1.2	-	-	-	-	-	-1.2	AE
22	12	-1.5	-2.0	-2.0	-2.0	-	-	-2.0	-2.0	-	-	-	-2.0	AE
22	33	-1.1	-1.3	-1.3	-1.4	-1.4	-	-	-	-	-	-	-1.4	AE
23	12	-2.3	-2.5	-2.4	-2.3	-	-	-	-	-	-	-	-2.3	AE
23	34	-2.9	-2.3	-2.0	-1.7	-1.6	-1.6	-1.6	-	-	-	-	-1.6	AE
24	11	-2.8	-2.8	-2.8	-	-	-2.8	-2.8	-	-	-	-	-2.3	E
25	32	-0.5	-0.6	-0.6	-0.6	-	-	-	-0.6	-0.6	-	-	-0.6	E
26	35	-2.7	-2.9	-	-	-	-	-3.2	-3.2	-	-	-	-3.2	AE
27	34	-1.5	-1.4	-1.4	-1.3	-	-	-	-	-1.3	-1.3	-1.3	-1.3	E
29	34	-3.2	-2.5	-2.1	-1.9	-	-	-1.9	-1.9	-	-	-	-1.9	AE
31	33	-	-	-	-	-	-	-0.9	-0.9	-	-	-	-0.9	E
32	34	-1.7	-1.4	-1.3	-1.2	-	-	-1.1	-1.1	-	-	-	-1.1	AE

TRIS-HCl BUFFER SERIES (KCl SERIES)

Transfers between 0.1m HCl and

1. 0.2m TRIS + 0.1m HCl
2. 0.1m TRIS + 0.05m HCl + 0.05m KCl
3. 0.02m TRIS + 0.01m HCl + 0.09m KCl

Electrodes:	1, 3, 4, 6, 19, 22, 23, 24
Runs:	3, 9, 10

Transfers from 0.1m HCl into Buffer 1														
No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
1	10	-1.5	-0.5	-0.1	0	0	0	0	-	-	-	-	0	AB
1	10	-3.0	-1.5	-0.5	0	0	0	-	-	-	-	-	0	AB
3	9	-	-	-	0	0	0	0	0	-	-	-	0	AB
4	10	0.1	0.1	0	0	0	0	-	-	-	-	-	0	B
6	3	0.3	0.4	0.5	0.5	0.5	0.5	-	-	-	0.5	0.5	0.5	AE
6	9	0.4	0.4	0.4	0.4	-	-	-	-	0.4	0.4	-	0.4	E
19	9	0.1	0.1	0.1	0.1	0.1	0.1	0.1	-	-	-	-	0.1	B
22	10	0	0.3	0.2	0.2	-	-	-	0.2	0.2	-	-	0.2	AE
22	10	-0.1	0	0.1	0.1	-	-	-	-	0.1	0.1	-	0.1	B
23	10	-0.3	0.1	0.4	0.6	-	0.7	0.7	-	-	-	-	0.7	AC1
24	9	0.1	0	0	0	-	-	0	0	-	-	-	0	B

Transfers from Buffer 1 into 0.1m HCl														
No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
1	10	-1.0	-0.6	-0.2	-	-	-	-	0	0	-	-	0	AB
3	3	-	-	0	0	0	0	0	-	-	-	-	0	AB
3	9	-0.6	-0.3	-0.1	0	0	0	0	0	-	-	-	0	AB
4	10	-1.5	-1.2	-1.0	-0.7	-	-	-	-	0	0	0	0	D1
6	3	-0.7	-0.5	-0.4	-0.4	-	-	-0.4	-0.4	-	-	-	-0.4	AE
6	9	-0.1	-0.2	-0.3	-0.4	-	-	-	-0.4	-	-	-	-0.4	AE
19	3	-0.5	-0.3	-0.1	-0.1	-0.1	-	-	-0.1	-0.1	-	-	-0.1	AB
19	9	-0.5	-0.3	-0.1	-0.1	-	-	-0.1	-0.1	-0.1	-	-	-0.1	AB
22	10	0.3	0.7	0.3	0	-0.1	-	-	0	0	-	-	0	AB
22	10	-0.4	-0.1	-0.1	-0.1	-	-	-0.1	-0.1	-	-	-	-0.1	AB
23	10	-0.2	-0.5	-0.6	-0.7	-0.7	-	-	-	-	-	-	-0.7	AB
24	9	0.1	0	0	0	0	0	-	-	-	-	-	0	B

Transfers from 0.1m HCl into Buffer 2

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
1	10	0	0.3	0.4	-	-	-	-	-	0.7	0.7	0.7	0.7	C1
1	10	1.0	1.3	-	0.9	0.7	0.7	0.7	-	-	-	-	0.7	C2
3	3	-0.5	-0.4	-0.2	-0.1	0	0	0	0	-	-	-	0	AB
3	9	-0.3	-0.2	-0.1	0	0	0	0	-	-	-	-	0	AB
4	10	0.9	0.7	0.5	0.3	0.2	-	0.2	0.2	-	-	-	0.2	AB
6	3	0.4	0.8	0.8	0.7	-	0.5	0.5	-	-	-	-	0.5	AE
6	9	0.5	0.6	0.7	0.5	0.4	-	-	0.4	0.4	-	-	0.4	AE
19	3	0.3	0.1	0.1	0	0	0	0	-	-	-	-	0	AB
19	9	0.1	0.2	0.2	0.2	-	-	-	0.2	0.2	-	-	0.2	E
22	10	0.2	0.2	0.2	0.2	0.2	0.2	-	-	-	-	-	0.2	E
22	10	0.3	0.2	0.2	0.2	0.2	-	-	-	-	-	-	0.2	E
23	10	2.0	1.4	1.2	1.1	1.2	1.2	-	-	-	-	-	1.2	AE
24	9	2.9	2.6	2.3	-	1.8	1.8	-	-	-	-	-	1.8	AE

