A STUDY OF THE ELECTRICAL IMPEDANCE OF A GLASS ELECTRODE IN ADVERSE ENVIRONMENTS

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Finally, I must thank my parents and girlfriend for their kind patience and encouragement throughout the project.

Abstract

The frequency response of pH-sensitive glass electrodes has been measured over the range 0.01 to 100 Hz using an SCE counter electrode. Observations were made firstly in standard buffers (pH2, 4, 7 and 9) with electrodes as supplied and secondly with electrodes having membranes which had suffered abrasion or surface contamination. These later observations were intended to simulate effects which might well be encountered when electrodes of this type were used in harsher commercial environments. Surface abrasion was simulated by scratching the surface with emery paper, and surface contamination by smearing it with petroleum jelly or causing a precipitate to form over it. The precipitate employed was that of aluminium hydroxide brought down by the addition of aqueous sodium hydroxide to a solution of hydrochloric acid and aluminium chloride.

The glass electrodes employed were Polymetron type 8404S and 8400B and in a standard buffer the frequency response of the former comprised two semi-circles when plotted in the complex plane and that of the latter a single semi-circle. Impedances on the real axis ranged from virtually zero at the highest frequency to values of about 300 to 500 MΩ at the lower frequency, and on the imaginary axis they peaked at values between 150 and 300 MΩ. Precise values varied both between electrode types and between electrodes of the same type. Ageing and pH values were also found to affect impedances, by up to some 20%, but did not change the shape of the curves.

Abrasion had little effect on the impedance characteristics, and petroleum jelly appeared to have a "stopping off" effect, increasing impedance values but not impairing electrode integrity. The precipitate, however, caused severe distortion of both the impedance characteristic and the pH response.

It was concluded that frequency response could be developed into a method of electrode integrity testing.

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CHAPTER 1 INTRODUCTION

The chemical and allied industries, probably more than any other industry at present, rely heavily for their operations on the use of automation, or as it is more usually known in this context, process control. The aim of process control is to maintain a set of variables at some pre-determined set of values or pattern of values which correspond to the optimum operating condition, however 'optimum' may be defined.

In its most elementary form, control is exercised by a loop, by means of which the measured value of the variable is passed to a controller, which compares it with the desired value and if necessary takes action by changing the setting of an item of plant, a valve for instance, which is capable of influencing the variable. The new value of the variable is then detected, fed back to the controller and the 'loop' thereby closed.

The operation of such a control loop clearly requires that information on the value of the control variable be fed to the controller either at suitable intervals or, if possible, continuously. For a continuous supply of information it is necessary to have a measuring device which is 'on-line', and for the control of variables such as temperature, pressure, flow-rate and pH, this policy is virtually always pursued.

On-line measuring devices bring with them the problem of integrity. With an off-line measuring device it is obviously possible, periodically, to run a check on its accuracy as a routine laboratory exercise, but the on-line device is more or less locked into the plant and such a check poses difficulties. A check on the behaviour of an orifice plate for example cannot be carried out without, to some extent, affecting the operation of the plant. Fortunately, in most instances measuring devices are relatively reliable. particularly those used for temperature, pressure and flow measurement. This is primarily because they are either mechanically robust if directly exposed to the process environment, e.g the orifice plate, or if fragile can be shielded from it, e.g the use of a thermometer pocket.

The measurement of pH is an exception, however, and carries much less confidence. The devices employed are almost exclusively based on glass electrodes, which are clearly not robust and, being direct measuring devices, cannot be shielded from their environment. It is the latter which is more problematical. The action of a glass electrode depends upon the condition of its surface which, being exposed to the environment it is monitoring, may be adversely affected by conditions which are characteristic of this environment or created by an abnormal excursion. For instance the presence of a fine suspension may have an abrasive effect, oil in minute traces may collect as a film or a precipitate may form a coating. Under these circumstances there is a possibility that the signal from the electrode will become increasingly in error, and unless experience dictates otherwise, it is not uncommon practice to install multiple electrodes to allow for cross checking and to enable routine rotational off line testing of their integrity. Such a system, however, is costly in both capital and labour and in addition is not a satisfactory solution to a temporary adverse condition which could affect all the electrodes to the same degree.

There is therefore a strong incentive to develop an on-line technique for testing their integrity, particularly one which would consume only a small fraction of on-line time. The aim of the present study was to investigate whether or not electrode impedance determined from frequency response measurements could form the basis of such a technique.

CHAPTER 2 IMPEDANCE AND FREQUENCY RESPONSE

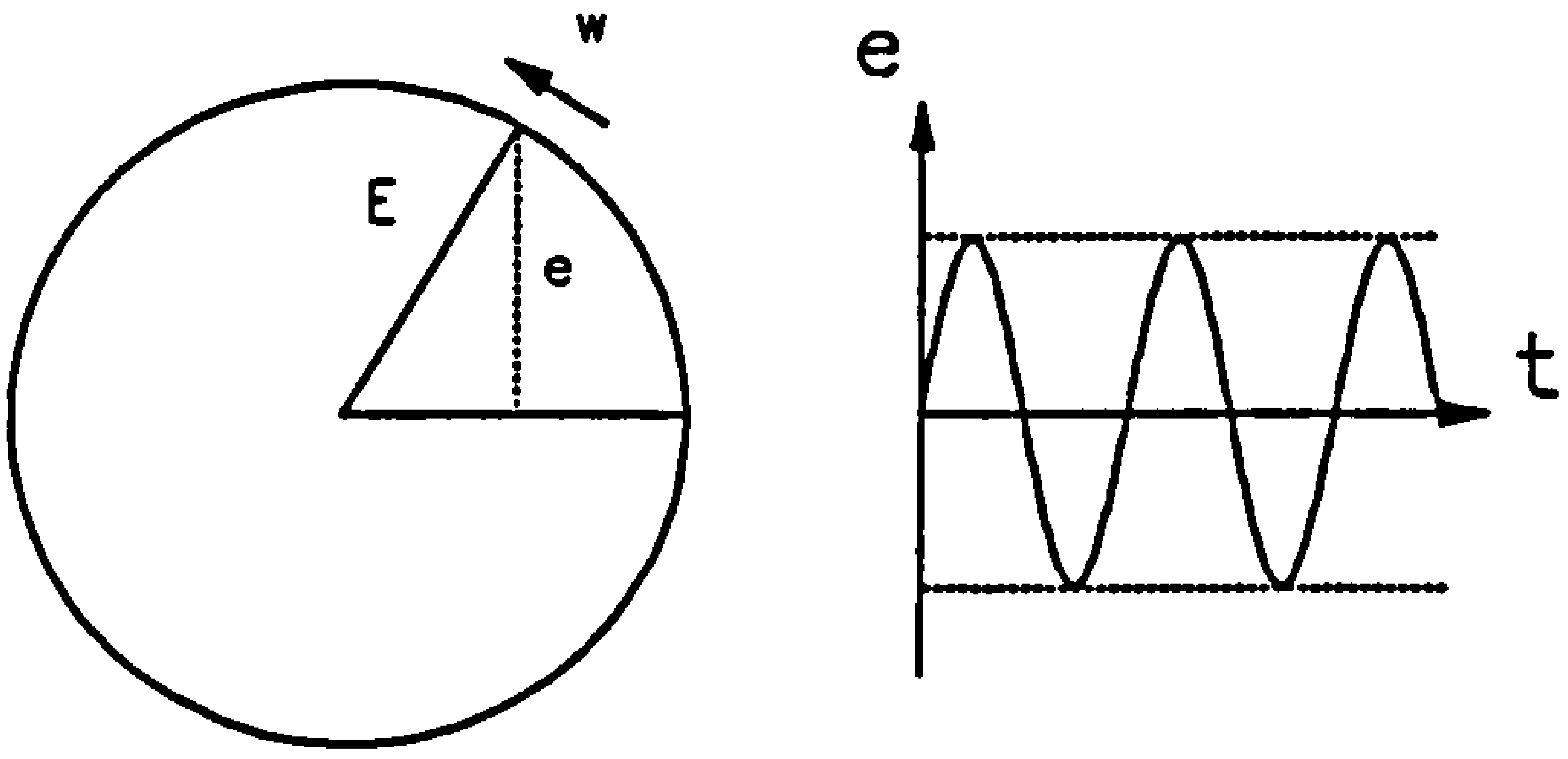
2.1 A.C Circuitry Methods

The alternating perturbations employed in the present investigations, in common with the majority of electrodic investigations depending upon impedance measurements, were small amplitude potentials, sinusoidal with time, which can be represented by the equation:

$$e = E \sin wt \qquad - (1)$$

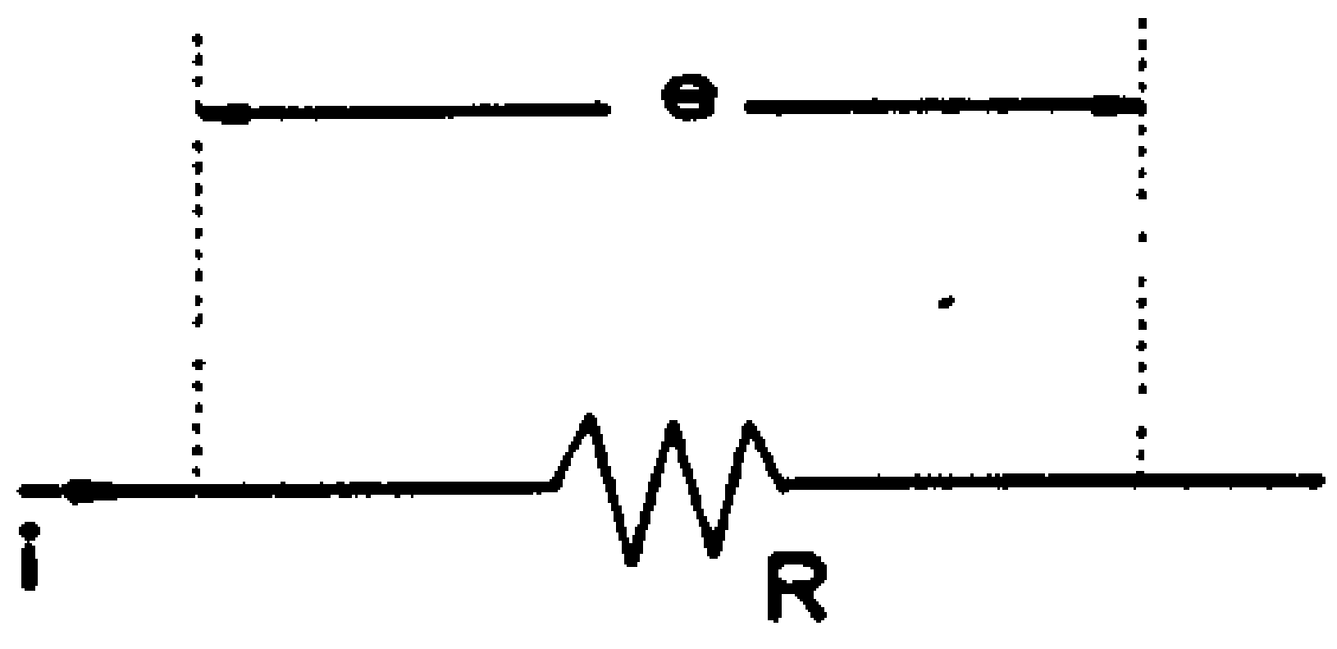
where e is the potential input at a time t, and E and w are constants. Since the maximum value of sin wt is unity, it is clear that the maximum value of e, i.e the amplitude, is E. Its period is $2\pi/w$ seconds, or conversely its frequency is $w/2\pi$ Hertz (i.e cycles per second).

It is conventional to represent an input of this type by a 'phasor', of length E, rotating with an angular velocity w, the value of e being the projection of E on any chosen axis as shown below.



a) Analytical Methods

i) Simple resistor



From Ohm's Law

$$e = i R$$

therefore $E \sin wt = i R$

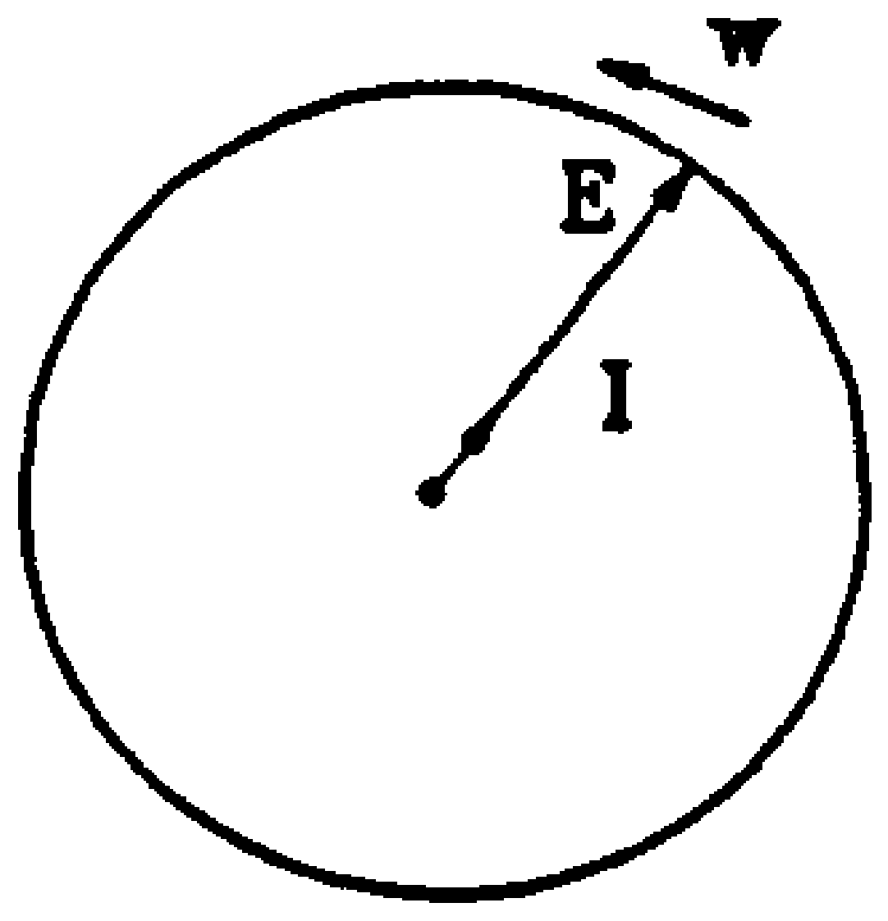
or $i = \frac{E}{R} \sin wt$

Denoting $\frac{E}{R}$ by the phasor I, the equation becomes

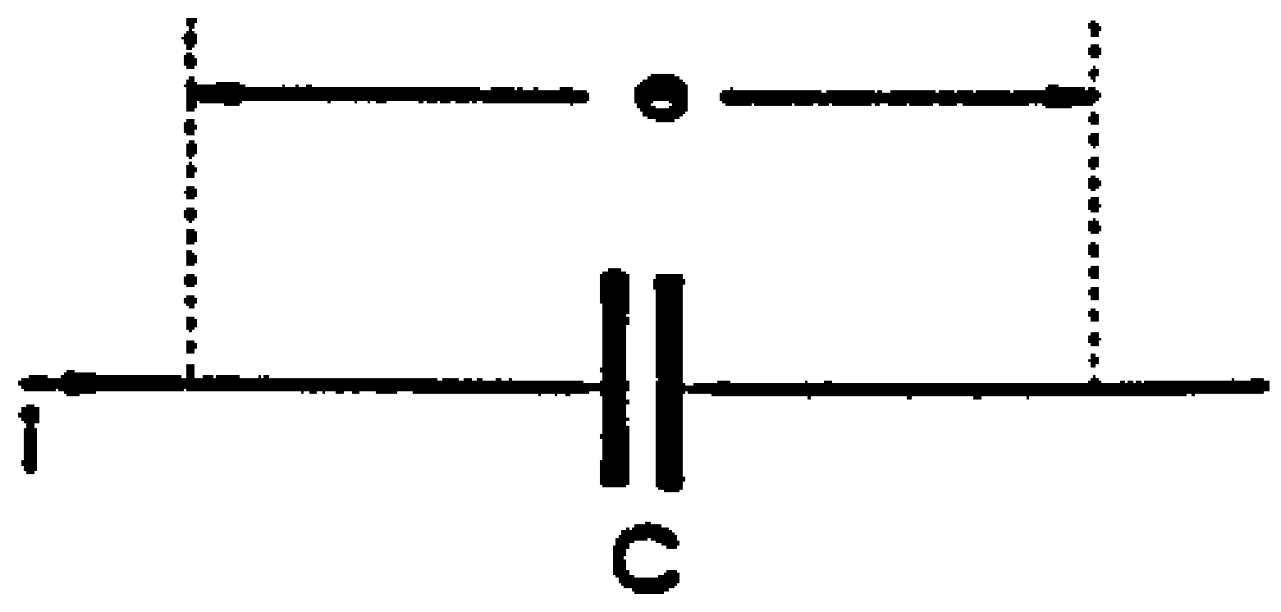
$$i = I \sin wt \qquad - (2)$$

and $E = I R$ - (3)

By comparing (2) with (1) it is evident that an a.c potential input to a resistor gives rise to an a.c current output which is in phase with the input, as indicated in the following phasor diagram.



(ii) Simple capacitor



The potential difference, e, and charge, Q, on the capacitor are related to the capacity, C, by

$$e = \frac{Q}{C}$$

differentiating with respect to time, t

$$\frac{de}{dt} = \frac{1}{C}\frac{dQ}{dt} = \frac{i}{C}$$

Hence

$$\frac{E\,d(\sin wt)}{dt} = \frac{i}{C}$$

or

$$E\,w\cos wt = \frac{i}{C}$$

However $\cos wt = \sin(wt + \pi/2)$

and so $i = E\,w\,C\sin(wt + \pi/2)$

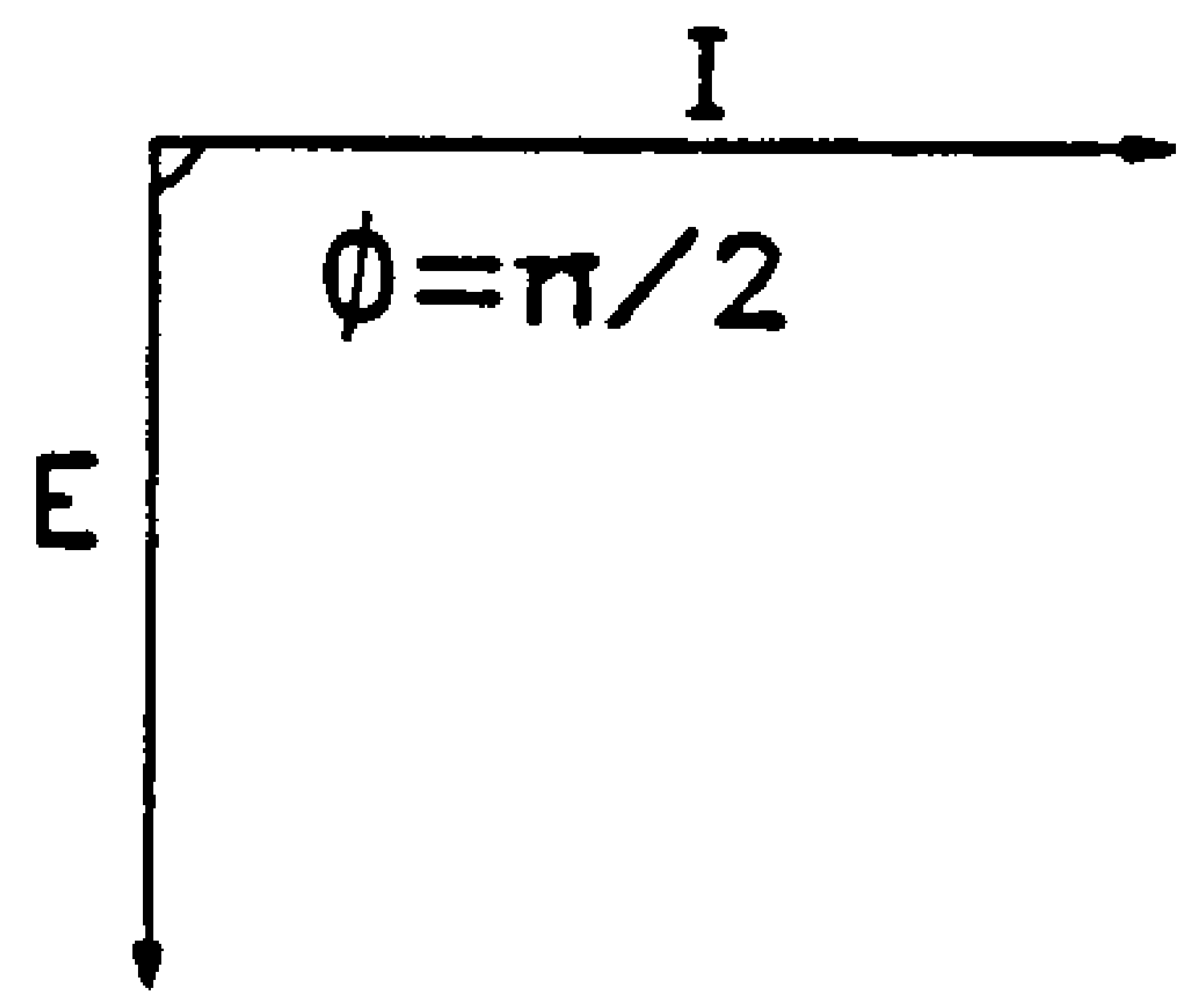
or $i = I\sin(wt + \pi/2)$ - (4)

where $I = wCE$

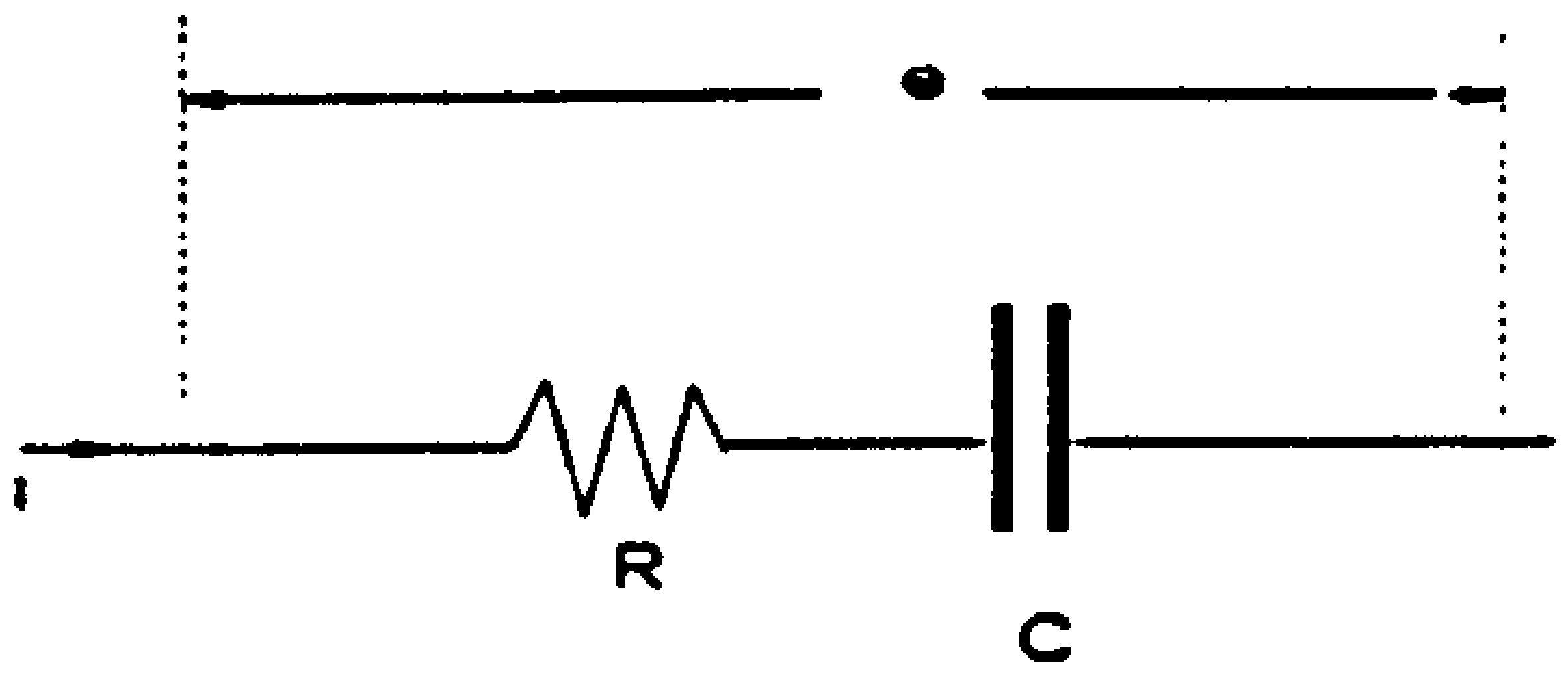
Denoting $1/wC$ by X_C, referred to as the capacitive reactance, the above becomes

$$E = X_C . I \qquad - (5)$$

By comparing (1) and (4) it is seen that in applying an a.c potential to a capacitor the resulting current i is out of phase with e, leading it by the angle $\pi/2$. The corresponding phasor diagram, omitting the circumscribing circle is as follows:



(iii) Resistor and Capacitor in series



The potential e will be described by the equation

$$e = Ri + \frac{Q}{C}$$

Differentiating with respect to time t,

$$\frac{de}{dt} = R\frac{di}{dt} + \frac{i}{C}$$

The solution to this equation is

$$i = \frac{RE}{[R^2 + 1/w^2C^2]} .\sin wt + \frac{1/wCE}{[R^2 + 1/w^2C^2]} .\cos wt$$

Converting this equation to the form $i = k \sin(wt + \phi)$ gives

$$i = \frac{E}{\sqrt{R^2 + (1/wC)^2}} . \sin(wt + \phi) \qquad - (6)$$

$$\text{where } \tan\phi = 1/wRC \qquad - (7)$$

However, $$X_C = 1/wC \qquad - (8)$$

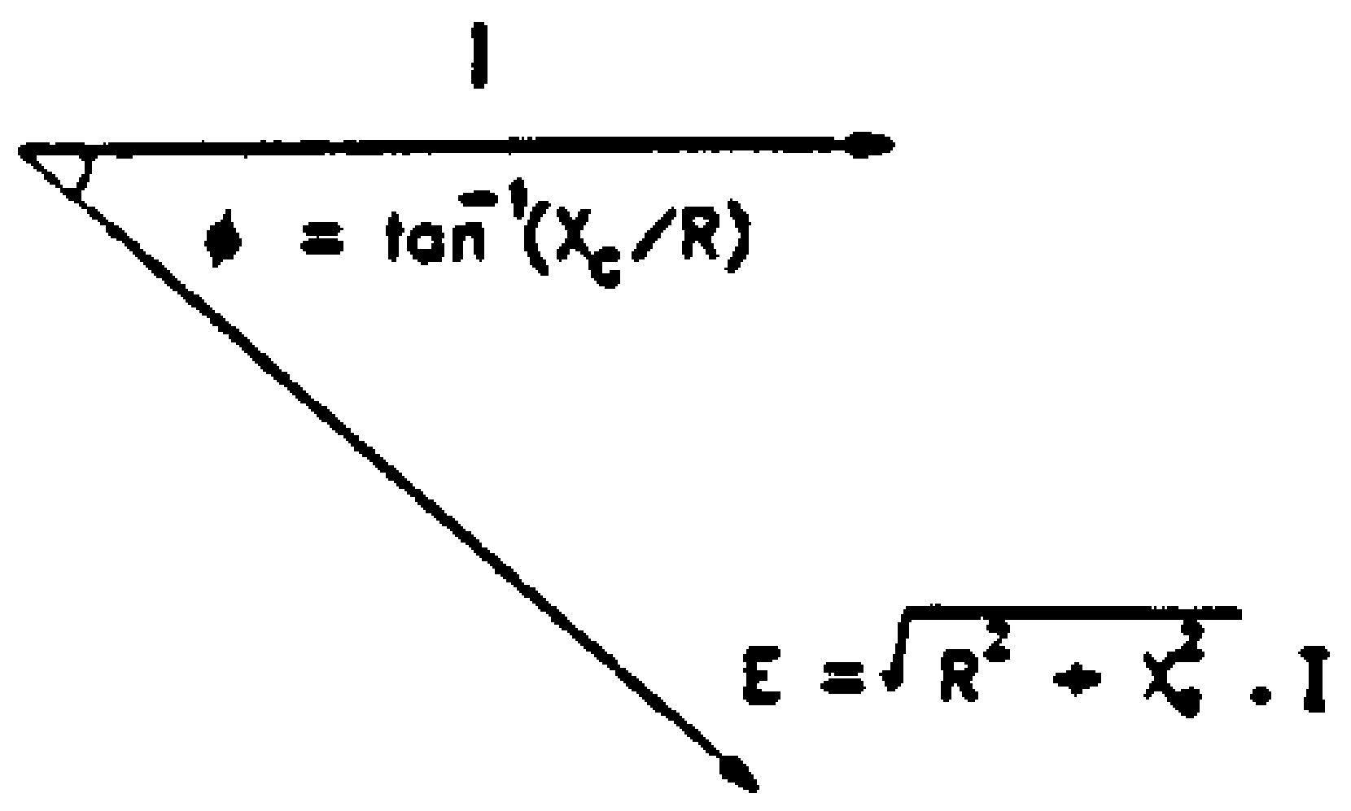
therefore $$i = \frac{E}{\sqrt{R^2 + X_C^2}} .\sin(wt + \phi) \qquad - (9)$$

or $$i = I \sin(wt + \phi) \qquad - (10)$$

where $$E = \sqrt{R^2 + X_C^2} . I \qquad - (11)$$

and $$\tan\phi = \frac{X_C}{R} \qquad - (12)$$

Comparing (1) and (10) it can be seen that the current i leads the potential e by an angle ϕ equal to $\tan^{-1}(X_C/R)$, which in phasor terms is represented as follows



The quantity $\sqrt{R^2 + X_C{}^2}$ is referred to as the impedance, Z, of the circuit, and may be regarded as the total a.c resistance of the circuit. Hence equation (11) can be re-expressed in the form

$$E = Z\,I \qquad - (13)$$

Clearly the impedance of a single resistor is R and of a single capacitor, X_C.

As the circuits become more complex the mathematics becomes progressively more tedious, and a more convenient method of achieving a solution is afforded by the so-called Steinmetz notation using a complex plane.

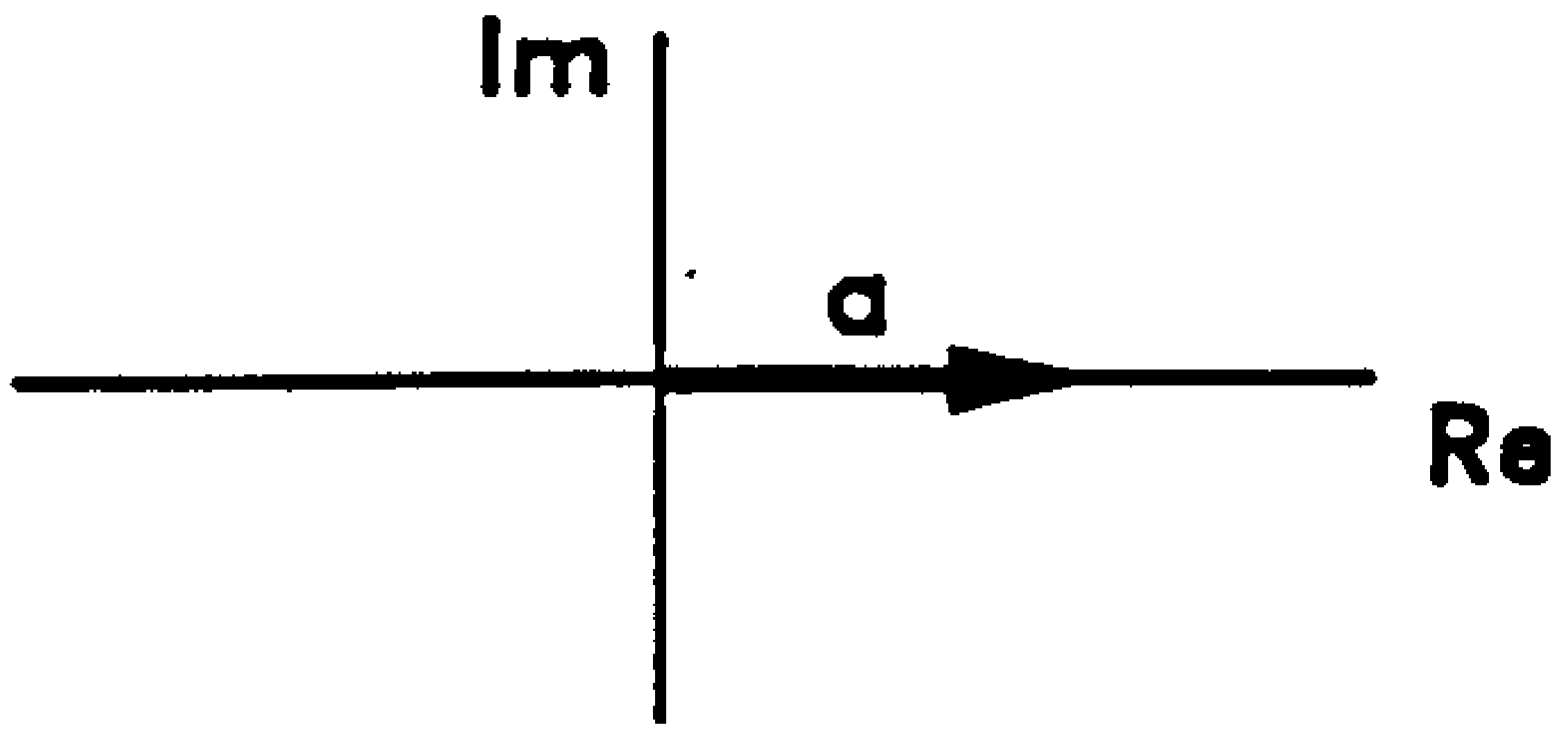
(b) Complex plane method

Steinmetz proposed a symbolic notation in which E, I and Z are treated as vectors comprising two mutually perpendicular components, a and b, one horizontal and the other vertical. Using this notation, Z for instance is expressed by

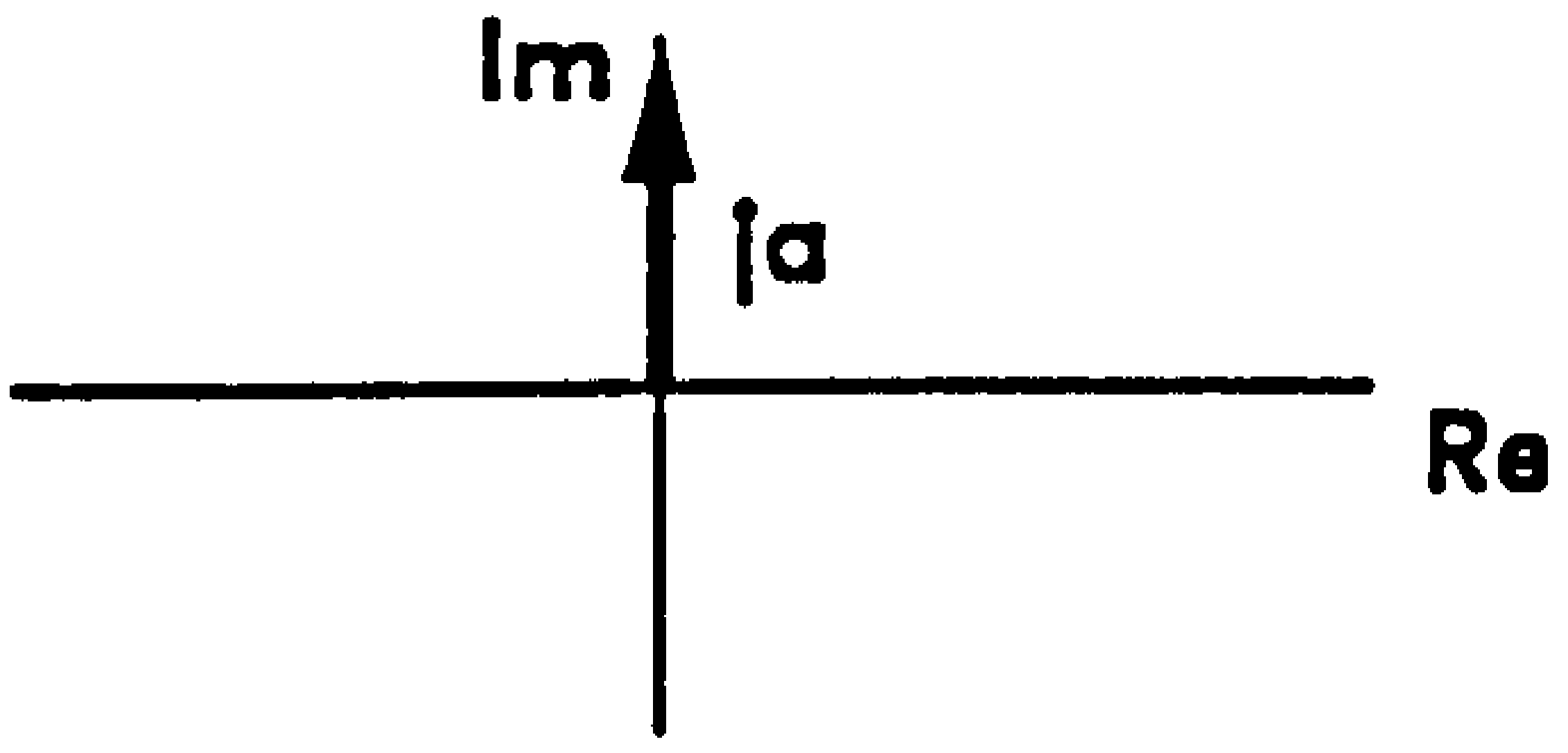
$$Z = a + jb \qquad - (14)$$

where j, denoting $\sqrt{-1}$, is employed as an operator to indicate that component b is at right angles to component a. The logic of using j to symbolise rotation through 90° can be seen from the following sequence where a vector of length a is depicted in four different directions with respect to mutually perpendicular axes labelled 'real' (Re) and 'imaginary' (Im):

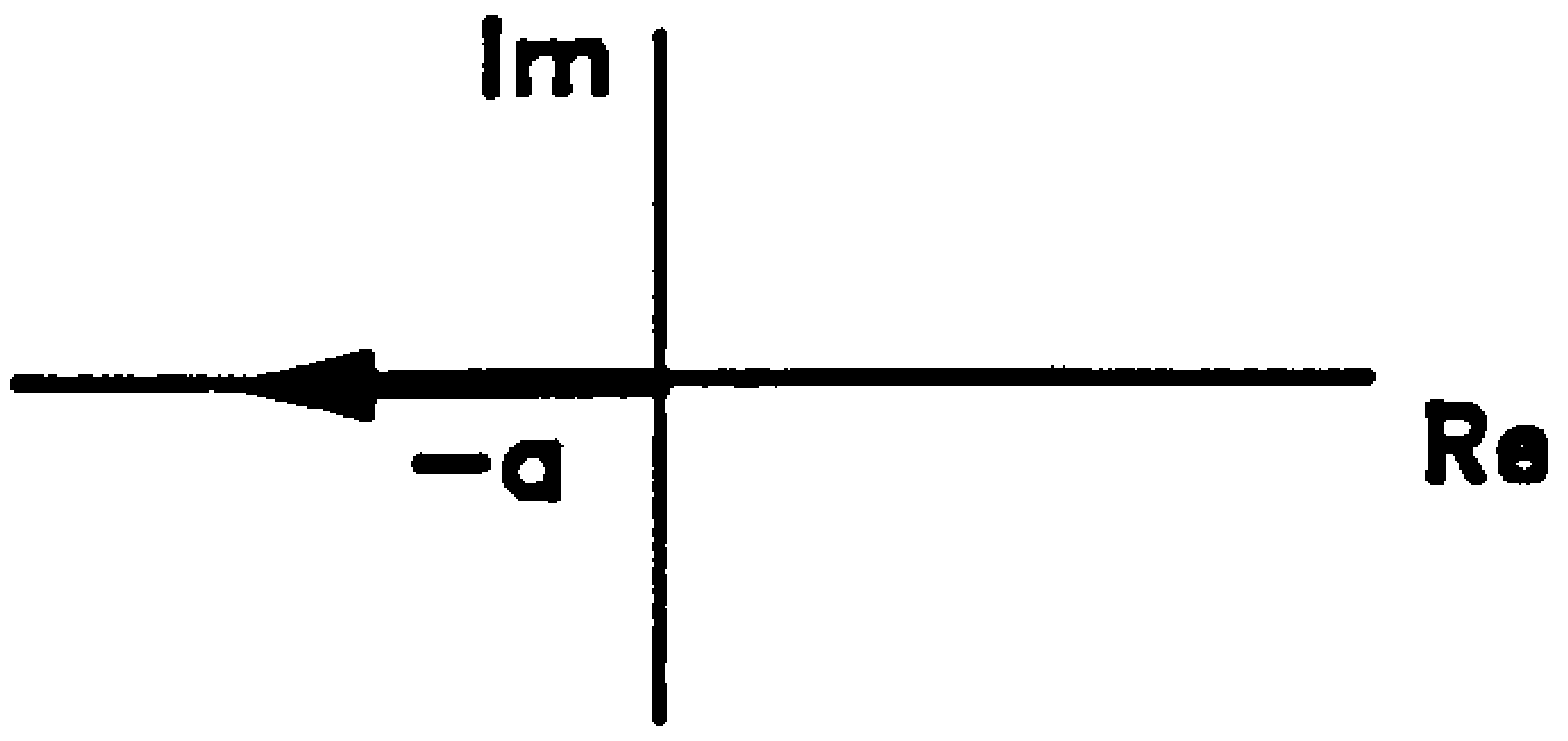
a



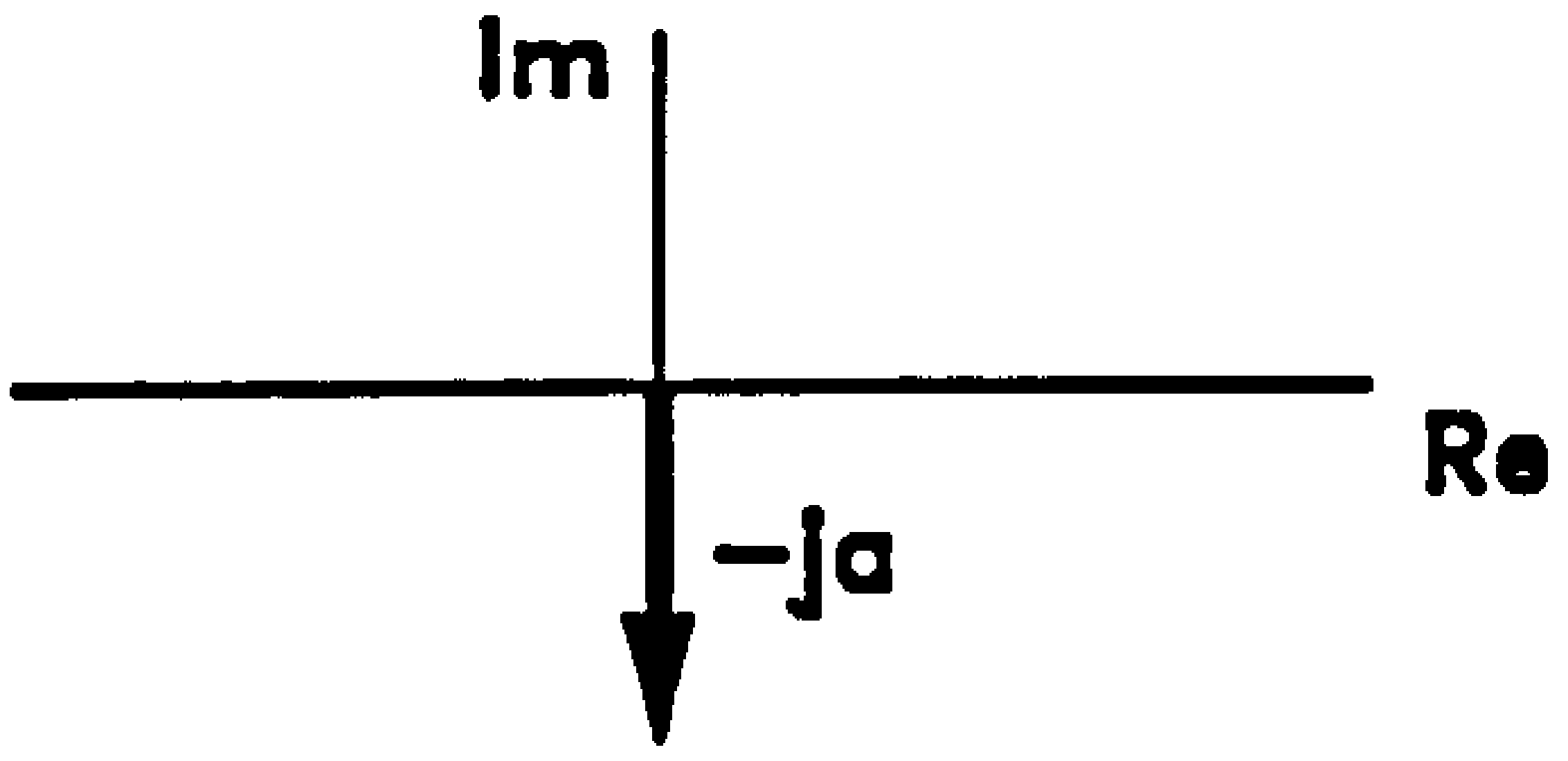
ja



$j^2 a = -a$



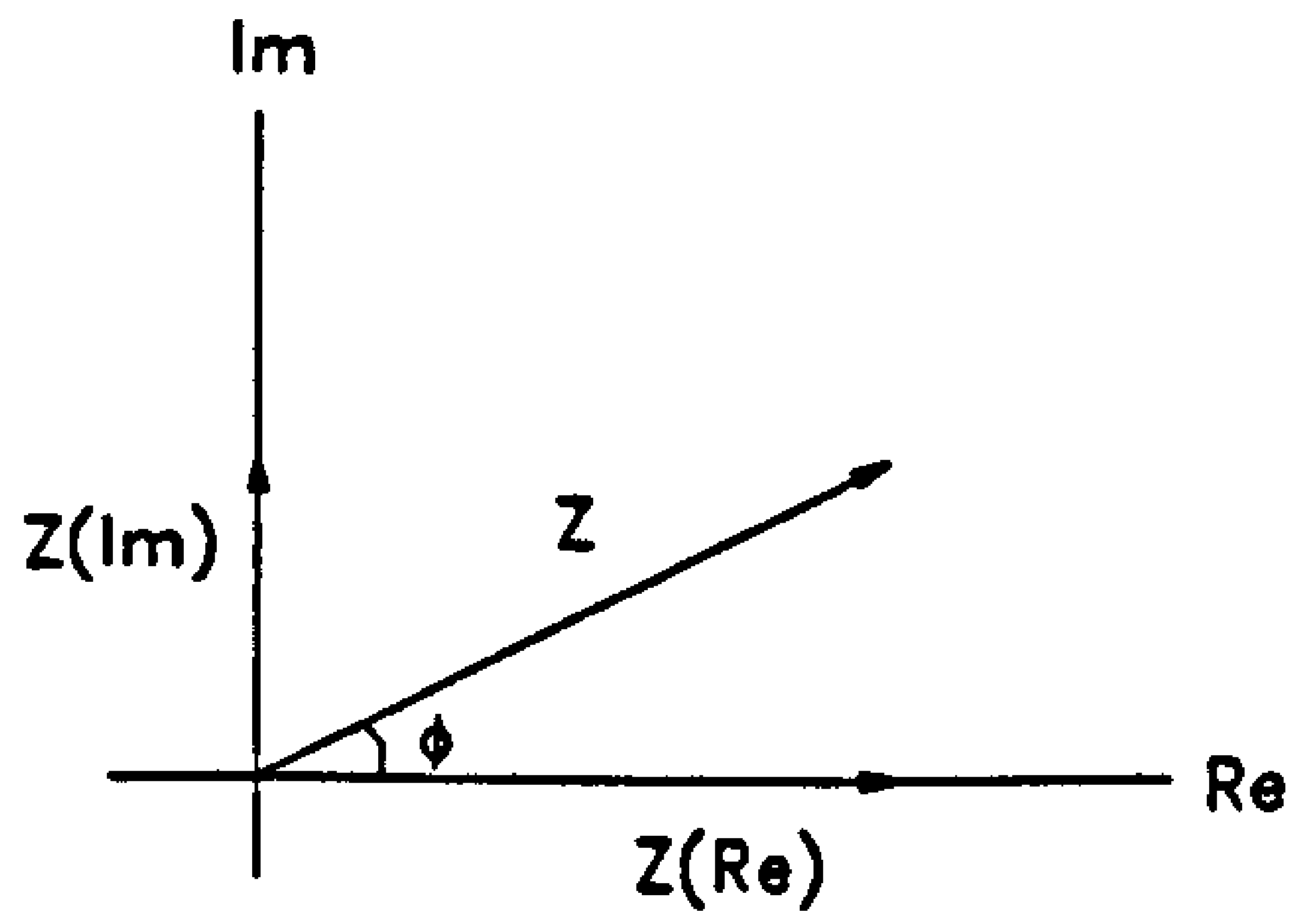
$j^3 a = -ja$



Using Z(Re) instead of a and Z(Im) instead of b, equation **(14)** becomes

$$Z = Z(Re) + jZ(Im) \qquad - (15)$$

and is depicted on the complex plane thus



Similarly E and I are expressed by

$$E = E(Re) + jE(Im) \quad , \qquad I = I(Re) + jI(Im) \qquad - (16)$$

The magnitudes of E and I are calculated from, (see eqn. 13),

$$|E| \quad = \quad |Z| \quad |I| \qquad - (17)$$

where

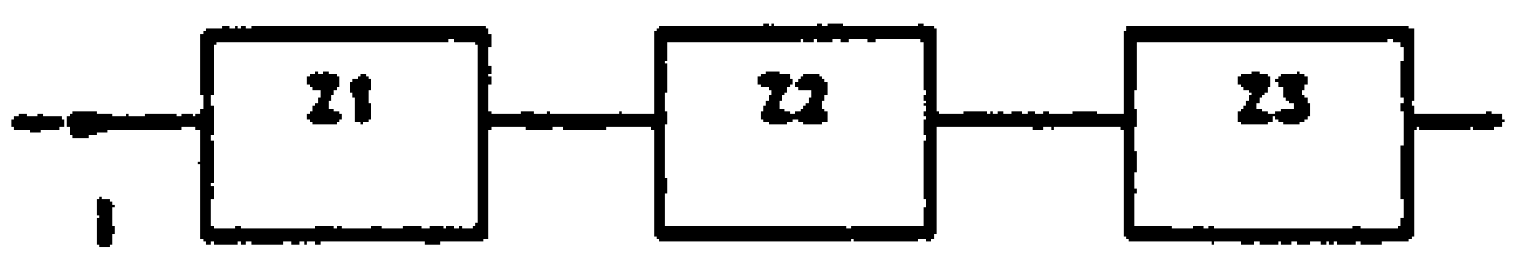
$$|Z| \quad = \quad \sqrt{Z^2(Re) + Z^2(Im)} \qquad - (18)$$

and the absolute symbols round Z, E and I are used to distinguish between vector and scalar quantities.

The phase angle ϕ by which E leads I is given by

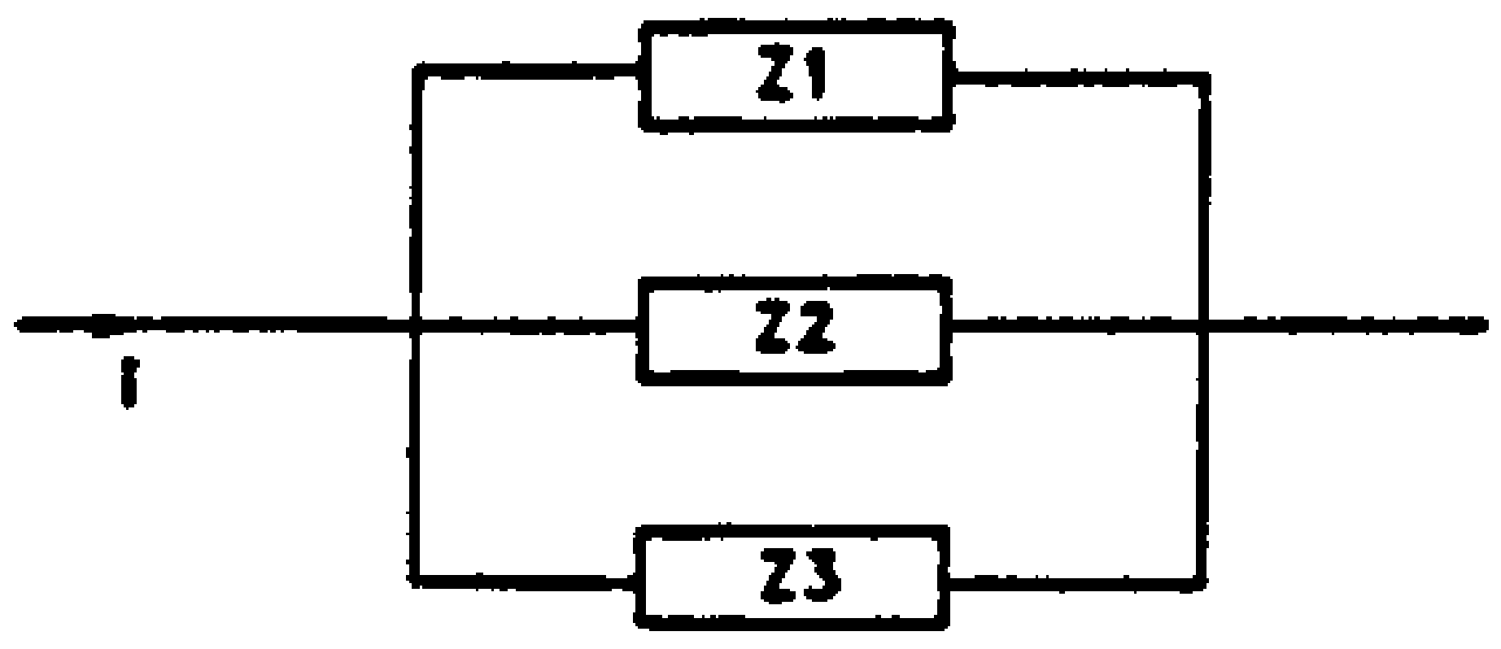
$$\tan \phi \quad = \quad \frac{Z(Im)}{Z(Re)} \qquad - (19)$$

The total impedance of a series-connected circuit is equal to the vector sum of the individual impedances, thus;



$$Z_{total} = Z1 + Z2 + Z3 + ...$$

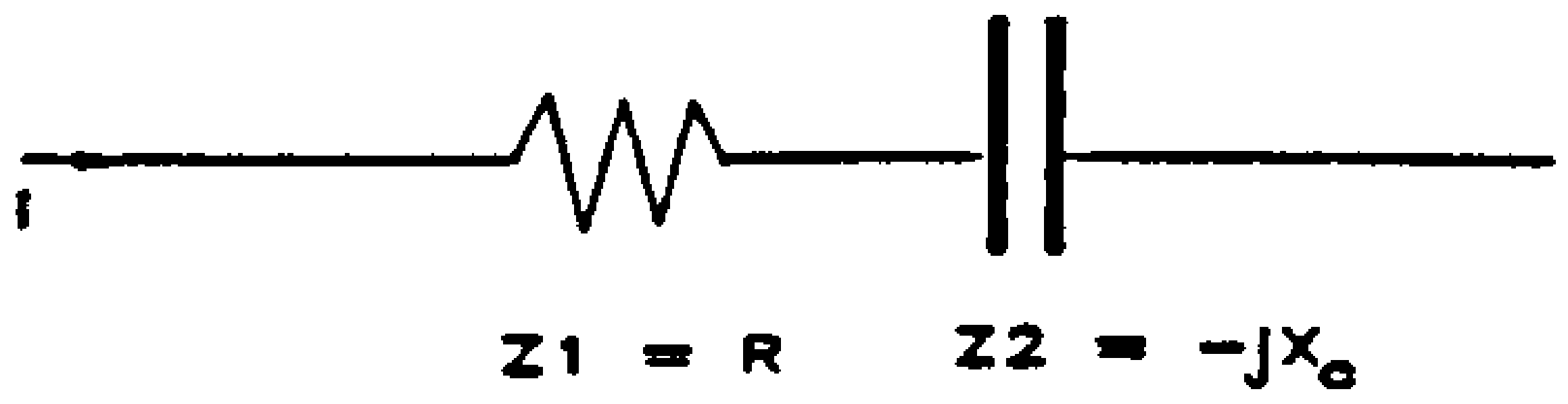
and for a parallel-connected circuit is obtained by inverting the vector sum of the reciprocals of the individual impedances:



$$\frac{1}{Z_{total}} = \frac{1}{Z1} + \frac{1}{Z2} + \frac{1}{Z3} + ...$$

These principles are illustrated below for a resistor and capacitor connected in series and parallel.

(i) Resistor and capacitor in series:



The total impedance, $Z = Z_1 + Z_2 = R - jX_C$

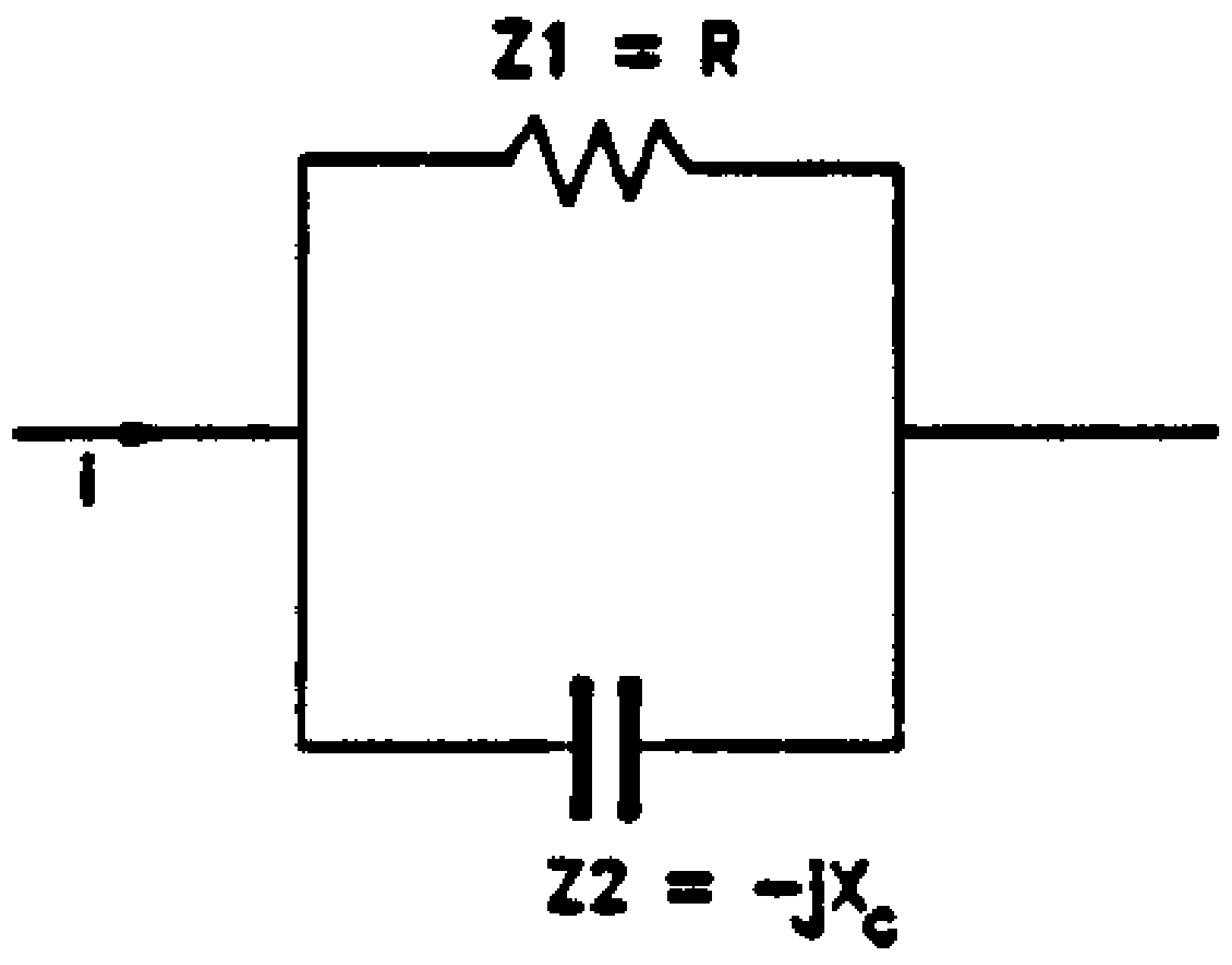
$$|Z| = \sqrt{Z^2(\text{Re}) + Z^2(\text{Im})} = \sqrt{R^2 + X_C{}^2} \qquad - (20)$$

$$|E| = \sqrt{R^2 + X_C{}^2} \,.\, |I| \qquad - (21)$$

$$\tan\phi = \frac{Z(\text{Im})}{Z(\text{Re})} = -\frac{X_C}{R} \qquad - (22)$$

Equations (21) and (22) compare with (11) and (12) but have been derived with much less fuss. The negative sign in (22) implies that E lags I by ϕ.

(ii) Resistor and Capacitor in parallel



the total impedance is give by

$$\frac{1}{Z} = \frac{1}{Z_1} + \frac{1}{Z_2} = \frac{1}{R} - \frac{1}{jX_C}$$

therefore

$$\frac{1}{Z} = \frac{jX_C - R}{jX_C R}$$

or

$$Z = \frac{jX_C R}{jX_C - R}$$

Rationalising

$$Z = \frac{jX_C R\ (jX_C + R)}{(jX_C - R)(jX_C + R)} = \frac{-RX_C{}^2 + jR^2X_C}{-R^2 - X_C{}^2}$$

or

$$Z = \frac{RX_C{}^2}{R^2 + X_C{}^2} - j.\frac{R^2X_C}{R^2 + X_C{}^2} \qquad - (23)$$

or

$$Z(Re) = \frac{RX_C^2}{[R^2 + X_C^2]}$$

$$Z(Im) = \frac{-R^2X_C}{[R^2 + X_C^2]} \qquad - (24)$$

from which

$$|Z| = \sqrt{Z^2(Re) + Z^2(Im)}$$

$$= \frac{\sqrt{R^2X_C^4 + R^4X_C^2}}{[R^2 + X_C^2]}$$

or

$$|Z| = \frac{RX_C}{(R^2 + X_C^2)}$$

and

$$|E| = \frac{RX_C}{(R^2 + X_C^2)} \cdot |I| \qquad - (25)$$

with

$$\tan \phi = \frac{Z(Im)}{Z(Re)} = -\frac{R}{X_C} \qquad - (26)$$

Again the negative sign implies that E lags I by the phase angle ϕ.

Denoting the product RC by J, the so-called time constant for the circuit, equations (24) can be re-written in the form:

$$Z(Re) = \frac{R}{1 + w^2J^2}$$

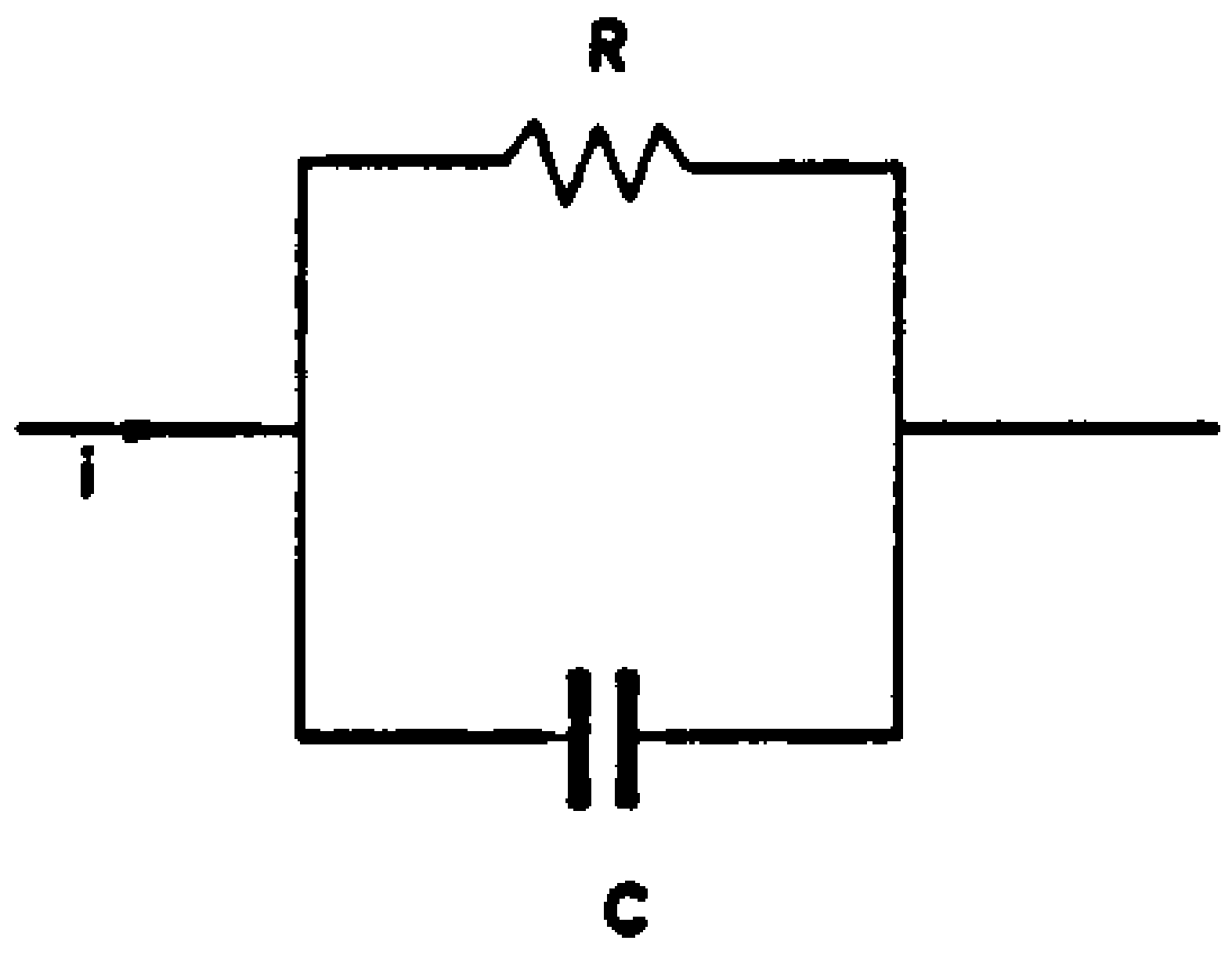
$$Z(Im) = \frac{-wRJ}{1 + w^2J^2} \qquad - (27)$$

from which it is seen that J is the decisive factor in determining the behaviour of Z(Re) and Z(Im), with R acting as a scale factor.