Transfers from Buffer 2 into 0.1m HCl

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
1	10	0.6	-0.1	-0.4	-0.5	-	-	-	-0.5	-0.5	-	-	-0.5	AE
1	10	1.0	-0.1	-0.8	-0.9	-	-	-0.7	-0.7	-	-	-	-0.7	AC2
3	3	-	-0.2	-0.2	-0.1	-	-	-	0	0	0	-	0	AB
3	9	-0.4	-0.2	-0.1	0	0	-	-	-	-	0	-	0	AB
4	10	-2.0	-1.7	-1.5	-	-	-0.6	-0.6	-	-	-	-	-0.6	AE
6	3	-0.6	-0.5	-0.5	-	-	-0.6	-0.6	-	-	-	-	-0.6	E
6	9	-0.3	-0.4	-0.4	-	-	-0.4	-	-	-	-	-	-0.4	E
19	3	-0.8	-0.4	-0.2	-	-	-	-	0	0	-	-	0	AB
19	9	-0.7	-0.4	-0.3	-0.1	-	-	-	-	0	0	-	0	AB
22	10	-	-	-	-	-	lost	-	-	-	-	-	-	-
22	10	-0.9	-0.3	-0.2	-0.2	-0.2	-0.2	-	-	-	-	-	-0.2	AE
23	10	-2.0	-1.5	-1.3	-1.2	-	-	-	-1.2	-	-	-	-1.2	AE
24	9	-3.1	-2.8	-2.5	-2.3	-2.1	-1.9	-1.9	-1.9	-	-	-	-1.9	D1

Transfers from 0.1m HCl into Buffer 3

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
1	10	4.5	2.9	2.1	1.7	-	-	1.3	1.3	-	-	-	1.3	D1
3	3	-0.1	0	0.3	0.4	0.5	-	-	-	-	0.4	0.4	0.4	AE
3	9	0.2	0.2	0.2	0.3	-	-	-	-	0.2	0.2	-	0.2	E
4	10	2.8	-	-	-	-	1.7	1.7	-	-	-	-	1.7	AE
6	3	1.9	2.4	2.1	-	-	1.5	1.4	-	-	lost	-	-	D2
6	9	1.6	2.3	2.3	1.6	-	1.1	1.0	-	0.8	0.8	-	0.8	D2
19	3	1.6	1.4	1.2	1.0	0.8	-	-	1.0	1.0	-	1.1	0.7*	D2
19	9	1.4	1.2	1.0	0.6	0.5	-	0.4	0.4	-	-	-	0.4	D1
22	10	1.3	1.0	1.0	1.0	1.0	-	-	1.0	-	-	-	1.0	AE
23	10	2.2	2.8	2.8	2.6	-	-	2.3	2.3	-	-	-	2.3	C2
24	9	3.5	3.3	3.0	2.8	-	-	3.3	3.5	3.5	-	-	3.5	C2

* Extrapolated to t=o

Transfers from Buffer 3 into 0.1m HCl

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
1	10	-	-	-	-1.9	-1.6	-	-	-	-1.3	-1.3	-	-1.3	D1
3	3	-0.9	-0.8	-	-0.6	-	-	-	-	-0.7	-0.7	-	-0.7	AE
3	9	-1.0	-0.7	-0.5	-0.3	-0.3	-0.3	-	-	-	-	-	-0.3	AE
4	10	2.8	-2.4	-2.3	-2.2	-2.2	-2.2	-	-	-	-	-	-2.2	AE
6	3	-1.2	-1.1	-1.1	-1.1	-1.1	-1.1	-	-	-	-	-	-1.1	E
6	9	-0.9	-0.9	-0.8	-0.8	-	-	-0.8	-0.8	-	-	-	-0.8	E
19	3	-1.3	-1.0	-0.9	-	-	-1.0	-	-1.4	-1.7	-	-	-0.7*	D2
19	9	-0.5	-0.5	-0.4	-0.4	-	-	-0.5	-0.5	-	-	-	-0.5	E
22	10	-1.0	-1.1	-1.0	-1.0	-1.0	-	-	-	-	-	-	-1.0	E
23	10	-	-3.3	-2.9	-	-	-2.4	-2.4	-	-	-	-	-2.4	D1
24	9	-4.1	-3.8	-3.6	-3.3	-3.3	-3.3	-	-	-	-	-	-3.3	AE

* Extrapolated to t=o

TRIS-HCl BUFFER SERIES (Me_4NCl SERIES)

Transfers between 0.1m HCl and

1a. 0.2m TRIS + 0.1m HCl

2a. 0.1m TRIS + 0.05m HCl + 0.05m Me_4NCl

3a. 0.02m TRIS + 0.01m HCl + 0.09m Me_4NCl

Electrodes: 1, 3, 4, 6, 19, 22, 23, 24

Runs: 13, 14

Transfers from 0.1m HCl into Buffer 1a

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
1	14	-	-1.7	-0.7	-0.1	0.1	0.1	0.1	-	-	-	-	0.1	AB
3	13	-0.5	-0.3	-0.1	0	0.1	0.1	-	-	0.1	0.1	-	0.1	AB
3	14	-0.3	-0.2	-0.1	0	0	0	0	-	-	-	-	0	AB
4	14	0.2	0.1	0.1	-	-	0.1	0.1	-	-	-	-	0.1	B
6	13	0.2	0.3	0.3	0.4	0.5	-	0.5	0.5	-	-	-	0.5	AE
19	13	-0.3	-0.1	0	0	-	-	-	0	0	-	-	0	AB
22	14	0.2	0.2	0.2	0.1	0.1	0.1	-	-	-	-	-	0.1	AB
23	14	0.1	0.2	0.3	0.4	0.5	0.65	0.7	0.7	-	-	-	0.7	C1
24	13	0.3	0.2	0.1	0.1	-	-	0	0	-	-	-	0	AB