2.2 Equivalent Circuits

Since the impedance of any circuit can be reduced to a real and an imaginary component it follows that any circuitry will have an equivalent circuit comprising a resistor and capacitor (or inductance if the imaginary component is positive) of appropriate values connected in series.

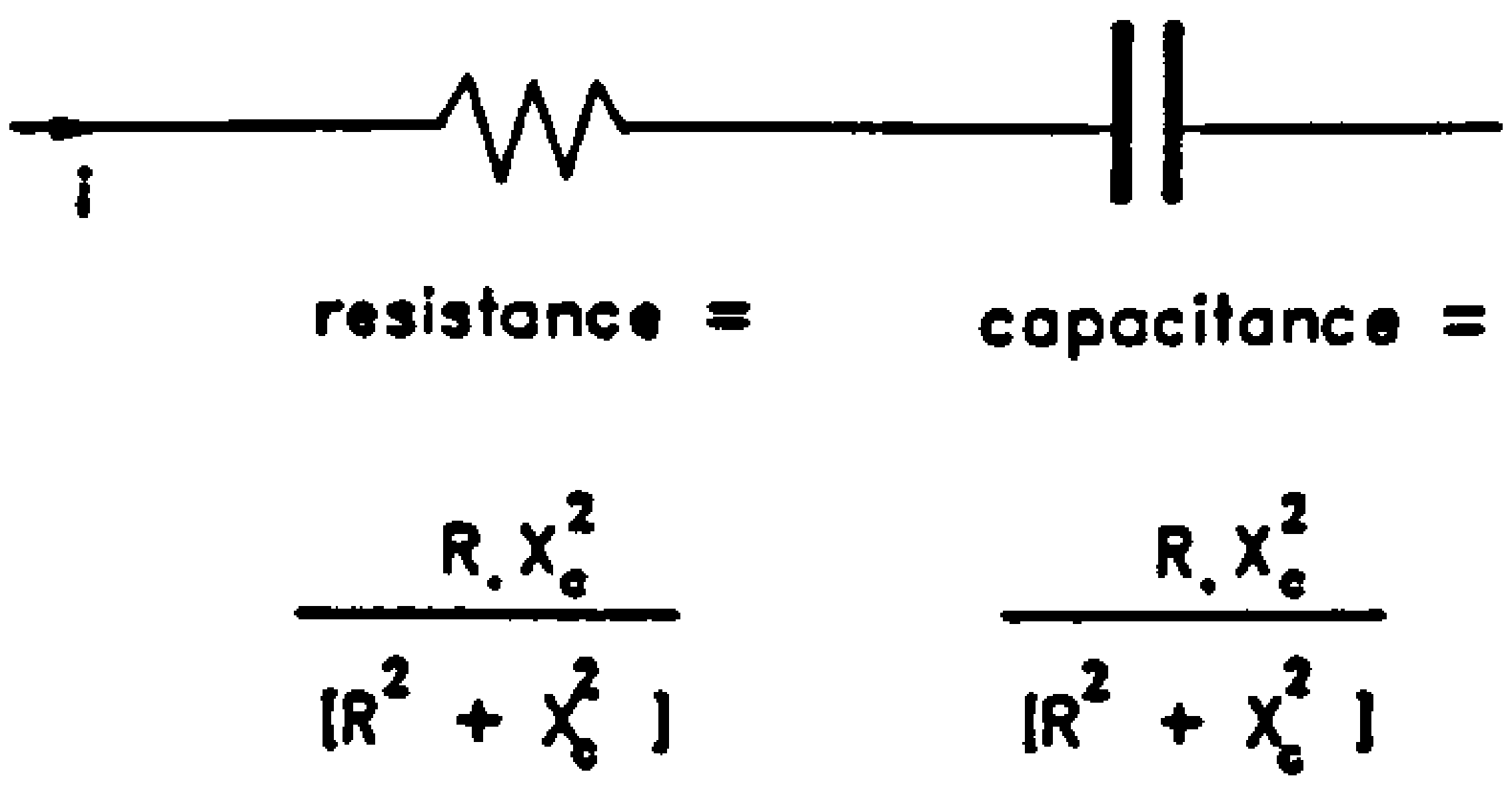
For instance a resistor and capacitor arranged in parallel,



has been shown in the previous section to have an impedance (equation 23) given by

$$Z = \frac{RX_C^2}{[R^2 + X_C^2]} - j.\frac{R^2X_C}{[R^2 + X_C^2]}$$

and therefore has the same characteristic as the following series circuit:

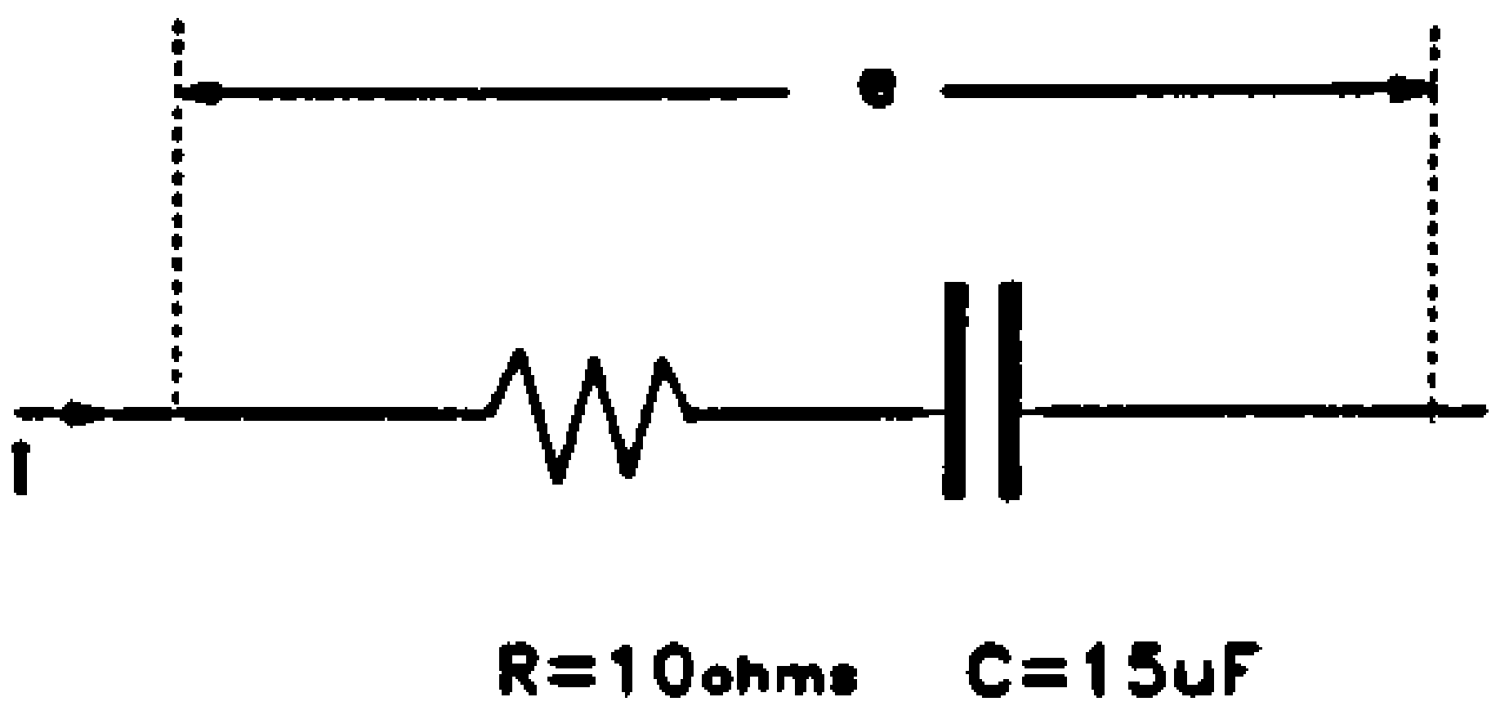


As a corollary any series circuit has an equivalent parallel circuit, and in fact any circuit can be reproduced by any number of series and parallel combinations using components of appropriate values.

2.3 Frequency response

Since capacitive reactance is dependent upon the frequency of the applied , or input, a.c potential difference it follows that the impedance is frequency dependent too. This dependence is termed the frequency response of the circuit, and some examples are as follows:

a) Resistor and capacitor in series



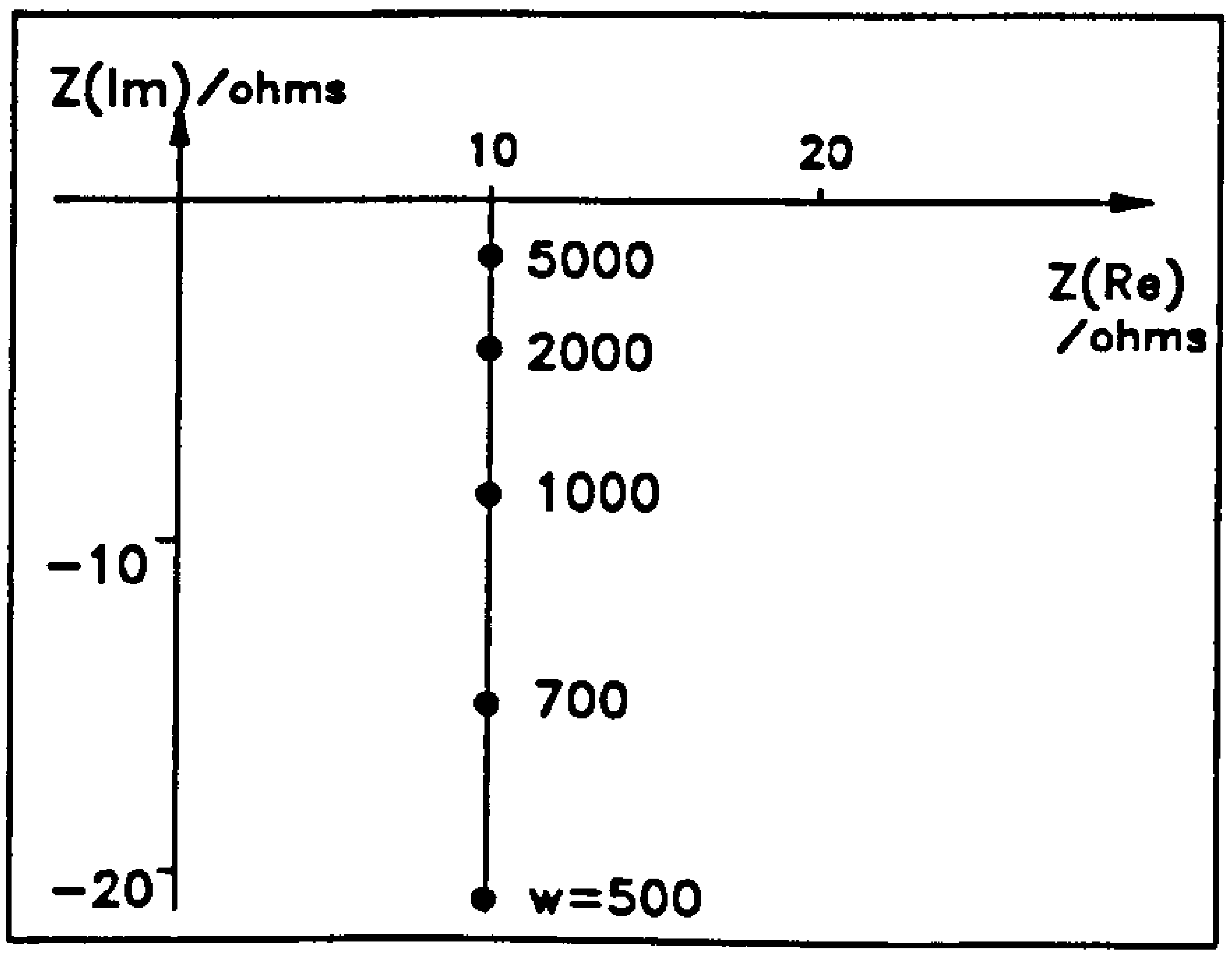
From equation (20) $Z = R - jX_C$

where $jX_C = 1/jwC$

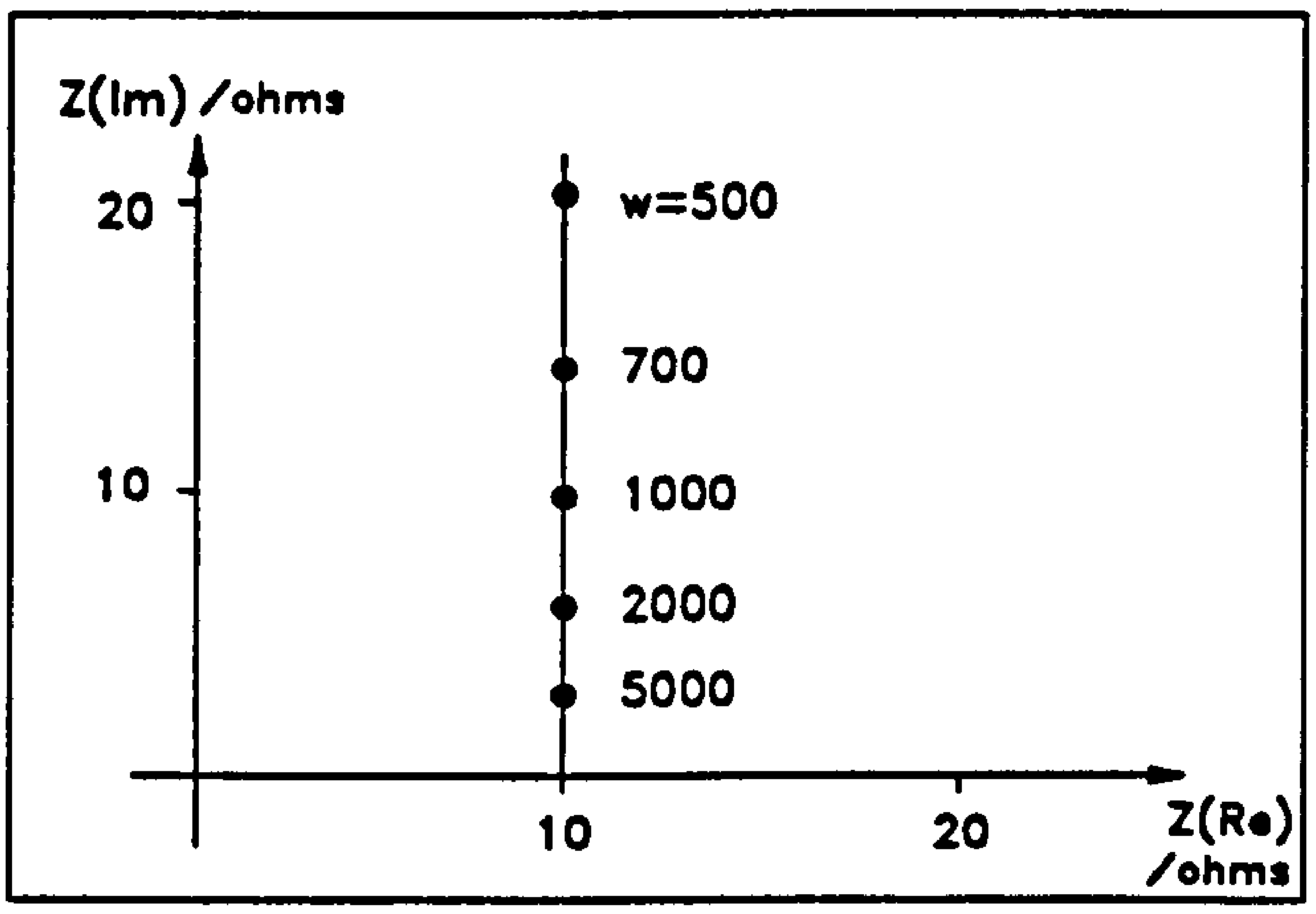
and so $Z(Re) = R = 10\Omega$

$Z(Im) = -X_C = -1/wC = -\dfrac{1}{1.5x10^{-5}.w}\ \Omega$

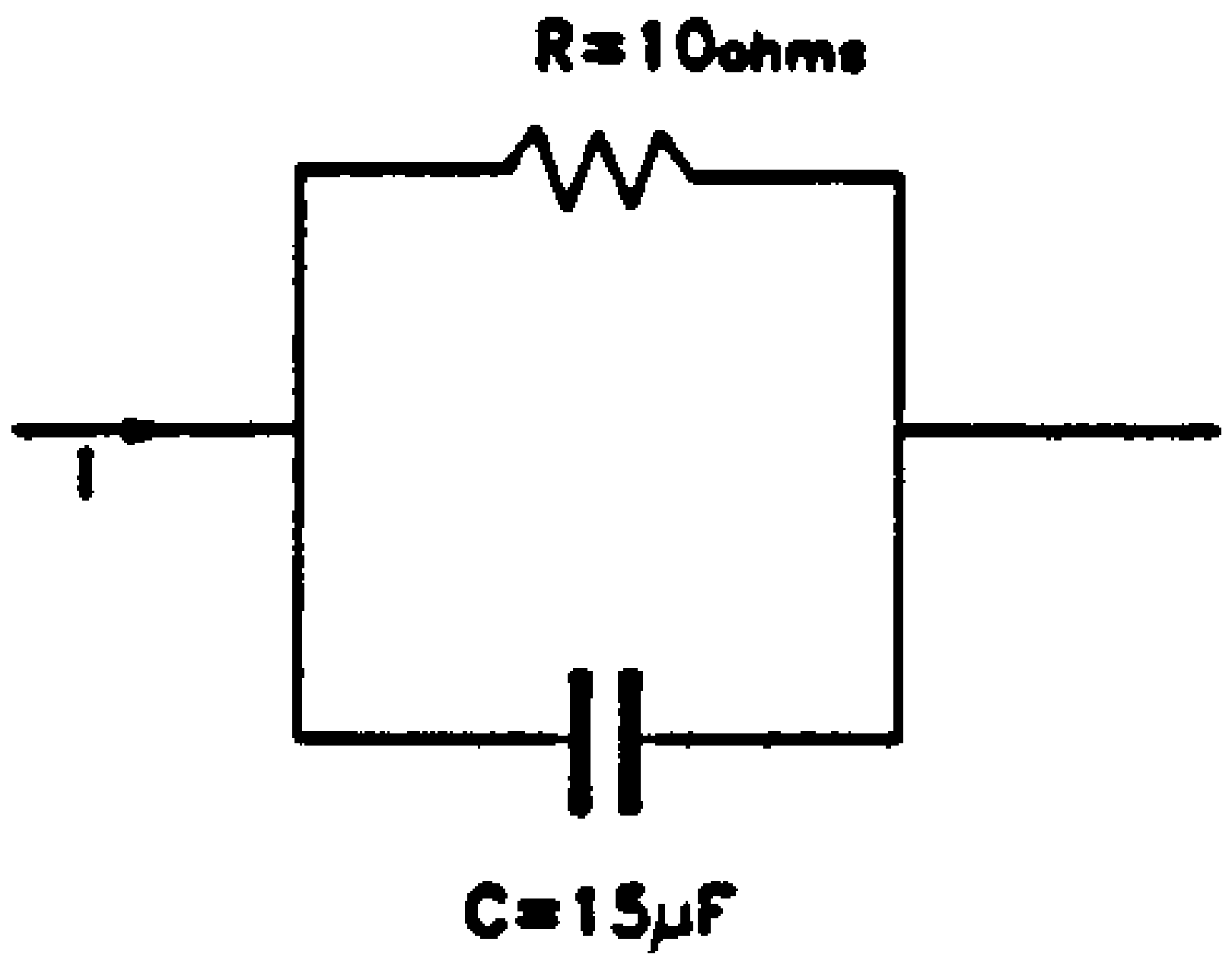
The frequency response is conventionally represented by a plot of Z(Im) against Z(Re) with frequency in Hertz as a parameter, and for the above circuit is as follows:



If there are no inductive components present in the circuitry it is convenient to ignore the negative sign on Z(Im) and transfer the plot to the first quadrant, thus:



(b) Resistor and Capacitor in parallel



From equation (24)

$$Z(Re) = \frac{RX_C{}^2}{[R^2 + X_C{}^2]}$$

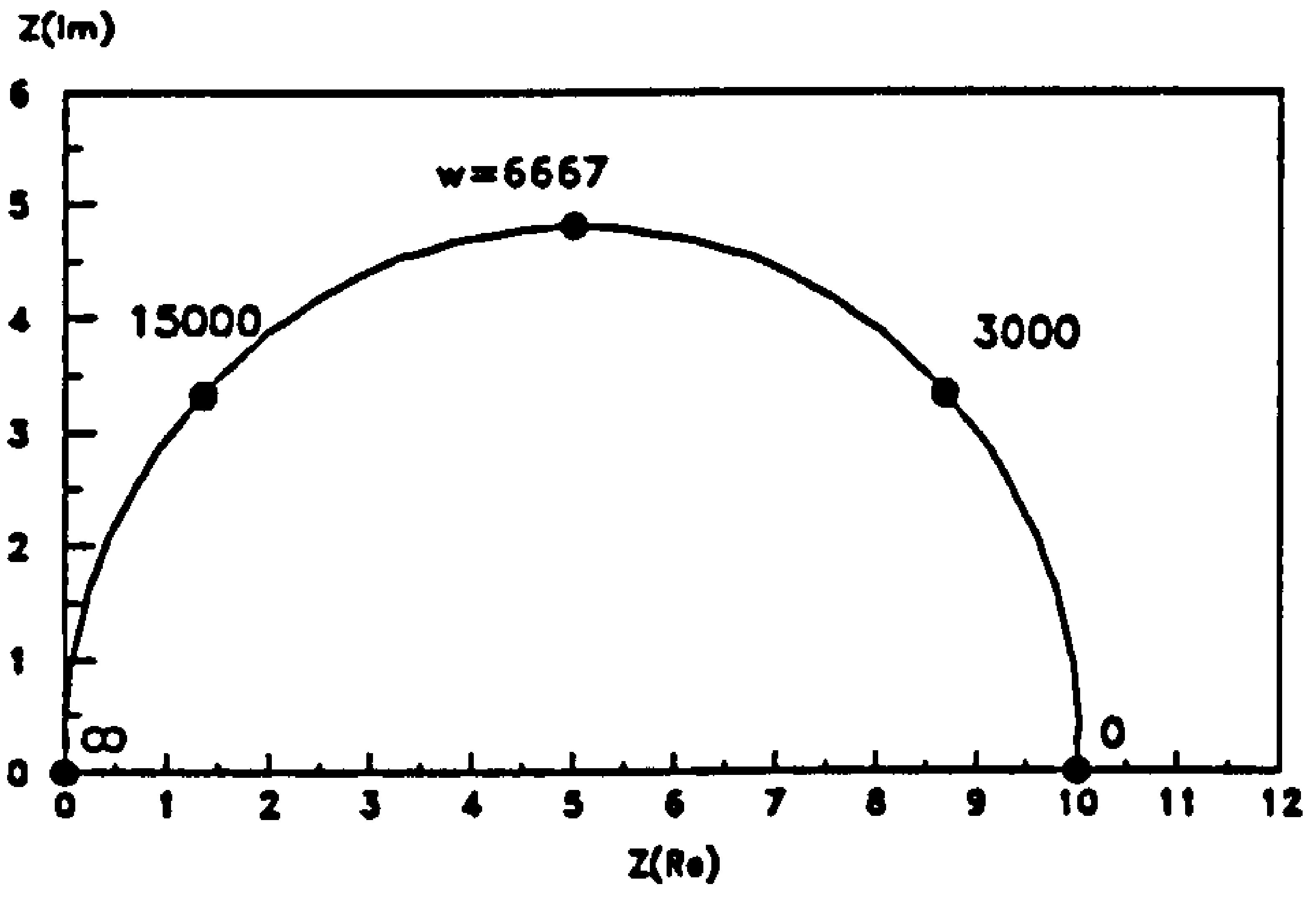
$$Z(Im) = \frac{R^2X_C}{[R^2 + X_C{}^2]}$$

therefore

$$Z(Re) = \frac{10 \times (1/1.5x10^{-5}.w)^2}{10^2 + (1/1.5x10^{-5}.w)^2]}$$

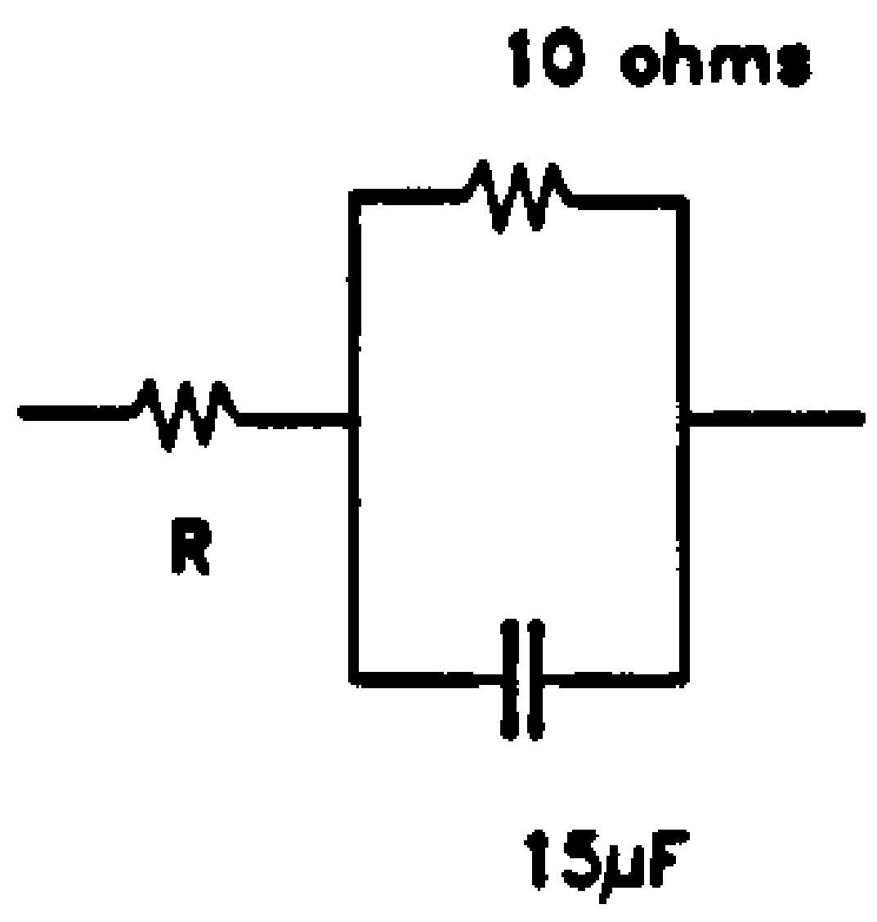
$$Z(Im) = \frac{-\ 100 \times (1/1.5x10^{-5}.w)}{[10^2 + (1/1.5x10^{-5}.w)^2]}$$

The frequency response plot takes on a semi-circular form as follows, with the maximum at $w = 1/J$.

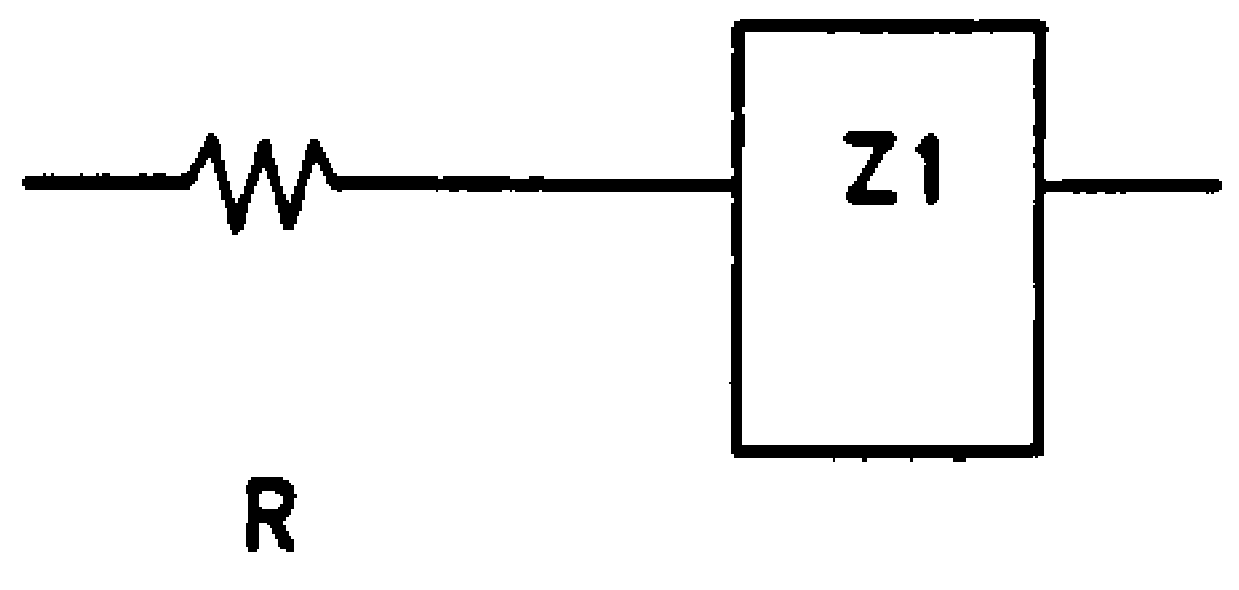


If a resistor were connected in series with the above parallel circuit,

i.e



or

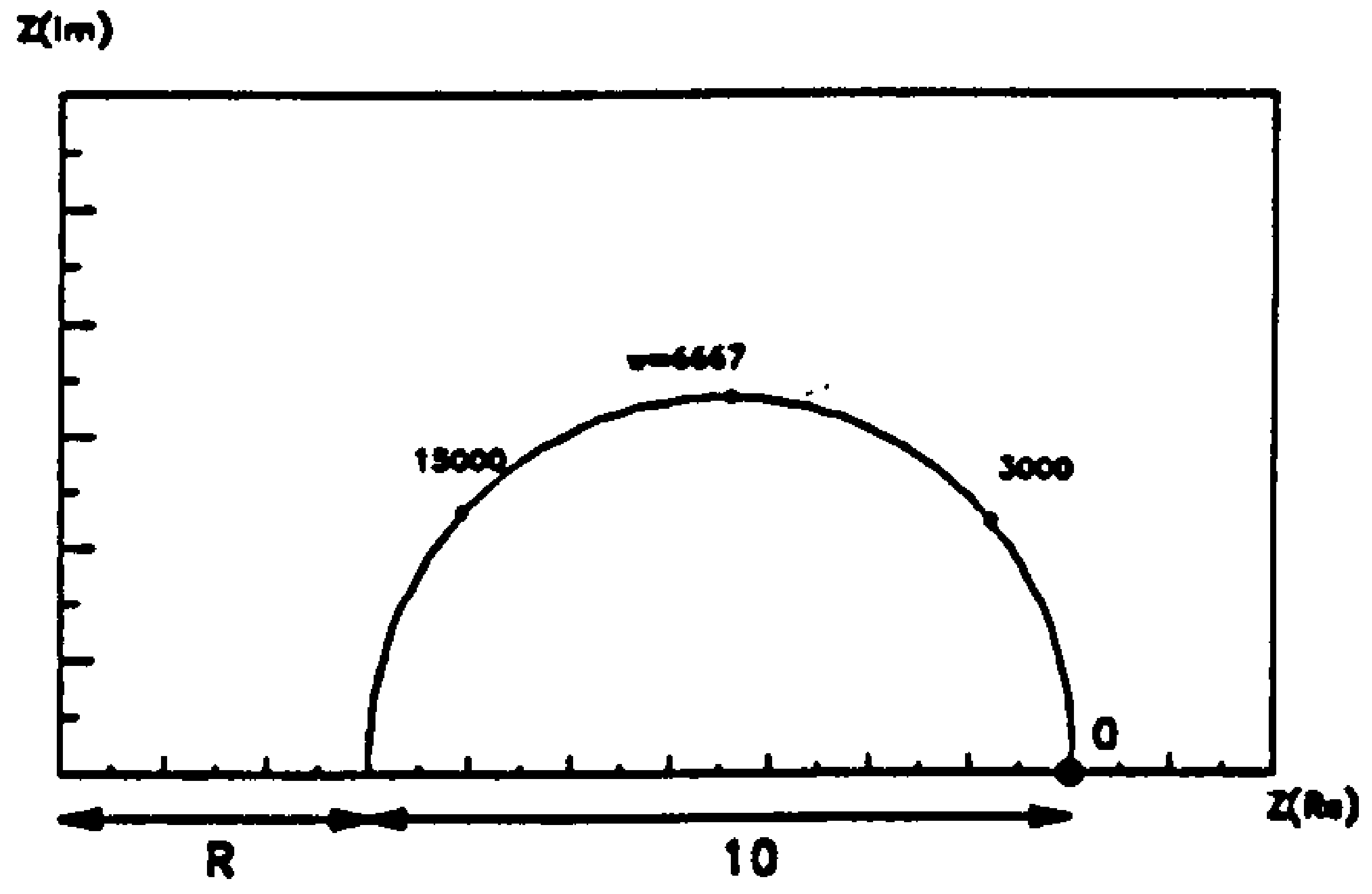


the resulting total impedance would be, $Z_T = Z + R$

In consequence $Z_T(Re) = Z(Re) + R$

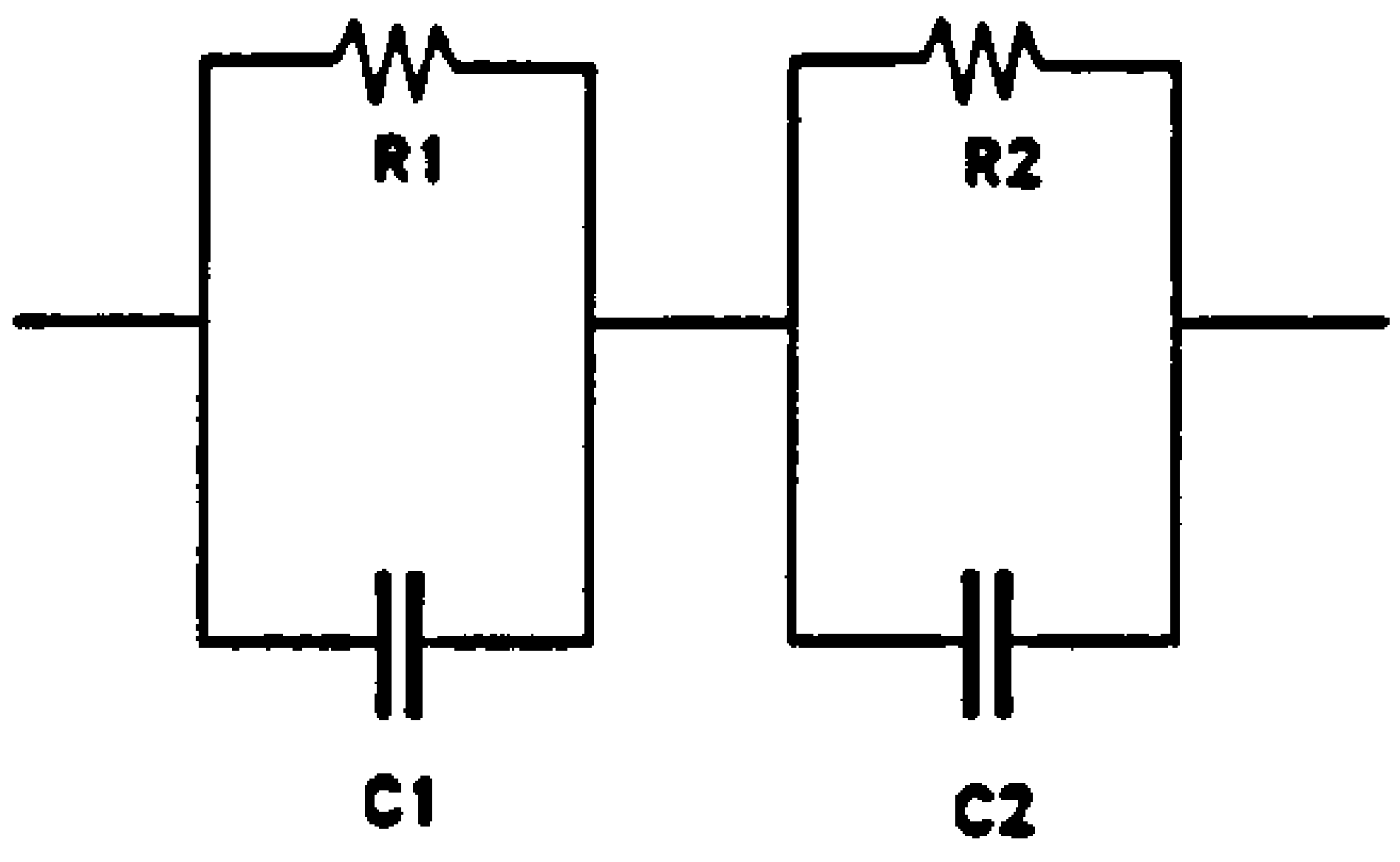
and $Z_T(Im) = Z(Im)$

The effect of connecting R in series is therefore to displace the plot along the real axis by an amount R, but the shape of the plot would be unchanged.



(c) Parallel R-C circuits in series:

These circuits take the form



The real and imaginary components will be given by

$$Z(Re) = Z_1(Re) + Z_2(Re) \qquad - (28)$$

$$Z(Im) = Z_1(Im) + Z_2(Im) \qquad - (29)$$

which from equation (24), neglecting the negative sign, will become

$$Z(Re) = \frac{R_1 X_{C1}^2}{R_1^2 + X_{C1}^2} + \frac{R_2 X_{C2}^2}{R_2^2 + X_{C2}^2} \qquad - (30)$$

$$Z(Im) = \frac{R_1^2 X_{C1}}{R_1^2 + X_{C1}^2} + \frac{R_2^2 X_{C2}}{R_2^2 + X_{C2}^2} \qquad - (31)$$

and replacing X_C by $1/wC$ gives

$$Z(Re) = \frac{R1}{1 + w^2 R_1^2 C_1^2} + \frac{R2}{1 + w^2 R_2^2 C_2^2} \qquad - (32)$$

$$Z(Im) = \frac{wR_1{}^2C_1}{1 + w^2R_1{}^2C_1{}^2} + \frac{wR_2{}^2C_2}{1 + w^2R_2{}^2C_2{}^2} \qquad - (33)$$

or by replacing RC by the time constant J,

$$Z(Re) = \frac{R1}{1 + w^2J_1{}^2} + \frac{R2}{1 + w^2J_2{}^2} \qquad - (34)$$

$$Z(Im) = \frac{wR_1J_1}{1 + w^2J_1{}^2} + \frac{wR_2J_2}{1 + w^2J_2{}^2} \qquad - (35)$$

If $J_1 = J_2 = J$ then equations (34) and (35) simplify to

$$Z(Re) = \frac{(R1 + R2)}{1 + w^2J^2} \qquad - (36)$$

$$Z(Im) = (R1 + R2) \cdot \frac{wJ}{1 + w^2J^2} \qquad - (37)$$

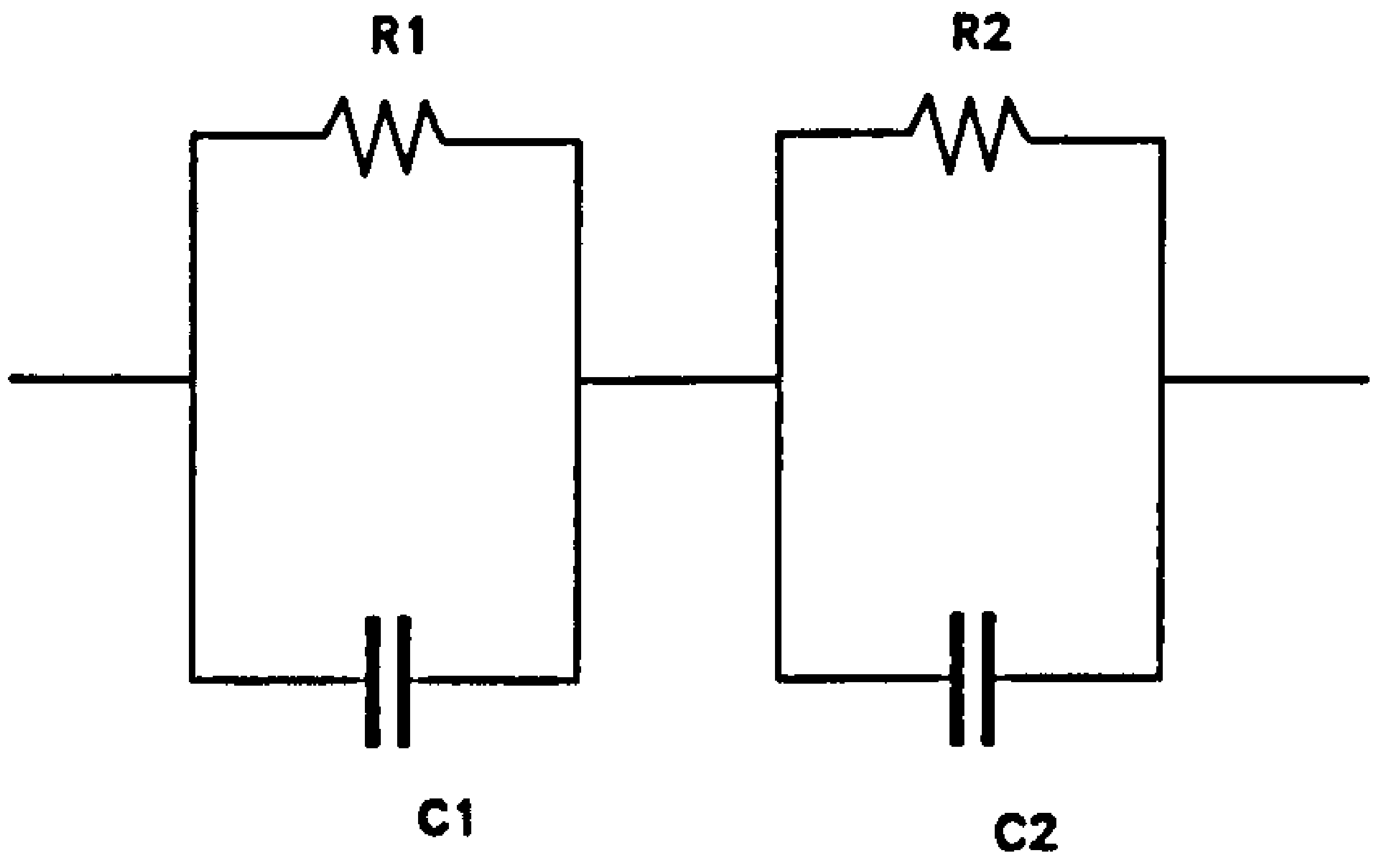
Denoting $R_1 + R_2$ by R_T, these reduce to

$$Z(Re) = \frac{R_T}{1 + w^2J^2}$$

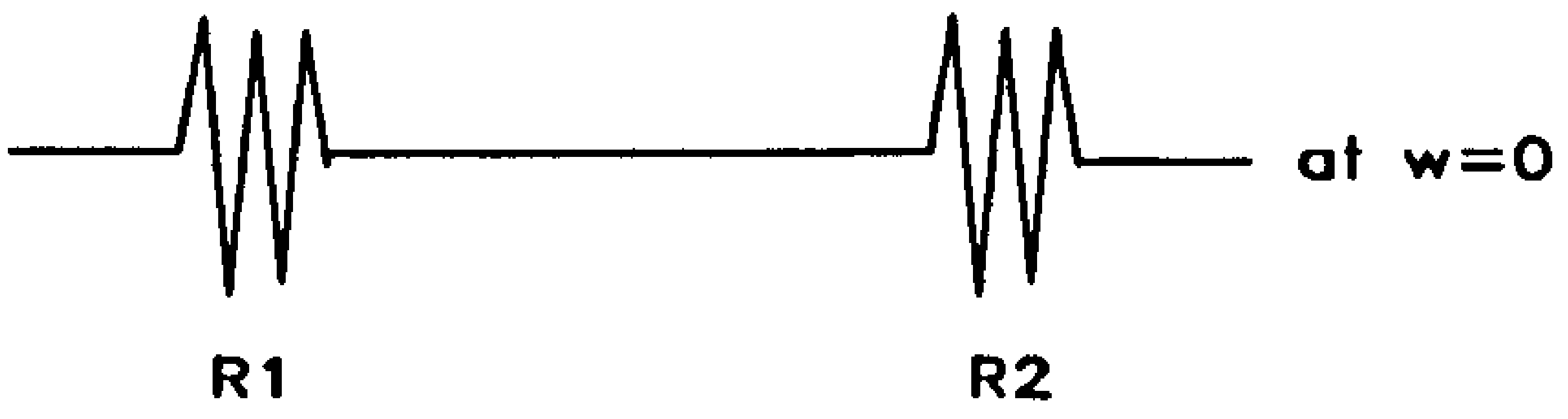
$$Z(Im) = \frac{wR_TJ}{1 + w^2J^2} \qquad - (38)$$