Transfers from Buffer 1a into 0.1m HCl

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
1	14	1.3	0.6	0.2	0	-	-	0.1	0.1	0.1	-	-	0.1	AB
3	13	1.5	0.7	0.3	0	0	0	-	-	-	-	-	0	AB
3	14	-0.1	-0.2	-0.2	-	-	-	0	0	-	-	-	0	B
4	14	-1.4	-1.1	-0.9	-0.8	-	-	-	-	-0.4	-0.4	-	-0.4	D1
6	13	0.1	-0.1	-0.2	-0.2	-	-0.2	-0.2	-	-	-	-	-0.2	E
19	13	0.4	0.2	0.1	0	-	-	-	0	0	-	-	0	AB
22	14	-0.3	-0.2	-	-	0	0	0	-	-	-	-	0	AB
23	14	-0.7	-0.7	-0.7	-0.7	-0.7	-	-	-	-	-	-	-0.7	E
24	13	0.2	0.1	0	0	-	-	0	0	-	-	-	0	AB

Transfers from 0.1m HCl into Buffer 2a

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
1	14	-	-	-	-	-	-	-	0.5	0.5	0.5	-	0.5	AE
3	13	-0.1	-0.1	0	0	0	-	-	0	0	-	-	0	B
3	14	-0.2	-0.1	0	0	-	-	-	0	0	-	-	0	AB
4	14	0.6	0.5	0.4	0.3	0.2	0.2	-	-	-	-	-	0.2	AE
6	13	0.6	0.6	0.6	0.5	-	-	0.4	0.4	-	-	-	0.4	AE
19	13	0.1	0.1	0.1	-	-	-	0	0	-	-	-	0	B
22	14	0.2	0.3	0.3	-	-	0.3	0.3	0.3	-	-	-	0.3	B
23	14	0.3	0.4	0.5	-	-	0.8	-	-	-	-	-	0.8	AE
24	13	0.2	0.1	0.1	0.1	-	-	0.1	0.1	-	-	-	0.1	B

Transfers from Buffer 2a into 0.1m HCl

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
1	14	0.7	0.2	-0.1	-	-0.4	-0.4	-0.4	-	-0.4	-0.4	-0.4	-0.4	AE
3	13	1.5	0.4	0.1	0	0	0	-	0	0	-	-	0	AB
3	14	-0.3	-0.2	-0.1	-	-	-	-	-	-0.1	-	-	-0.1	AB
4	14	-1.6	-1.2	-0.9	-0.8	-	-	-	-0.2	-0.2	-0.2	-	-0.2	AE
6	13	-0.2	-0.3	-0.3	-0.3	-0.3	-	-	-0.2	-0.2	-0.2	-	-0.2	E
19	13	0.2	0	-0.1	-0.1	-0.1	-	-	0	0	-	-	0	AB
22	14	-0.1	-0.2	-0.2	-	-	-0.2	-0.2	-	-	-	-	-0.2	E
23	14	-0.7	-0.7	-0.8	-	-0.8	-0.8	-	-	-	-	-	-0.8	E
24	13	0.2	0.1	0	0	-	-	-	0	0	-	-	0	AB

Transfers from 0.1m HCl into Buffer 3a

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
1	14	1.0	1.0	1.0	-	1.2	1.3	-	1.2	1.2	1.2	-	1.2	AE
3	13	0.4	0.3	0.2	0.1	-	0.1	0.1	0.1	-	-	-	0.1	AB
4	14	1.5	1.4	1.3	-	-	-	-	-	1.5	1.5	-	1.5	E
6	13	1.5	1.4	1.5	-	-	1.4	1.4	1.4	-	-	-	1.4	E
19	13	0.9	0.7	0.6	0.4	-	0.4	0.4	-	-	-	-	0.4	AE
22	14	1.0	1.1	1.3	1.5	1.5	1.4	-	1.3	1.3	-	-	1.3	AE
23	14	1.3	-	-	1.4	1.6	-	1.7	1.7	-	-	-	1.7	AE
24	13	0.8	0.7	0.7	-	0.7	0.8	-	0.8	-	-	-	0.8	E

Transfers from Buffer 3a into 0.1m HCl

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
1	14	-2.3	-1.5	-1.2	-1.0	-	-1.0	-	-1.0	-	-	-	-1.0	AE
3	13	0.2	-0.1	-0.2	-0.2	-	-	-0.1	-	-	-	0	0	AE
4	14	-2.5	-	-	-	-1.8	-	-1.9	-1.6	-	-1.5	-1.5	-1.5	D1
6	13	-1.3	-1.3	-1.3	-1.3	-	-1.2	-	-1.2	-1.2	-	-	-1.2	E
19	13	0	-0.1	-0.2	-0.3	-	-	-	-0.6	-0.6	-	-	-0.6	AE
22	14	-1.5	-1.4	-1.3	-1.3	-	-	-1.3	-1.3	-	-	-	-1.3	AE
23	14	-1.6	-1.6	-1.6	-1.6	-	-1.6	-1.6	-	-	-	-	-1.6	E
24	13	-0.7	-0.7	-	-	-	-1.0	-1.0	-	-	-	-	-1.0	AE

BORAX BUFFER SERIES

Transfers between 0.1m HCl and

1. 0.05m $Na_2B_4O_7$ + 0.1m KCl
2. 0.01m $Na_2B_4O_7$ + 0.1m KCl
3. 0.005m $Na_2B_4O_7$ + 0.1m KCl

Electrodes: 3, 6, 19

Run: 2

Transfers from 0.1m HCl into Buffer 1

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
3	2	0.2	0.3	0.3	0.3	0.3	-	-	0.3	0.3	0.3	-	0.3	E
6	2	0.4	0.6	0.6	0.5	-	-	-	0.4	0.4	-	-	0.4	AE
19	2	1.0	0.35	0.15	0	-	-	-	0	0	-	-	0	AB

Transfers from Buffer 1 into 0.1m HCl

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
3	2	-0.5	-0.6	-	-	-0.6	-0.6	-	-	-0.6	-	-	-0.6	E
6	2	-0.3	-0.6	-0.5	-0.4	-0.4	-0.4	-0.4	-	-	-	-	-0.4	AE
19	2	-1.5	-0.5	-0.2	-0.1	-	-	-	0	0	-	-	0	AB

Transfers from 0.1m HCl into Buffer 2

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
3	2	-0.6	-0.2	0	0.15	-	-	0.2	0.2	0.2	-	-	0.2	AE
6	2	1.2	1.7	1.6	0.8	-	-	0.3	0.3	-	-	-	0.3	C2
19	2	0.2	0.1	0.15	0.2	0.2	-	0.3	0.3	-	-	-	0.3	E

Transfers from Buffer 2 into 0.1m HCl

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
3	2	-0.4	-0.35	-0.25	-0.2	-0.2	-	-	-0.2	-	-	-	-0.2	AE
6	2	-0.3	-0.3	-0.3	-0.3	-	-	-0.3	-0.3	-	-	-	-0.3	E
19	2	-1.2	-0.6	-0.3	-0.2	-	-0.3	-0.3	-	-	-0.3	-0.3	-0.3	AE

Transfers from 0.1m HCl into Buffer 3

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
3	2	0.7	0.4	0.3	0.3	-	-	-	-	0.4	0.4	-	0.4	AE
6	2	1.0	0.9	0.7	0.7	0.7	-	-	-	0.7	0.7	-	0.7	AE
19	2	-0.5	0	0.2	0.3	-	-	-	-	-	0.3	0.3	0.3	AE

Transfers from Buffer 3 into 0.1m HCl

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
3	2	-0.4	-0.3	-0.5	-0.5	-0.5	-0.5	-0.5	-	-	-	-	-0.5	E
6	2	-1.0	-0.8	-0.7	-0.7	-	-	-	-0.9	-0.9	-	-	-0.9	D2
~~19~~	~~2~~	~~-1.0~~	-0.3	0.1	0.2	-	-	-	-	-0.6	-0.6	-0.6	-0.6	D2

MIXED BUFFER SERIES

Consecutive transfers from 0.1m HCl into

1. 0.05m K tetroxalate + 0.1 m KCl
2. 0.05m KH phthalate + 0.1 m KCl
3. 0.025m KH_2PO_4 + 0.025m Na_2HPO_4 + 0.1m KCl
4. 0.01m $Na_2B_4O_7$ + 0.1 m KCl

Electrodes:	1, 3, 4, 6, 19, 22, 23, 24, 25, 26, 27, 29, 30, 31, 32.
Runs:	36, 37, 38, 39

Transfers from 0.1m HCl into tetroxalate buffer

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
3	36	-0.5	-0.4	-0.2	-	-	-	-	-	0	0	0	0	AB
4	36	0	0.1	0.1	0.1	lost							0.1?	B?
6	39	0.7	0.4	0.2	0.1	0	0	0	-	-	-	-	0	AB
19	37	-1.5	-0.7	-0.2	-0.1	-	-	-	-	-0.1	-0.1	-0.1	-0.1	AB
22	37	0.7	0.7	0.3	-	-	-	-	-	0	0	0	0	AB
23	38	-0.2	-0.1	0	0	0.05	-	0.1	0.5	-	0.15	-	0	B
24	39	0.4	0.3	0.2	0.1	-	0	0	0	-	-	-	0	AB
25	38	-2.0	-0.5	-	-	-	-	-	-	-	0.1	0.1	0.1	AB
26	38	-0.7	-0.3	0	-	-	-	-	-	-0.1	-0.1	-0.1	-0.1	AB
27	38	0	0	-	-	0.1	0.1	-	0.2	0.2	0.2	-	0.2	AB
29	38	-0.3	-0.1	0	-	-	0	0	-	-	-	-	0	AB
30	38	0.2	0.1	0	0	lost							0?	AB?
31	38	0.4	0	0	0	-	-	-	-	0	0	-	0	AB
32	38	0	-0.1	-0.1	-0.1	-	-	-0.1	-0.1	-	-	-	-0.1	B

Transfers from tetroxalate buffer into phthalate buffer

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
1	36	lost												
3	36	-	-1.2	-0.4	-0.1	-	-	-	-	-	0.2	0.2	0.2	AE
4	36	lost												
6	39	-0.4	-	-	0.4	0.4	0.4	0.4	-	-	-	-	0.4	AE
19	37	-0.2	0	0.2	0.2	0.2	-	-	-	0.2	0.2	0.2	0.2	AE
22	37	-0.2	0.2	0.3	0.3	0.3	-	-	0.3	0.3	-	-	0.3	AE
23	38	-	-	-	-	-	0.3	0.4	0.4	0.4	0.4	-	0.4	E
24	39	0.8	0.7	-	-	-	-	-	-	0.1	0.1	-	0.1	AB
25	38	-0.4	-	-	-	-	-	-	-	-	0.4	0.4	0.4	AE
26	38	1.3	1.1	1.0	0.9	-	-	-	0.5	0.5	0.5	-	0.5	D1
27	38	0.9	0.5	0.3	0.2	0.2	-	-	0.2	0.2	-	-	0.2	AE
29	38	2.8	1.1	0.7	-	-	-	-	-	0.3	0.3	-	0.3	AE
30	38	0	0.1	0.1	0.1	0.1	-	0	0	-	-	-	0	B
31	38	-0.3	-0.2	0	0.2	-	-	-	0.2	0.2	-	-	0.2	AE
32	38	0.6	0.4	0.3	-	-	-	0.4	0.4	-	-	-	0.4	AE