Comparisons of equations (38) and (27) show that such a system would be the same as a single R-C parallel circuit with R equal to R_T and $J = R_1C_1 = R_2C_2$. Its frequency response would therefore be a semicircle, with a diameter on the real axis equal to R_T and a maximum at $w = 1/R_1C_1 = 1/R_2C_2$

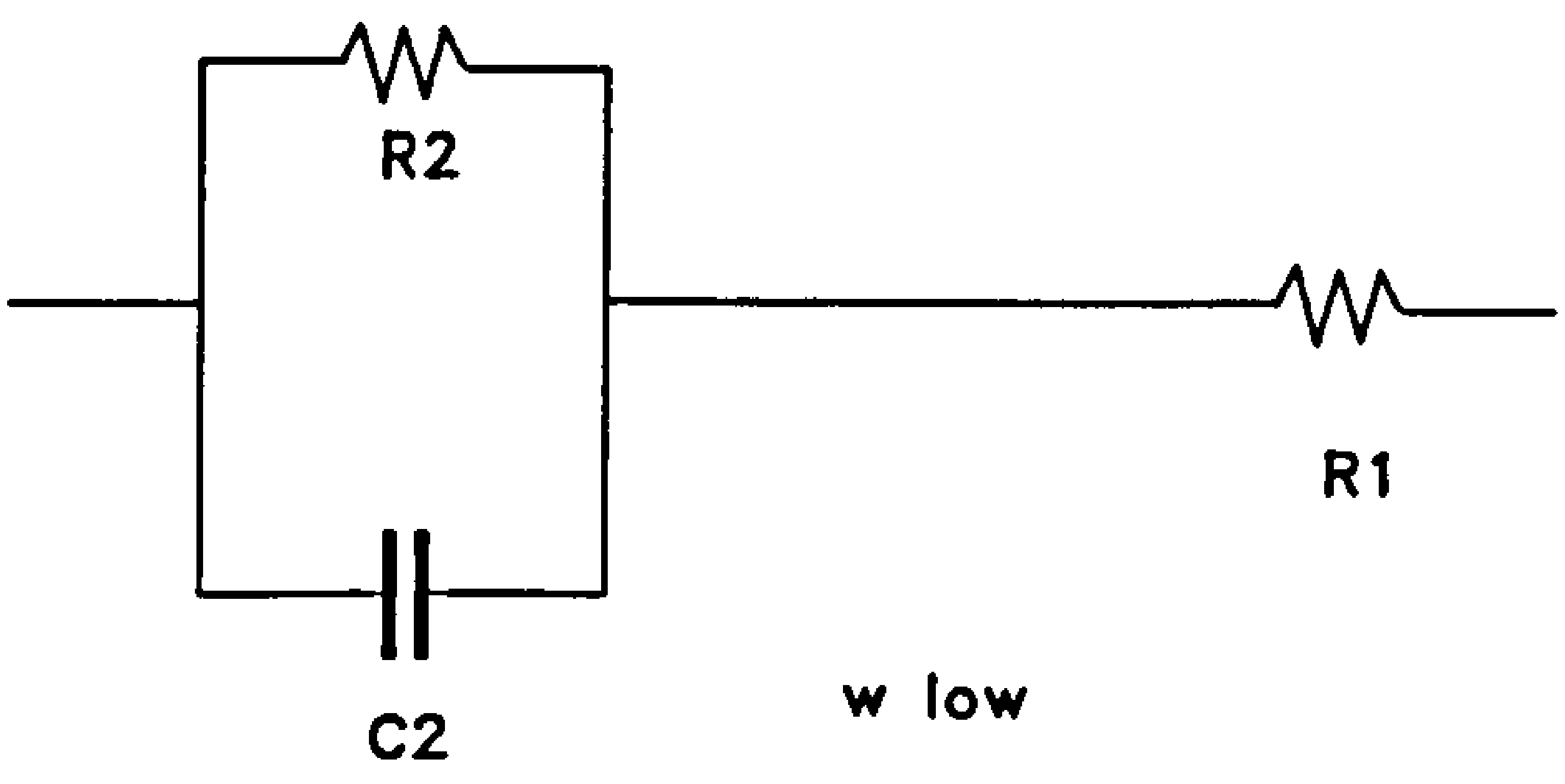
If J_1 is not equal to J_2 the shape of the response is that of two semi-circles which overlap if J_1 is not too different from J_2, but separate as the difference becomes more marked. The reason for this can be seen as follows:



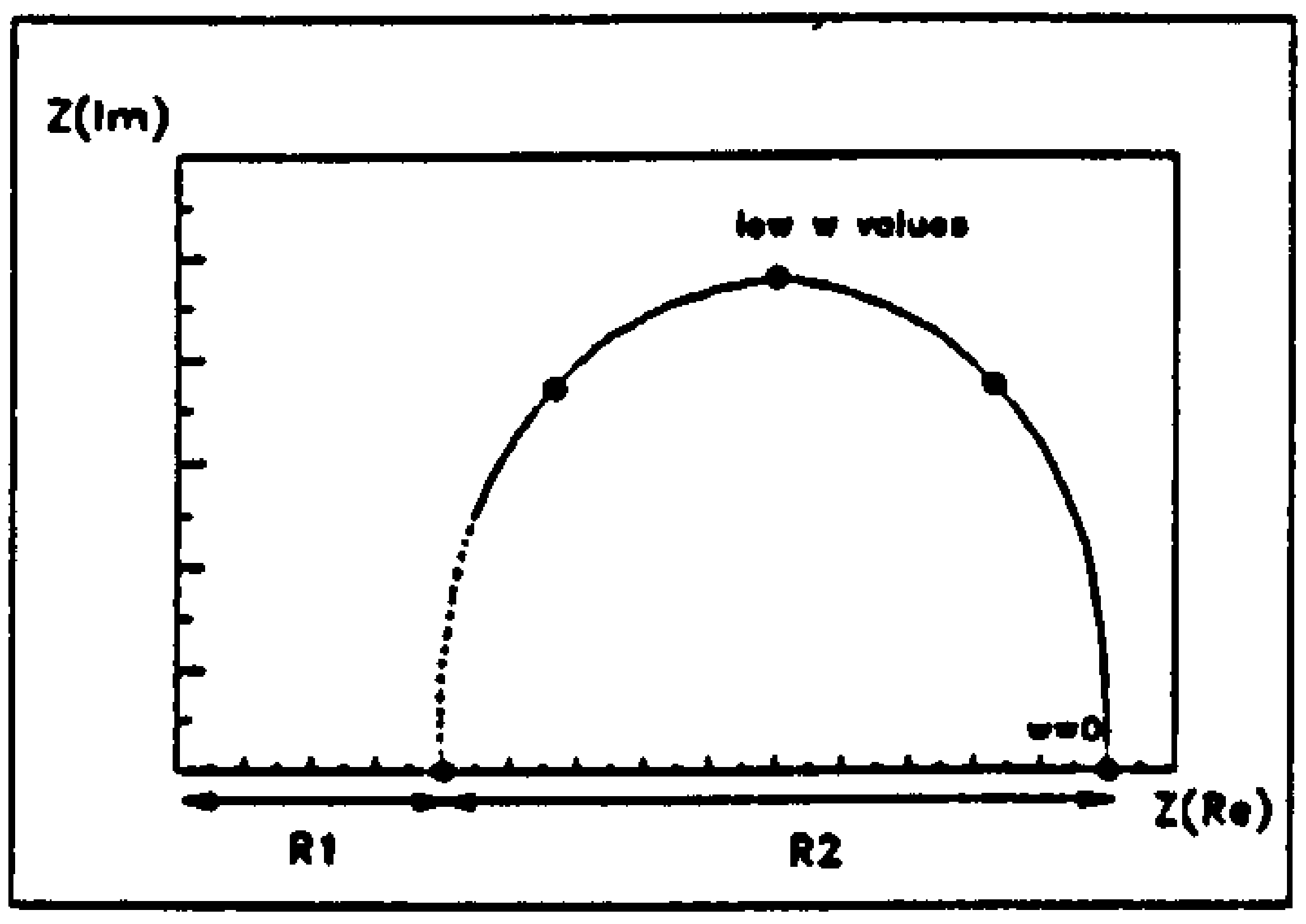
Under D.C. conditions, i.e w = 0, the circuit behaves as follows, and the impedance is simply $R_1 + R_2$



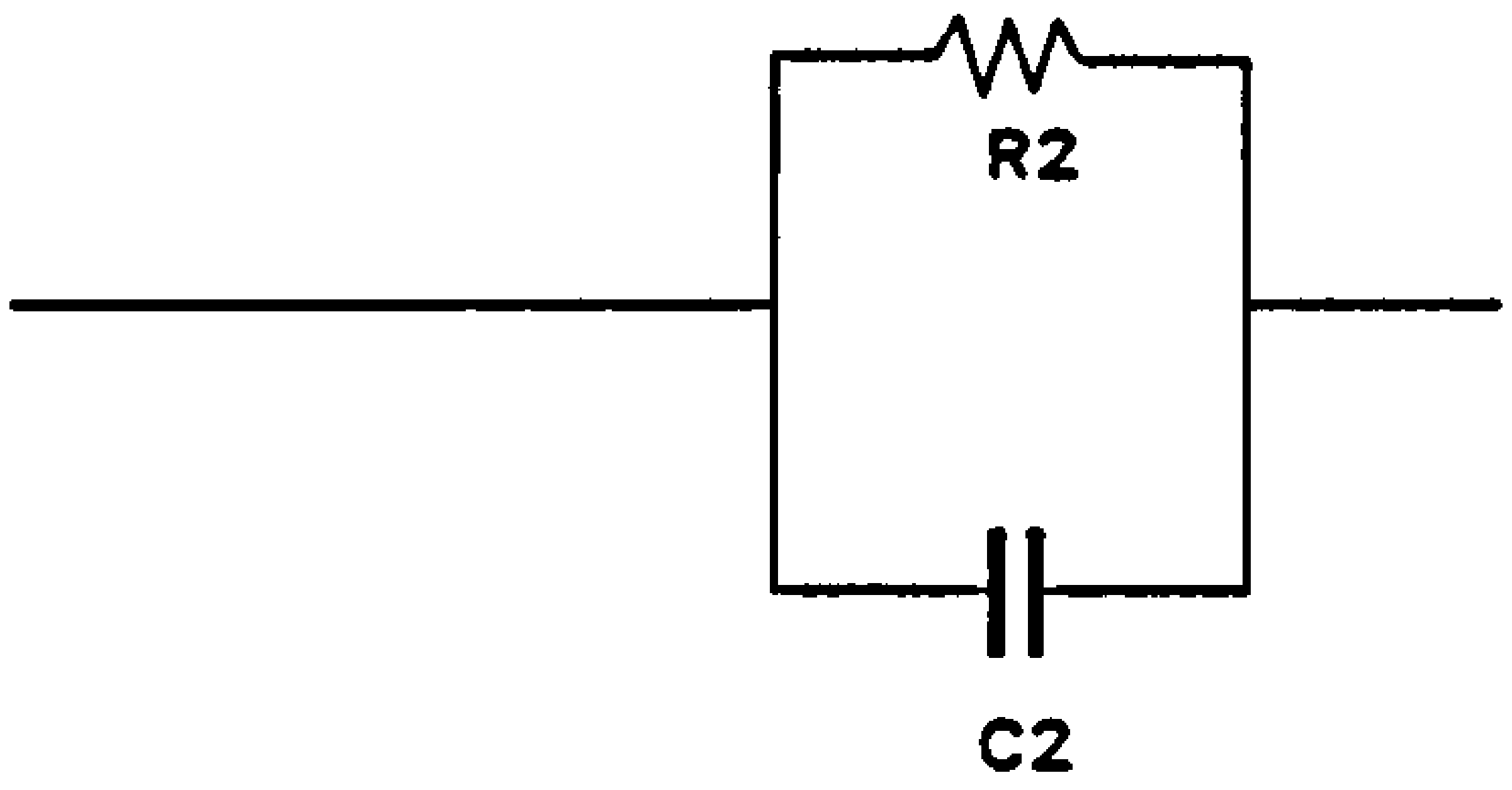
If, however $C_1 >> C_2$ (or $R_1 >> R_2$ i.e $J_1 >> J_2$) circumstances will be such that over the lower range of frequencies, moving up from zero, $1/wC_1$, will be comparable to R_1 while $1/wC_2$ is still much greater than R_2. The circuit then approximates to the following:



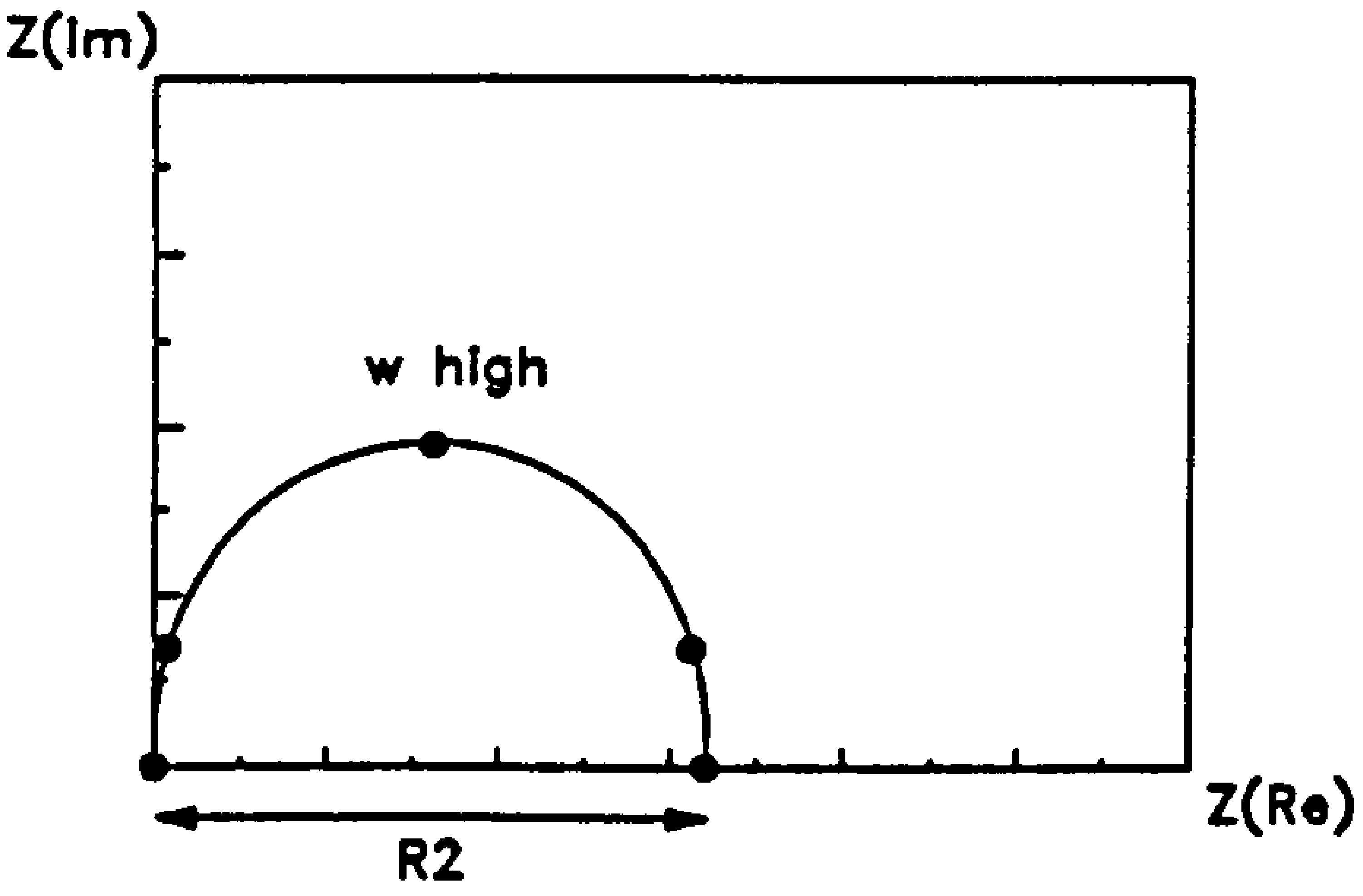
and the frequency response will be of the form as shown below :



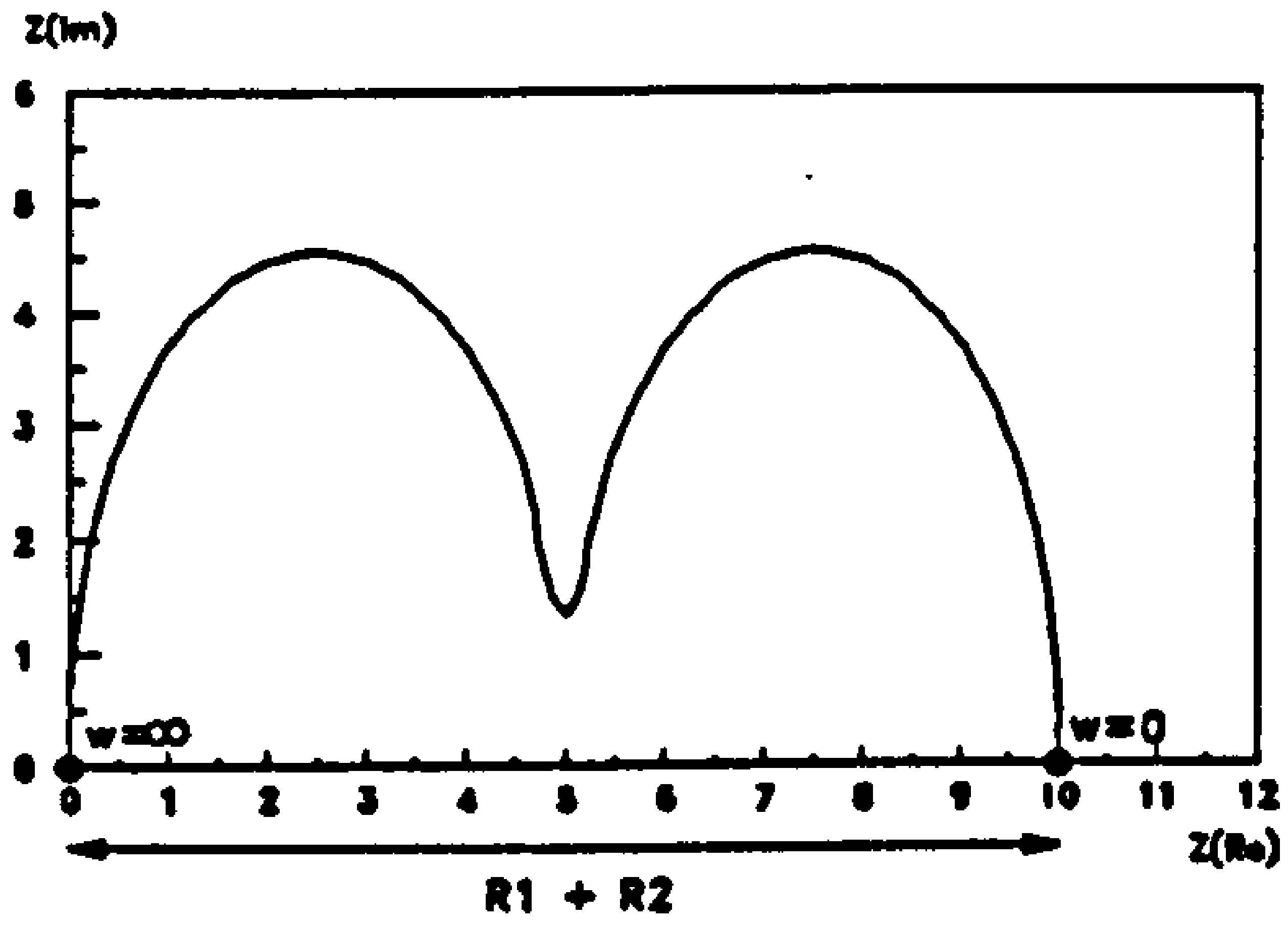
At high frequencies $1/wC_1 << R_1$ and acts as a short, the resulting circuit converging to



with a frequency response of the form



Summing these responses over the whole range of w gives:



With a clear separation of the semicircles, as shown, the maxima occur for w = $1/R_1C_1$ and w = $1/R_2C_2$ and, with $R_1C_1 \gg R_2C_2$, at Z(Re) = $R_2 + 0.5R_1$ and Z(Re) = $0.5R_2$.