Transfers from phthalate buffer into phosphate buffer

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
1	36	-	-2.5	-0.6	0	0 – 0.1 at 50 min				-0.25 at 90 min			0	AB
3	36	0.3	0.1	0.1	0.1	-	-	-	0.2	0.2	0.2	-	0.2	AE
4	36	0.1	0	0	0	-	-	0.2	0.2	-	-	-	0.2	E
6	39	0.8	0.7	0.6	-	-	-	-	-	-0.1	-0.1	-0.1	-0.1	AB
19	37	-1.0	-0.3	-0.1	0.1	-	-	-	0.1	0.1	0.1	-	0.1	AB
22	37	0.3	0.2	0.1	0.1	0.1	-	-	-	0.1	0.1	-	0.1	AB
23	38	-	-	-	-	-	-	0.15	0.2	0.2	0.25	-	0.1	B
24	39	0.9	0.8	0.7	0.6	-	-	-	0.4	0.4	-	-	0.4	D1
25	38	-0.1	0	0.1	0.1	0.1	-	-	-	-	-	-	0.1	B
26	38	1.5	1.4	1.4	-	-	-	-	-	-	0.5	0.5	0.5	D1
27	38	0.2	0	-0.1	-	-	-	-	0.1	0.1	-	-	0.1	AB
29	38	4.3	3.4	2.4	-	-	-	-	0.3	0.3	0.3	-	0.3	D1
31	38	-1.7	-0.9	-	-	-	0.1	0.1	0.1	0.1	-	-	0.1	AB
32	38	1.2	0.8	0.4	0.1	-	0	0	-	-	-	-	0	AB

Transfers from phosphate buffer into borax buffer

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
1	36	-	-3.0	0	1.0	1.2	1.2	-	-	-	1.2	1.2	1.2	AE
3	36	0.2	0	0.1	0.1	0.1	0.1	0.1	-	-	0.1	-	0.1	AB
4	36	-	-	-	-	1.0	1.0	1.0	-	-	-	-	1.0	AE
6	34	2.2	1.6	1.3	-	-	-	-	0.7	0.7	-	-	0.7	AE
19	37	-1.0	-0.3	0	-	-	-	-	-	0	0	-	0	AB
22	37	-	-	-	0.3	0.3	0.3	-	-	-	-	-	0.3	E
23	37	6.0	5.0	-	-	-	-	-	1.5	1.5	1.5	-	1.5	D1
24	39	4.7	4.6	4.6	5.0	-	-	-	7.0	7.6	8.0	-	5.7	D2
25	38	0.8	0.5	0.3	0.3	-	-	-	-	0.3	0.3	-	0.3	AE
26	38	1.7	1.5	1.3	1.2	-	1.0	1.0	1.0	-	-	-	1.0	D1
27	38	1.0	0.8	0.8	-	-	-	-	1.0	1.0	-	-	1.0	AE
29	38	5.9	4.9	3.8	-	-	-	-	0.6	0.6	-	-	0.6	D1
30	38	-0.4	-0.3	-0.2	0	0	-	0	0	-	-	-	0	AB
31	38	-0.5	0	0.3	0.5	-	-	-	0.6	0.6	0.6	-	0.6	AE
32	38	3.3	2.1	1.3	-	-	0.6	0.6	-	-	-	-	0.6	AE

Transfers from borax buffer into 0.1m HCl

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
1	36	2.3	0.2	-0.8	-1.3	-	-	-1.3	-1.3	-	-	-	-1.3	AE
3	36	-	-	-	-0.3	-0.3	-0.3	-	-	-	-	-	-0.3	E
4	36	-2.2	-2.4	-2.5	-2.3	-2.2	-2.2	-2.2	-	-	-	-	-2.2	AE
6	39	-0.6	-0.8	-0.9	-	-	-	-1.1	-1.1	-1.1	-	-	-1.1	AE
19	37	-1.6	-1.0	-0.7	-0.4	-0.2	-	0	0	0	0	-	0	AB
22	37	-0.6	-0.5	-0.4	-0.3	-0.3	-0.3	-0.3	-	-	-	-	-0.3	AE
23	38	-5.5	-4.3	-3.3	-	-	-	-2.2	-2.2	-2.2	-	-	-2.2	AE
24	39	-5.4	-5.3	-5.3	-5.6	-	--7.3 at 50 min			-7.6 at 110 min			-7.0	AE
25	38	-2.5	-0.9	-0.6	-	-	-	-	-0.2	-0.2	-0.2	-	-0.2	AE
26	38	-2.8	-2.6	-	-	-2.2	-2.2	-2.2	-	-	-	-	-2.2	AE
27	38	-1.5	-1.4	-1.5	-	-	-1.5	-1.5	-1.5	-	-	-	-1.5	E
29	38	-2.1	-2.0	-1.8	-	-	-	-1.4	-1.4	-1.4	-	-	-1.4	AE
30	38	-0.9	-1.1	-1.1	-	-	-	-	-1.2	-1.2	-1.2	-	-1.2	AE
31	38	-1.7	-1.4	-1.1	-	-0.8	-0.8	-0.8	-	-	-	-	-0.8	AE
32	38	-0.3	-0.5	-0.8	-	-0.9	-	-0.9	-	-	-	-	-0.9	AE

PHOSPHATE BUFFER SERIES

Transfers between 0.1m H_2SO_4 and

1. 0.05m KH_2PO_4 + 0.05m Na_2HPO_4 + 0.1m KCl
2. 0.025m KH_2PO_4 + 0.025m Na_2HPO_4 + 0.1m KCl
3. 0.0125m KH_2PO_4 + 0.0125m Na_2HPO_4 + 0.1m KCl
4. 0.0025m KH_2PO_4 + 0.0025m Na_2HPO_4 + 0.1m KCl

Electrodes: 1, 3, 19, 22, 23, 24

Runs: 17, 18

Transfers from 0.1m H_2SO_4 into Buffer 1

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
1	17	-1.0	0.5	0.7	-	-	-	-	0.2	0.2	-	-	0.2	AE
3	13	-0.7	-0.3	0	0.2	-	-	-	0.2	0.2	-	-	0.2	AE
19	17	0	0.4	0.4	0.4	0.4	0.4	0.4	-	0.4	-	-	0.4	AE
22	18	0	0.3	0.3	0.3	-	-	0.1	0.1	0.1	-	-	0.1	AE
23	13	-0.1	0	0.1	0.2	-	0.3	0.35	0.4	0.4	-	-	0.4	AC1
24	18	3.2	2.8	2.5	2.0	1.6	-	1.4	1.4	-	-	-	1.4	D1

Transfers from Buffer 1 into 0.1m H_2SO_4

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
1	17	2.2	0.6	-0.1	-0.3	-	-	-0.3	-0.3	-	-	-	-0.3	AE
3	18	-0.7	-0.5	-0.4	-0.3	-	-	-0.3	-0.3	-	-	-	-0.3	AE
19	17	-1.2	-0.7	-0.5	-0.3	-	-	-	-0.3	-0.3	-0.3	-	-0.3	AE
22	18	-0.7	-0.5	-0.4	-	-	-0.2	-0.2	-0.2	-	-	-	-0.2	AE
23	18	-1.2	-0.8	-0.6	-	-	-0.3	-0.3	-	-	-	-	-0.3	AE
24	18	-1.5	-1.5	-1.4	-	-	-1.4	-1.4	-	-	-	-	-1.4	AE

Transfers from 0.1m H_2SO_4 into Buffer 2

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
1	17	-1.3	0.6	0.9	0.8	-	-	0.4	0.4	-	-	-	0.4	AC2
3	18	-4.0	-1.2	-0.2	0.2	0.3	0.3	0.3	0.3	-	-	-	0.3	AC1
19	17	-0.1	0.2	0.3	0.4	-	-	0.4	0.4	-	-	-	0.4	AE
22	18	1.1	0.5	0.45	-	-	-	0.3	0.3	0.3	-	-	0.3	AE
23	13	-0.35	-0.2	-0.1	-	-	0.3	0.3	0.3	-	-	-	0.3	AE
24	18	2.5	2.2	1.9	-	-	1.4	1.4	1.4	-	-	-	1.4	D1

Transfers from Buffer 2 into 0.1m H_2SO_4

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
1	17	1.7	0.4	0	-0.1	-	-	-0.4	-0.4	-0.4	-	-	-0.4	AC1
3	18	-2.5	-1.4	-0.7	-0.4	-	-	-0.3	-0.3	-0.3	-	-	-0.3	D1
19	17	-0.8	-0.6	-0.4	-0.3	-0.3	-	-	-0.3	-0.3	-	-	-0.3	AE
22	18	-0.7	-0.4	-0.3	-	-	-	-	-	-	-0.3	-0.3	-0.3	AE
23	18	-0.7	-	-	-0.3	-0.3	-0.3	-	-	-	-	-	-0.3	AE
24	18	-1.4	-1.4	-1.4	-1.4	-	-1.4	-1.4	-	-	-	-	-1.4	E

Transfers from 0.1m H_2SO_4 into Buffer 3

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
1	17	3.3	2.5	1.6	0.7	-	-	-	0.3	0.3	-	-	0.3	D1
3	18	-0.2	0	0.2	0.3	-	-	-	-	0.3	0.3	0.3	0.3	AE
19	17	0.4	0.6	0.6	-	-	-	0.2	0.2	-	-	-	0.2	C2
22	18	-0.9	0.2	0.4	-	-	-	-	0.3	0.3	-	-	0.3	AE
23	18	0.65	-	-	0.4	-	0.5	0.5	-	-	-	-	0.5	AE
24	18	2.3	2.0	1.8	-	-	-	1.4	1.3	1.3	1.3	-	1.3	D1

Transfers from Buffer 3 into 0.1m H_2SO_4

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
1	17	2.1	0.4	-0.2	-	-	-	-0.3	-0.3	-0.3	-	-	-0.3	AE
3	18	-0.8	-0.5	-0.4	-	-	-0.4	-0.4	-	-	-	-	-0.4	AE
19	17	-0.6	-0.5	-0.5	-	-	-	-	-0.4	-0.4	-	-	-0.4	AE
22	18	-0.4	-0.2	-0.2	-0.2	-0.2	-	-0.2	-0.2	-0.2	-	-	-0.2	AE
23	18	-0.7	-	-	-0.6	-0.6	-	-	-	-	-	-	-0.6	E
24	18	-1.3	-1.3	-	-	-1.2	-1.2	-1.2	-	-	-	-	-1.2	E

Transfers from 0.1m H_2SO_4 into Buffer 4

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
1	17	0.2	1.4	1.9	2.0	-	-	1.3	1.2	1.2	-	-	1.2	C1
3	18	-	-	1.0	0.8	0.8	0.8	-	0.8	0.8	-	-	0.8	AE
19	17	1.7	1.5	-	-	-	-	0.6	0.6	0.6	-	-	0.6	D1
22	18	0.5	1.0	1.1	1.2	1.2	-	-	1.2	1.2	-	-	1.2	AE
24	18	3.8	3.1	-	-	2.1	2.1	2.1	-	-	-	-	2.1	AE

Transfers from Buffer 4 into 0.1m H_2SO_4

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
3	18	-0.8	-0.9	-0.8	-0.8	-	-	-	-0.8	-0.8	-	-	-0.8	E
19	17	-0.6	-0.7	-0.7	-0.7	-	-	-	-	-0.7	-0.7	-	-0.7	E
22	18	-1.0	-1.2	-1.2	-1.2	-	-	-1.2	-	-	-	-	-1.2	E
24	18	-1.9	-2.0	-2.0	-2.0	-2.0	-	-	-	-	-	-	-2.0	E

PHOSPHATE BUFFER SERIES

Transfers between 0.1 m H_2SO_4 and

1. 0.05m KH_2PO_4 + 0.05m Na_2HPO_4
2. 0.025m KH_2PO_4 + 0.025m Na_2HPO_4

Electrodes: 3, 23, 28

Runs: 41, 43

Transfers from 0.1m H_2SO_4 into Buffer 1

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
3	41	-0.1	0.1	0.2	0.3	-	-	0.3	0.3	-	-	-	0.3	AE
28	41	-3.0	-0.6	100 - 250 min 0.3									0.3	AE