CHAPTER 3 GLASS ELECTRODES

3.1 Introduction

The glass electrode is a specific type of ion selective electrode (ISE) and is inextricably linked with the measurement of pH. In the present chapter a brief introduction is given to the definition of pH, which is followed by a description of the structure of a glass electrode and its behaviour with respect to the hydrogen ion.

3.2 Concept of pH

The concept of pH has closely paralleled the development of an understanding of acids and bases. Prior to Arrhenius our understanding of acids and bases was extremely vague , and at best acids were defined in terms of their sour taste and their behaviour in reactions with other substances. Once a satisfactory definition of acids and bases was firmly founded on the hydrogen ion, however there was an immediate search for methods to measure its concentration. At first it was in the form of coloured indicators, but this method later gave way to the use of physical methods as improvements in potentiometry came along together with electrodes which were sensitive to hydrogen ion concentrations.

In 1909, Sorenson researching acid-dependant enzymatic processes in the brewing industry, noted a difference between the total acid added to s system and the resulting degree of acidity, which he measured by both colormetric and electrometric method. He denoted the "power" of the hydrogen ion by the symbol P_H^+, later replaced by pH, which he defined according to the following relationship

$$\text{pH} \quad = \quad -\log\,[\text{H}^+] \qquad\qquad - (1)$$

and this definition was the starting point from which our present concept of pH evolved.

Sorenson's original definition of pH(25) contains an inherent difficulty in that measuring devices respond to hydrogen ion activity rather than its concentration, and when the concept of activity was formulated, largely through the efforts of Lewis and Randall, Sorenson and Linderstrom-Lang(26) redefined pH as the negative of the log of the hydrogen ion activity.

$$\text{pH} \quad = \quad -\log\,a_H{}^+ \qquad\qquad - (2)$$

Unfortunately individual values of activity cannot be evaluated without moving from sound scientific principles into the realms of assumption and so pH defined in terms of activity cannot be rigourously related to experimental observation. Consequently an operational scale of pH, or acidity, has been defined by the National Bureau of Standards(11) based on practical rather than theoretical quantities. It has its roots in the electrochemical behaviour of the hydrogen ion.

The e.m.f of an electrode (for instance the Pt/H_2 electrode) which is reversible to the reaction

$$H_2(1\ \text{atm}) \longleftrightarrow 2H^+ + 2e \qquad - (3)$$

is given, according to Nernst, by

$$E_H = E_H^{\circ} - \frac{RT}{F} \ln a_{H^+} \qquad - (4)$$

where E° is the standard potential, corresponding to unit activity. From equation (2), this relationship may be re-written as

$$E_H = E_H^{\circ} + \frac{2.303\ RT}{F} .\ pH \qquad - (5)$$

If the hydrogen responsive electrode were made one half of a complete cell the e.m.f of the cell, e, would be given by

$$E = E_H - E_C$$

where E_C, is the e.m.f of a counter electrode unresponsive to hydrogen ions. Hence

$$E = E_H^{\circ} - E_C + \frac{2.303\ RT}{F} .\ pH \qquad - (6)$$

If E were the e.m.f of the cell when it contained a solution of unknown pH, and E_S its value when it contained a reference solution having a known value of pH equal to pH_S, it follows from equation (6) that

$$E - E_S = \frac{2.303\ RT}{F} .\ pH - pH_S$$

or

$$pH = pH_S + \frac{F.(E - E_S)}{2.303\ RT} \qquad - (7)$$

Equation (7) has been adopted by the NBS as the operational definition of pH in aqueous solution and it has specified the composition and pH_S values for six different reference solutions, or standard buffers, covering the range $pH_S = 3$ to 10. The pH_S values were determined using the following cell, which has the advantage of having no liquid junction.

$$\text{Pt } H_2(1\text{ atm}),\ H^+\ Cl^-\ (\text{plus } K^+\ Cl^-),\ AgCl(s)\ Ag \qquad -\ (8)$$

The e.m.f of this cell is given by

$$E = E^{\circ} - 0.000198T\ \log\{f_{H^+}\ .\ f_{Cl^-}\ [H^+]\ [Cl^-]\} \qquad -\ (9)$$

where E° is the standard potential of the cell.

Rearranging,

$$-\log(a_{H^+}\ .\ f_{Cl^-}) \quad = \quad \frac{E - E^{\circ}}{0.000198T} + \log\{Cl^-\} \qquad -\ (10)$$

The quantities on the right hand side can be measured or calculated, and $\log(a_{H^+}\ .\ f_{Cl^-})$ therefore evaluated. If this is done for various concentrations of Cl^- and the results extrapolated back to zero concentration the value of $(a_{H^+}.f_{Cl^-})$ for the standard buffer under chloride-free conditions is obtained. This value is denoted by $(a_{H^+}.f_{Cl^-})^{\circ}$, and pH_S under chloride-free conditions is determined from

$$pH_S \quad = \quad -\log(a_{H^+}\ .\ f_{Cl^-})^{\circ} = \log(f_{Cl^-})^{\circ} \qquad -\ (11)$$

The asymptotic value $(f_{Cl^-})^{\circ}$ can be estimated from the equation

$$-\log(fCl^-)^{\circ} \quad = \quad \frac{A\ .\sqrt{u}}{1 + 1.5\sqrt{u}} \qquad -\ (12)$$

where A is the Debye-Huckel parameter which is dependant upon temperature and u is the ionic strength of the solution at zero chloride concentration.

By the use of equation (11) pH_S values are as closely linked to a_{H+} as is at present possible, thereby preserving the spirit of the Sorenson definition. The fact that equation (11) requires the estimation of an individual activity coefficient does, however, deprive the resulting value of pH_S of thermodynamic exactitude.

The uncertainty in pH_S values is taken as 0.005 pH units up to 60°C rising to 0.008 at 95°C. This does not include errors arising from liquid junction which, in practice, are almost invariably present when measuring pH.

3.3 Liquid Junctions(4,5,6,7)

Out of practical necessity electrolytic cells, for whatever purpose, usually include junctions between liquid phases of different compositions and their existence creates a potential difference which arises as follows. Consider the junction shown in Fig 3.1 between solutions containing HCl in different concentrations.

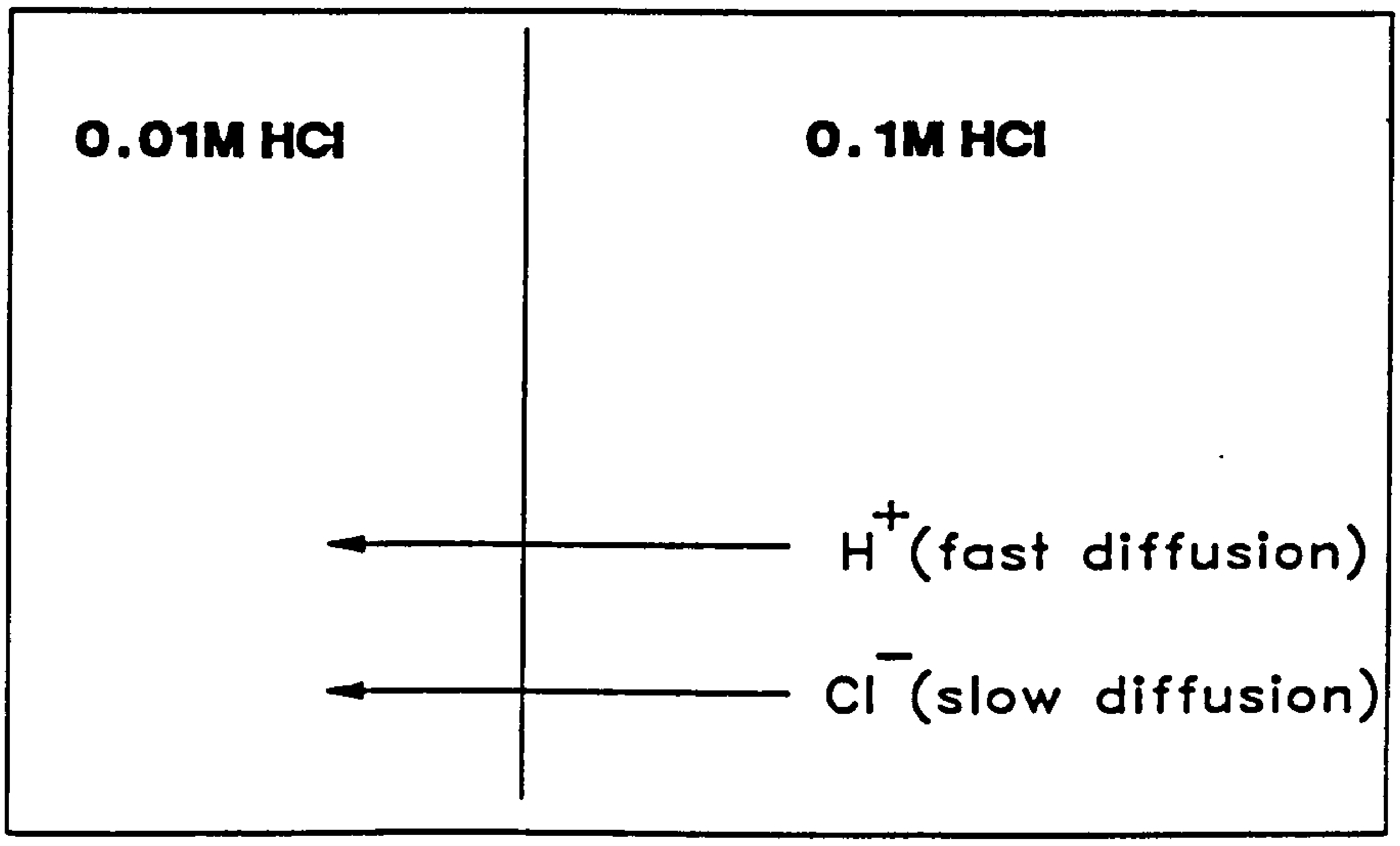


Fig 3.1 Development of a Liquid Junction Potential

Due to the difference in concentration at the junction there will be a net transfer of H^+ and Cl^- ions by diffusion from right to left, but since H^+ has a greater mobility than Cl^- the migration of the former will outstrip the latter thereby bestowing a positive charge on the dilute phase and a negative charge on the more concentrated phase. The process is self limiting because the electric field produced in this way will retard the H^+ ions and accelerate the Cl^- ions. The magnitude of the potential difference which develops across the junction as a result of this process depends upon the ions involved but can be of the order of tens of millivolts.

The junction in Fig 3.1 is termed a type 1 junction because it consists of like ions in each phase. If only one of the ions is common it is referred to as type 2, and if neither are common as type 3.

e.g

type 1 $HCl \mid HCl$

type 2 $HCl \mid KCl$

type 3 $HCl \mid KNO_3$

Type 1 junctions are amenable to a reasonably rigourous analysis, but types 2 and 3 can only be treated in a somewhat approximate manner, and moreover only in a few cases, since their analysis depends upon the way the junction is formed.

In order to minimise junction potentials it is usual to employ a salt bridge comprising a fairly concentrated solution of anions and cations which have roughly equal mobility. Their high concentrations means that these ions will dominate conditions at the interface, and their comparable mobilities results in a minimal potential difference. The fact that this condition will exist at both ends of the salt bridge but with opposing polarities reduces the combined effect of the junction potential still further, down perhaps to 1 or 2 millivolts.

In measurements such as pH the over-riding requirement is that the junction potential should remain constant between test and calibration solutions, but once again a difference of 1 - 2 mV usually cannot be avoided.

3.4 Glass Electrode Assembly

For over half a century the most common and convenient means of measuring pH has been based on the potential difference which develops between the surfaces of a glass membrane separating solutions of known and unknown acidity. Devices which make use of this phenomenon are termed "glass electrodes" and a typical construction is shown in Figure 3.2 following.

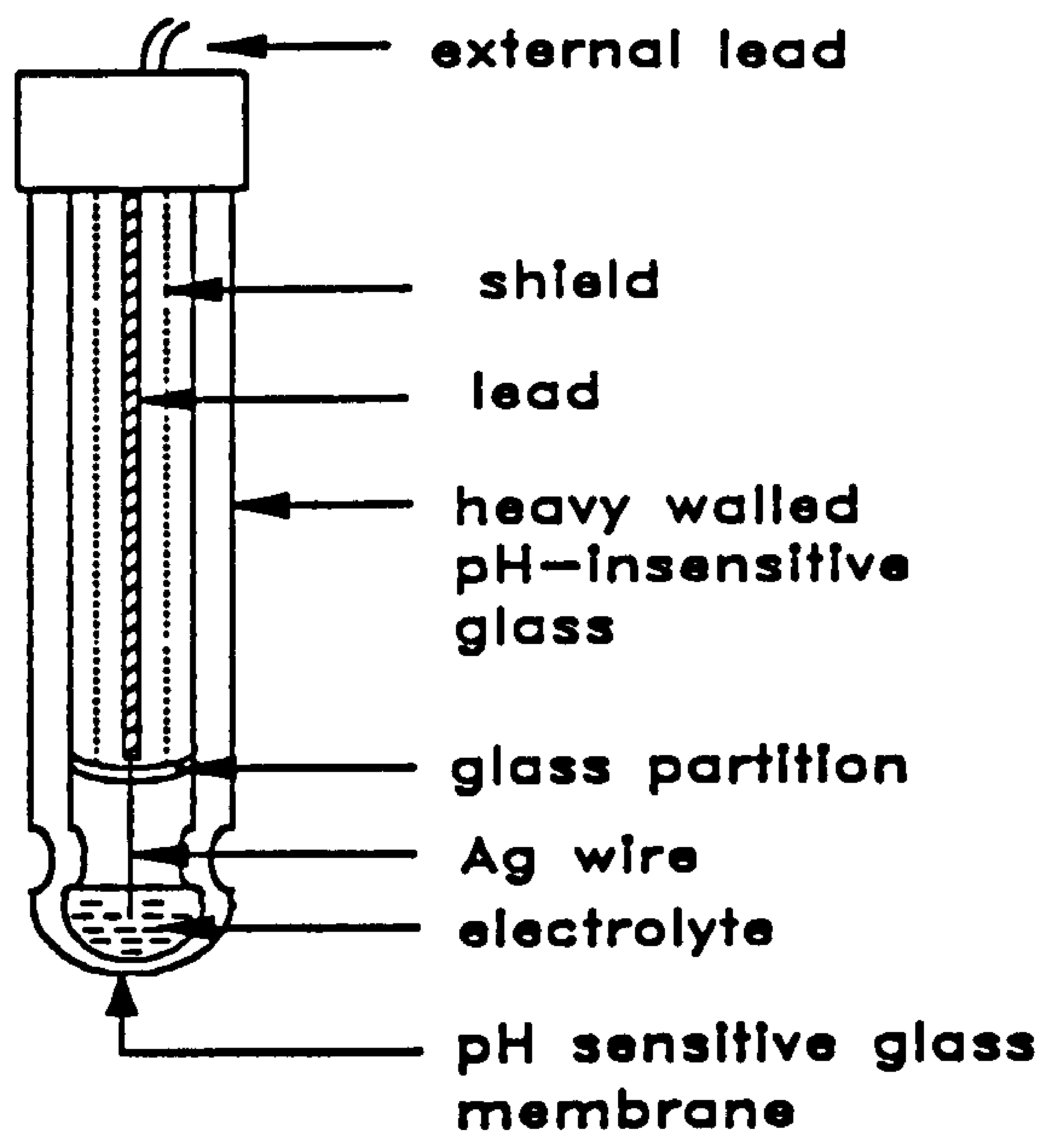


Figure 3.2 Typical Glass electrode[8]

It comprises a heavy-walled glass tube, unresponsive to pH, which is closed at one end by a plastic cap and sealed at the other to a pH-sensitive glass membrane. The membrane and that part of the wall to which it is attached are formed into a bulb which is filled with a reference electrolyte, usually either 0.1 M HCl or a chloride phosphate buffer of pH 7. In both cases the electrolyte is saturated with AgCl. This solution is restricted to the bulb by a glass partition which stretches across the tube just above the bulb. A silver wire dips into the electrolyte and a lead attached to the wire passes up the tube and through the cap so that the electrode can be connected to an external electrical circuit. The electrolyte performs two functions. Firstly, by reason of its silver chloride content it allows the silver wire to function as an Ag|AgCl reference electrode[27], referred to as the "internal reference", and secondly, it bathes the internal surface of the membrane with a solution of fixed pH. The lead passing up the tube is shielded by an earthed metal gauze to prevent interference from stray electric fields.

3.5 Behaviour of the Glass Electrode(9,10,11,12)

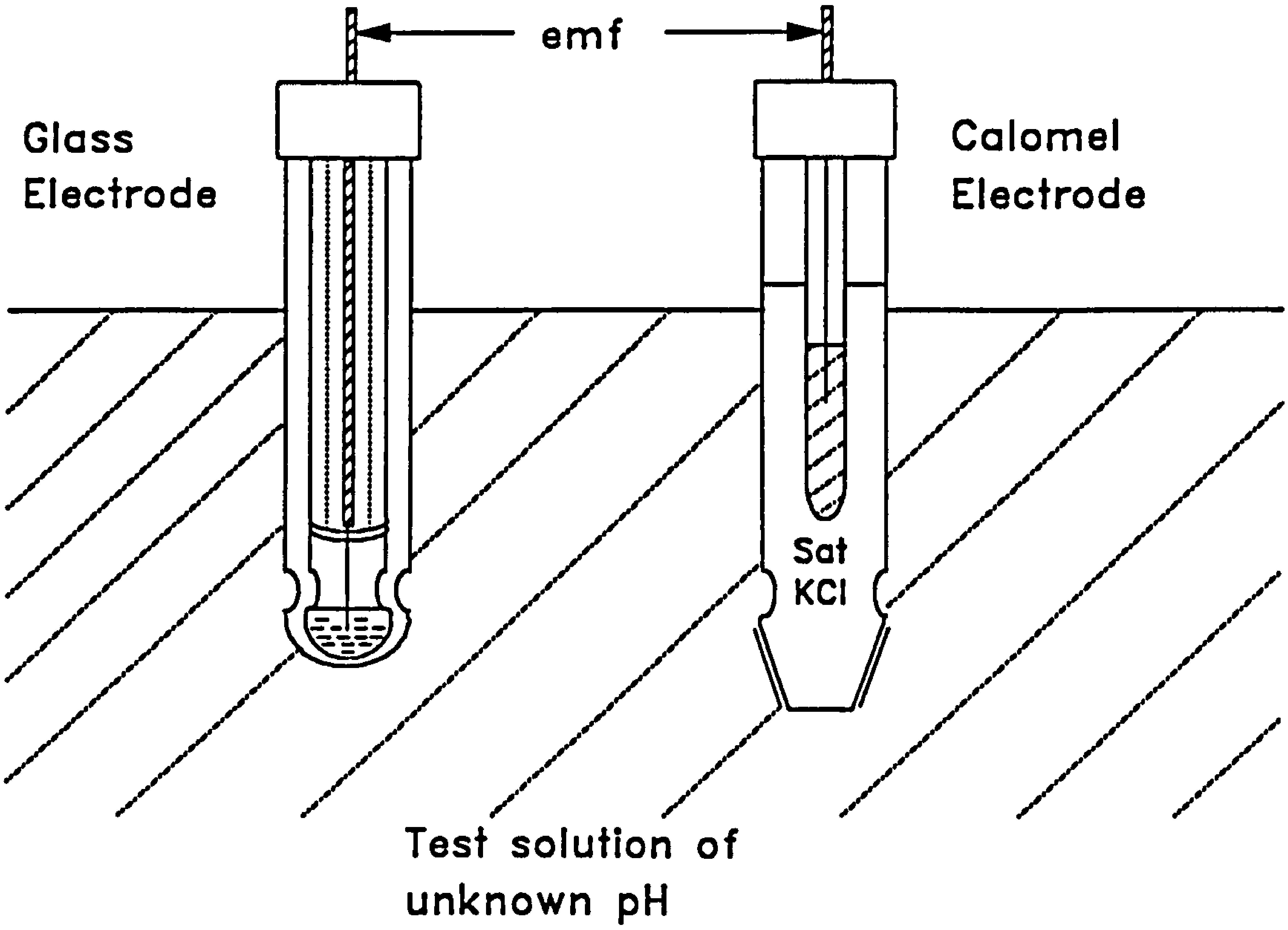


Fig 3.3 Electrode assembly for pH measurement

In order to determine pH the bulb of the glass electrode is immersed in the test solution, together with a reference electrode insensitive to H^+ ions, and the e.m.f developed between them is measured. The set up is shown in Fig 3.3, from which it is clear that pH measurement requires the use of two reference electrodes, namely the internal reference electrode within the glass electrode, and an external reference. If a saturated calomel electrode is used as the external reference, and the internal electrolyte is 0.1 M HCl, the resulting cell is as follows:

$$\underbrace{Hg|Hg_2Cl_2|KCl(sat)}_{\text{Calomel electrode}}|\text{Test soln}|\underbrace{\text{Glass membrane}|HCl(0.1M)|AgCl|Ag}_{\text{Glass electrode}}$$

The e.m.f of this cell, Ecell, will be made up in the following way:

$$\boxed{E_{cell} = E_{AgAgCl} + E_{asy} + E_b + E_j - E_{sce} \qquad - (13)}$$

where

E_{AgAgCl} = the electrode potential of the internal reference

E_{asy} = asymmetry potential, which will be discussed later

E_b = boundary potential i.e the difference in potential across the glass membrane

E_j = junction potential at the Sat'd KCl/test solution interface

E_{sce} = potential of the saturated calomel electrode

Of these potentials, the H+ concentration, and therefore the pH of the test solution, will only affect E_j and E_b, and so equation (13) reduces to:

$$\boxed{E_{cell} = \text{const} + E_j + E_b \qquad - (14)}$$

Since a saturated KCl bridge is used in the calomel electrode it is safe to assume that E_j will not only be small, but more importantly virtually constant, and so (14) becomes

$$E_{cell} = \text{const} + E_b \qquad - (15)$$

Errors arising from the inconsistency of the junction potential rarely exceed 2 mV.