Transfers from Buffer 1 into 0.1m H_2SO_4

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
28	41	-0.3	-0.2	-0.2	-0.1	-0.1	-	-	-	-	-	-	-0.1	AB

Transfers from 0.1m H_2SO_4 into Buffer 2

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
3	43	60 min 0.7 - 120 min 1.2											0.2	E
23	43	-0.6	-0.1	0.2	0.3	0.4	0.5	0.5	0.5	-	-	-	0.5	AE
23	43	-0.3	0	0.1	0.1	0.2	0.2	0.2	0.2	-	-	-	0.2	AE
28	43	0.5	0.4	0.4	0.4	0.3	0.3	0.2	0.2	0.2	0.2	-	0.2	AE

Transfers from Buffer 2 into 0.1m H_2SO_4

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
3	43	-0.3	-0.3	-0.2	-0.2	-	-	-0.1	0	0	0	-	0	AB
23	43	-0.3	-0.2	-0.2	-0.3	-	-	-	-0.4	-0.4	-0.4	-	-0.4	AE
23	43	0	-0.1	-0.2	-0.3	-0.3	-	-0.3	-	-0.2	-0.2	-	-0.2	AE
28	43	-0.6	-0.4	-0.4	-0.3	-0.3	-	-	-	-0.3	-0.3	-	-0.3	AE

PHTHALATE BUFFER SERIES

Transfers between 0.1m H_2SO_4 and

1. 0.1m KH Phthalate
2. 0.05m KH Phthalate
3. 0.01m KH Phthalate

Electrodes: 3, 23, 28

Runs: 42

Transfers from 0.1m H_2SO_4 into Buffer 1

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
3	42	-0.8	-0.4	-0.2	0	-	-	-	0.15	0.2	-	0.3	0	AB
23	42	-	-	-	0	0	0	0	-	-	-	-	0	B
28	42	-0.1	0	0	0	-	-	-	0	0	-	-	0	B

Transfers from Buffer 1 into 0.1m H_2SO_4

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
3	42	-	0	0	0	-	0	0	-	-	-	-	0	B
23	42	0.1	0	-	-	-	-	-0.1	-0.1	-	-	-	-0.1	B
28	42	-0.3	-0.2	-0.1	-	-	-	-	0	0	0	-	0	AB

Transfers from 0.1m H_2SO_4 into Buffer 2

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
3	42	-2.0	-	-	-	0	0	0	-	-	-	-	0	AB
23	42	-0.4	-0.2	0	0	-	-	0	0	0	-	-	0	AB
28	42	-0.2	-0.1	0	0	-	-	-	0	0	-	-	0	AB

Transfers from Buffer 2 into 0.1m H_2SO_4

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
3	42	-0.8	-0.4	-0.2	-0.1	0	-	-	0.1	-	-	-	0	AB
23	42	-0.1	-0.1	-0.1	-0.1	-0.1	-	-	0	0	-	-	0	B
28	42	-0.4	-0.2	-0.1	-0.1	-	-	-	-	-	0	0	0	AB

Transfers from 0.1m H_2SO_4 into Buffer 3

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
3	42	-1.0	-0.4	0	0.15	0.15	0.2	0.25	0.3	-	-	-	0	AB
23	42	-	-0.3	-0.1	0	0.1	-	-	0.1	0.1	0.1	0.1	0.1	AB
28	42	-0.3	-0.1	0.1	0.1	-	-	0.1	0.1	-	-	-	0.1	AB

Transfers from Buffer 3 into 0.1m H_2SO_4

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
3	42	-1.0	-0.6	-0.4	-0.2	-	lost							
23	42	-0.4	-0.2	-0.1	-0.1	-0.1	-	-	-0.1	-	-	-0.1	-0.1	AB
28	42	-0.1	-0.1	-0.1	-0.1	-0.1	-	-	-	-0.1	-0.1	-0.1	-0.1	B

PHTHALATE BUFFER SERIES

Transfers between 0.1m H_2SO_4 and

1. 0.01m KH Phthalate
2. 0.01m KH Phthalate + 0.1m KCl
3. 0.01m KH Phthalate + 0.1m $KClO_4$

Electrodes: 3, 23, 28

Run: 44

Transfers from 0.1m H_2SO_4 into Buffer 1

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
3	44	-	0	0	-	0	0	0	-	-	-	-	0	B
23	44	0.3	0.6	0.7	0.6	100 - 150 min 0.3							0.3	AE
28	44	-0.1	0.2	0.2	0.2	0.2	0.1	0.1	0	0	0	-	0	AB

Transfers from Buffer 1 into 0.1m H_2SO_4

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
3	44	-	0	0	0	-	0	0	-	-	-	-	0	B
23	44	-0.3	-0.3	-0.3	-0.4	-0.4	-	-	-	-0.3	-0.3	-0.3	-0.3	E
28	44	-0.2	-0.1	-0.1	0	-0.1	-	0	0	0	-	-	0	AB

Transfers from 0.1m H_2SO_4 into Buffer 2

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
2	44	-3.0	-1.0	-0.2	0	-	-	-	-	0.1	0.1	-	0.1	AB
23	44	-	0	0.3	-	-	0.3	0.3	0.4	0.4	-	-	0.4	AE
28	44	-0.3	-0.3	0	0.1	0.1	0.1	-	-	-	0	0	0	AB

Transfers from Buffer 2 into 0.1m H_2SO_4

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
3	44	0.1	0	0	0	-	-	0	0	0	-	-	0	B
23	44	-0.3	-0.3	-0.3	0.4	-0.4	-	-	-	-0.3	-0.3	-0.3	-0.3	E
28	44	-0.2	-0.1	-0.1	0	0	-	-	0	0	-	-	0	AB

Transfers from 0.1m H_2SO_4 into Buffer 3

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
3	44	-0.1	0	0.05	0.05	-	-	-	-0.15	-0.2	-	-0.3	0	AB
23	44	0	0.2	0.3	-	-	-	0.4	0.4	50 - 90 min 0			0	AB
28	44	-0.4	-0.1	0.1	0.1	0.1	-	-	-	0.1	0.1	-	0.1	AB

Transfers from Buffer 3 into 0.1m H_2SO_4

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
3	44	0	0	0	0	-	0	0	-	-	-	-	0	B
23	44	-0.2	-0.1	-0.1	-0.1	-0.1	-0.1	-	-0.1	-0.1	-	-	-0.1	B
28	44	0	0	0	-	-	-	-	0	0	-	-	0	B

PHOSPHATE BUFFER SERIES

Transfers between 0.1m H_2SO_4 and

1. 0.0025m Na_2 HPO_4 + 0.0025m KH_2PO_4

2. 0.0025m Na_2 HPO_4 + 0.0025m KH_2 PO_4 + 0.1m KCl

3. 0.0025m Na_2 HPO_4 + 0.0025m KH_2PO_4 + 0.1m $KClO_4$

4. 0.025m Na_2 HPO_4 + 0.025m KH_2PO_4

Electrodes: 3, 23, 28

Run: 45

Transfers from 0.1m H_2SO_4 into Buffer 1

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
3	45	-0.4	-1.2	0.1	1.1	-	-	0.8	0.8	0.8	-	-	0.8	AC2
23	45	lost												
28	45	0.2	0.5	0.6	0.8	0.8	0.7	-	-	-	0.7	0.7	0.7	AE

Transfers from Buffer 1 into 0.1m H_2SO_4

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
3	45	-0.3	-0.6	-0.7	-0.7	-	-	-	-0.7	-0.7	-	-	-0.7	AE
23	45	-0.3	-0.4	-0.5	-0.5	-	-	-	-0.5	-0.5	-	-	-0.5	AE
28	45	-0.6	-0.7	-0.6	-0.6	-	-	-	-0.6	-	-	-	-0.6	E

Transfers from 0.1m H_2SO_4 into Buffer 2

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
3	45	-1.5	-0.3	0.2	0.6	120 - 150 min 0.8							0.8	AE
23	45	-1.5	0	0.6	1.0	1.2	100 - 120 min 0.8						0.8	AC2
28	45	-1.5	-0.1	0.5	1.0	0.9	-	-	0.6	0.6	0.6	-	0.6	AC2

Transfers from Buffer 2 into 0.1m H_2SO_4

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
3	45	-1.0	-0.9	-0.9	-0.9	-	-	-1.2	-1.2	-1.2	-	-	-1.2	D2
23	45	-0.7	-0.8	-0.9	-	-	-	-0.9	-0.4	-	-	-	-0.9	C1
28	45	-0.6	-0.6	-0.6	-0.6	-	-	-0.6	-0.6	-0.6	-	-	-0.6	E

Transfers from 0.1m H_2SO_4 into Buffer 3

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
3	45	-3.0	-1.0	0	-	-	0.6	0.6	-	-	-	-	0.6	AC1
23	45	0.2	0.7	1.0	-	-	-	90 - 100 min 0.9					0.9	C1
28	45	-0.6	0.3	0.7	0.6	-	-	-	0.4	0.4	-	-	0.4	AC2

Transfers from Buffer 3 into 0.1m H_2SO_4

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
3	45	-1.5	-1.0	-0.8	-	-	-	-	-	-	-0.4	-0.4	-0.4	D1
23	45	-0.7	-0.6	-0.6	-0.6	-	-	-0.7	-0.7	-	-	-	-0.7	E
28	45	-0.7	-0.5	-0.4	-0.4	-0.4	-	-	-	-0.4	-0.4	-	-0.4	AE

Transfers from 0.1m H_2SO_4 into Buffer 4

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
3	45	-1.8	-0.6	0	0.2	0.1	0	0	-	-	-	-	0	AB
23	45	-0.5	-0.2	-	-	0.1	0.1	0.1	0.1	-	-	-	0.1	AB
28	45	0.6	0.5	0.4	0.4	-	-	-	-	-	0.3	0.3	0.3	AE

Transfers from Buffer 4 into 0.1m H_2SO_4

No.	Min. Run	½	1	2	5	10	15	20	30	40	50	60	ΔE	Type
3	45	-1.1	-0.6	-0.3	-0.2	0	0	0	-	-	-	-	0	AB
23	45	-0.3	-0.2	-0.1	-0.1	-0.1	-0.1	-0.1	-	-	-	-	-0.1	AB
28	45	-0.6	-0.4	-0.3	-0.3	-0.3	-	-	-0.3	-	-	-	-0.3	AE

PUBLICATIONS AND CITATIONS

PUBLICATIONS

The work described in Chapters 5 and 6 has been published;

1. 'Errors of Glass Electrodes in Certain Standard Buffer Solutions at High Discrimination'
   Beck, W.H., Bottom, A.E., Covington, A.K., Anal.Chem., (1968), 40, 501.

2. 'The Effect of the Solvent used for the Internal Reference Electrode System on the Response Characteristics of Hydrogen-responsive Glass Electrodes in Aqueous and Partially Aqueous Buffer Solutions'
   Bottom, A.E., Covington, A.K., J.Electroanal.Chem., (1970), 24, 251.

   An account of this work was presented at the IMEKO Symposium on Electrochemical Sensors held at the University of Chemical Industry, Veszprém, Hungary, October 3rd-5th, 1968.

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(l) 'Rapid Spectrophotometric Measurements based on the Dual Wavelength Technique'.
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2. J.Electroanal.Chem., (1970), 24, 251

(a) Covington, A.K., Electrochemistry, Vol. 1, The Chemical Society, 1970, 61.

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