The behaviour of the membrane is somewhat complicated(13,14,20,22). Glass is an irregular array of silicate tetrahedra ($SiO_4{}^{4-}$) which are connected to one another by the sharing of oxygen atoms to produce what is tantamount to an infinite network. The spaces in this structure are occupied by sufficient cations to neutralise the negative charge on the network. Cations of multiple charge (e.g Ca^{++}) are tightly anchored in the network and are immobile, but singly charged ions (e.g Na^+,Li^+,H^+) on the other hand are sufficiently mobile to give the glass a detectable electrical conductance. A typical glass electrode is about 0.03 to 0.1 mm thick and has a resistance of 50 to 100 Mohms. Corning 015 glass, which has enjoyed wide popularity in pH measurement, consists of approximately 22% Na_2O, 6% CaO and 72% SiO_2. At high pH values, however, it becomes sensitive to Na+ and loses its pH selectivity. Glasses in which sodium and calcium are replaced by lithium and barium to various extents have a much improved performance at the high pH end.

In order to respond to H+ ions, a glass membrane must be hydrated. Glasses which are not capable of being hydrated, as for instance Pyrex, show no response. The hydration of the membrane is the result of ion exchange in which monovalent cations in the glass are replaced by hydrogen ions. The immobility of the higher valency cations prevents them from taking part in this process. This ion exchange is usually depicted by the reversible reaction:

$$H^+ + Na^+Gl^- \longleftrightarrow Na^+ + H^+Gl^- \qquad - (16)$$

where Gl^- represents a cation bonding site in the glass.

The equilibrium for this process is so heavily weighted to the right hand side that the surface of the glass membrane consists of a silicic acid gel. These conditions are shown diagrammatically in Fig 3.4, which shows that H^+ is the dominant monovalent cation at the surface and that its presence decreases towards the interior falling to zero at a penetration of the order 50 to 100 Å. The centre of the membrane, which is the vast majority of it, is "dry".

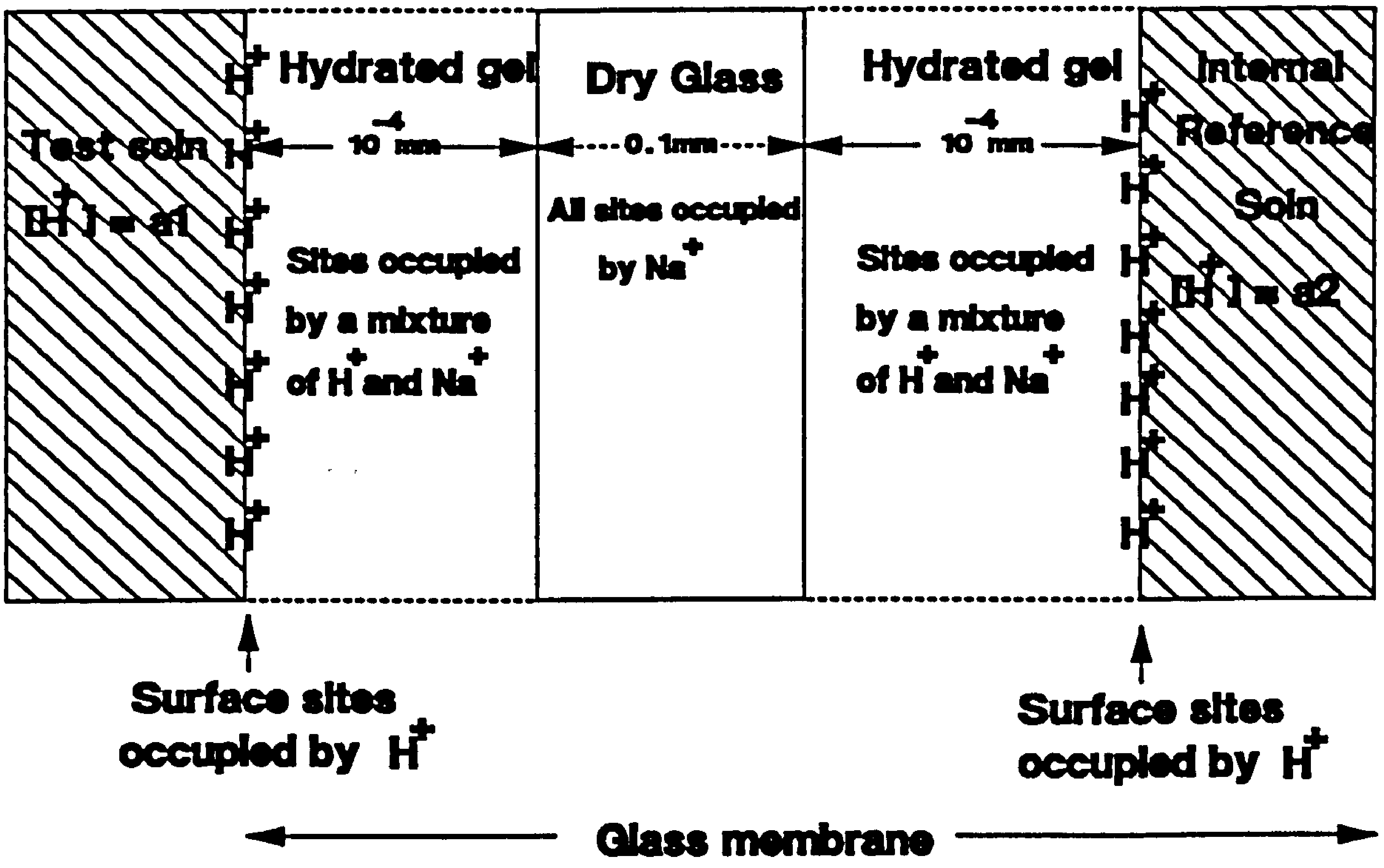


Fig 3.4 Conditions in a hydrated glass membrane(12)

This diagram is re-drawn in terms of contacting surfaces in Fig 3.5, where W_1 is the test solution, g_1 and g_3 the two silicic acid gels on either side of the membrane, g_2 the dry glass phase and W_2 the internal aqueous reference electrolyte.

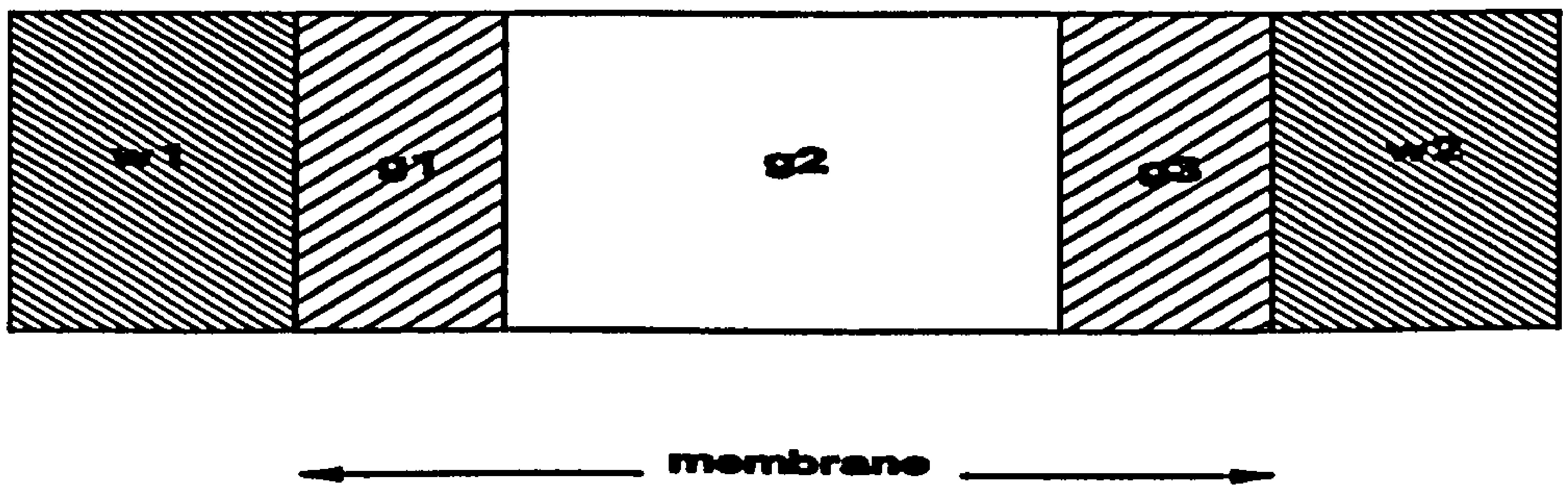


Fig 3.5 Contacting phases across a glass membrane

The value of E_b in equation (15) is made up as follows,

$$E_b = \blacktriangle\phi_{W1-g1} + \blacktriangle\phi_{g1-g2} + \blacktriangle\phi_{g2-g3} + \blacktriangle\phi_{W2-g3} \quad (17)$$

The interface between W_1 and g_1 and W_2 and g_3 are semipermeable in that they allow only the passage of monovalent cations. In the analysis of the glass electrode the potential differences $\blacktriangle\phi_{W1-g1}$ and $\blacktriangle\phi_{W2-g3}$ are therefore treated as Donnan equilibrium potentials. The potential differences $\blacktriangle\phi_{g1-g2}$ and $\blacktriangle\phi_{g2-g3}$ at the phase boundaries between g_1 and g_2 and between g_2 and g_3 are treated as internal diffusion potentials akin to type 2 liquid junction potentials, the mobility of H^+ and Na^+ in the gel and dry glass being substantially different. This approach leads to the relationship(24),

$$E_b = \text{constant} + \frac{RT}{F} \ln(a_{H^+,1} + K.a_{Na^+,1}) \quad (18)$$

where $a_{H^+,1}$ and $a_{Na^+,1}$, are the activities of the hydrogen and sodium ions, respectively, in the test solution. The quantity K is made up as follows:

$$K = Ke \frac{U_{Na}}{U_H} \quad - (19)$$

the terms U_{Na} and U_H being the mobilities of the sodium and hydrogen ions in the gel phase and K_e the equilibrium constant for the exchange reaction:

$$Na^+(aq) + H^+(gel) \quad {<}{-}{-}{-}{-}{>} \quad Na^+(gel) + H^+(aq)$$

i.e

$$K_e = a_{H^+}(aq) . a_{Na^+}(gel) / a_{H^+}(gel) . a_{Na^+}(aq) \qquad - (20)$$

From equation (18) it is clear that the membrane potential, E_b, responds to the presence of both Na^+ and H^+ in the test solution, the specificity being dependant on the value of K. If this is small enough $K.a_{Na^+,1} << a_{H^+,1}$, and to all intents and purposes the membrane will only be sensitive to H^+ ions. Under these circumstances,

$$E_b = \text{constant} + \frac{RT}{F} \ln(a_{H^+,1}) \qquad - (21)$$

and substitution in equation (15) leads to

$$E_{cell} = \text{constant} + \frac{RT}{F} \ln(a_{H^+,1}) \qquad - (22)$$

which for most practical purposes is equivalent to

$$E_{cell} = \text{constant} - \frac{2.303RT}{F} . \text{pH}$$

The constant is determined by the use of a standard buffer .

It might be pointed out that glass membranes can respond to other monovalent ions, for instance Li^+, K^+, Ag^+ etc, and the suppression of this response is achieved by adjusting the composition of the glass. Even with the best glasses available, however, there is still a so called "alkaline error" at pH 12 and above, the electrode reading too low by up to 0.5 of a pH unit. There is also an acid error at pH < 0, but this is not well understood.

3.6 <u>Asymmetry Potential</u>

If a glass electrode is dipped into a test solution of identical composition to the internal reference electrolyte, the potential difference across the membrane, Eb, should theoretically be zero. In practice, however, it is found that Eb has a value other than zero, and that the value changes very slowly with time. This difference is referred to as the asymmetry potential, and its origin is uncertain, although it may be due to mechanical strains in the surfaces of the membrane set up during manufacture. It is subsumed in the calibration procedure and presents no problem.

CHAPTER 4 ELECTRODE EQUIVALENT CIRCUITRY

4.1 Introduction

The present chapter describes how the behavioural characteristics of an electrode can be broken down into an equivalent circuit of resistors and capacitors, which can be used to interpret their frequency response.

The ideal polarised electrode is defined and the disposition of the charge in the electrode and surrounding electrolyte in the form of a "double layer" is seen to be equivalent to a simple capacitor.

The complications concomitant with the transfer of charge across the electrode/electrolyte interface are then described, and finally, against this background, the equivalent circuitry of the glass electrode is discussed.

4.2 Ideal Polarised Electrode

An electrode which cannot transfer charge to (or accept charge from) a surrounding electrolyte irrespective of the potential which is applied to it from an outside source is termed an "ideal polarised electrode". Changes in potential are accompanied only by an accumulation or depletion of charge on the electrode, and another of equal but opposite sign in the electrolyte. The phases on either side of the metal / electrolyte interface behave therefore like the plates of a capacitor. The result is depicted simplistically in Fig 4.1

for cathodic conditions where the charges represent an excess of electrons in the metal and an excess of cations over anions in the electrolyte. The distribution of charge in this way is referred to as the "double layer".

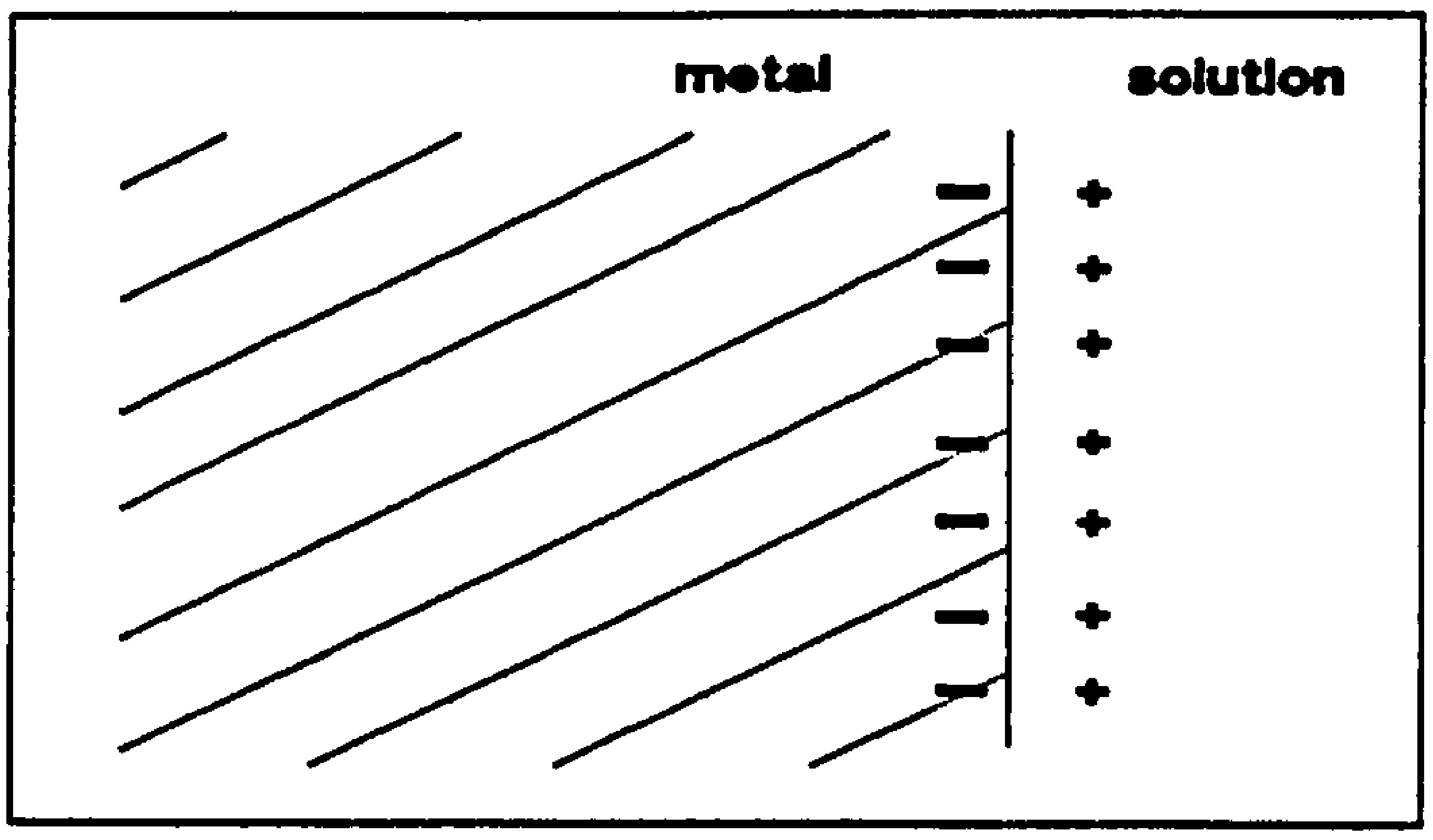


Fig 4.1 Distribution of excess charge on either side of a metal/electrolyte interface

As might be anticipated, however, the reality is somewhat more complicated than this, and the distribution of charge in the solution is thought to consist of two regions, which are shown in Fig 4.2.

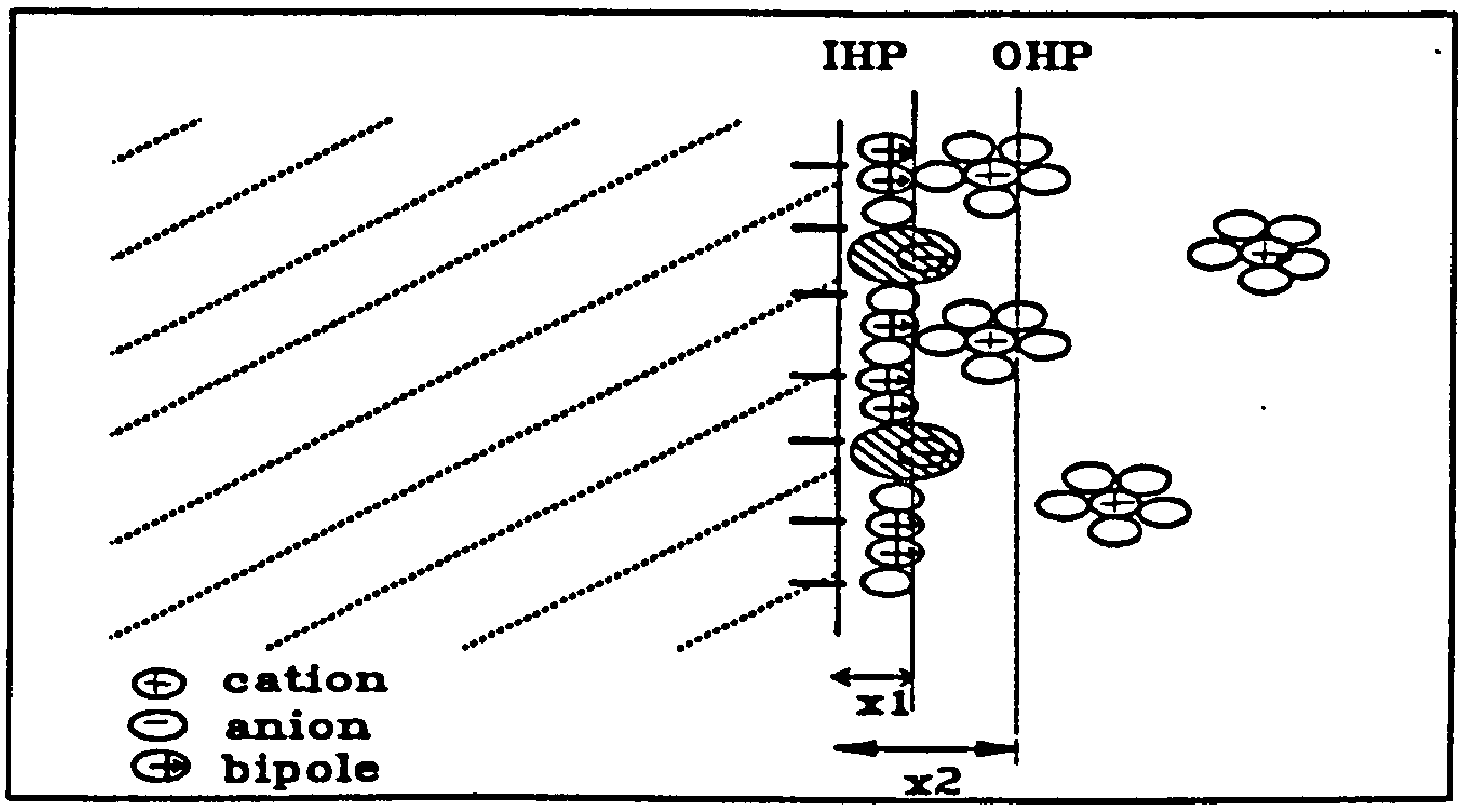


Fig 4.2 Compact and Diffuse layers in the Double Layer

One is termed the inner, compact or Helmholtz layer and the other the diffuse layer. The Helmholtz layer is immediately adjacent to the electrode and consists of solvent molecules, together with other molecular and ionic(usually anionic) species present in solution, tightly bound (i.e specifically adsorbed) to the electrode surface. The diffuse layer consists of solvated ions, which in the case of the cathode would be solvated cations. The solvating molecules limit the distance to which the ions can approach the electrode and therefore weaken the electrostatic forces of attraction. In consequence these ions are susceptible to thermal agitation and as a result occupy a region which extends over 300 Å away from the electrode surface. Referring to Fig 4.2 the distance x_1 is the distance from the electrode to the centre of the specifically adsorbed ions, and the plane at x_1 is termed the Helmholtz plane. The distance x_2 is the distance from the electrode to the solvated ions at their closest approach. The plane at x_2 is termed the outer Helmholtz plane. The solvent and other species specifically adsorbed are oriented as dipoles and contribute to the potential drop between solution and electrode.

From the behaviour described it is clear that the equivalent circuit of an ideal polarised electrode is simply a capacitor as shown in Fig 4.3., of value Cd, which is termed the "double-layer" capacity.

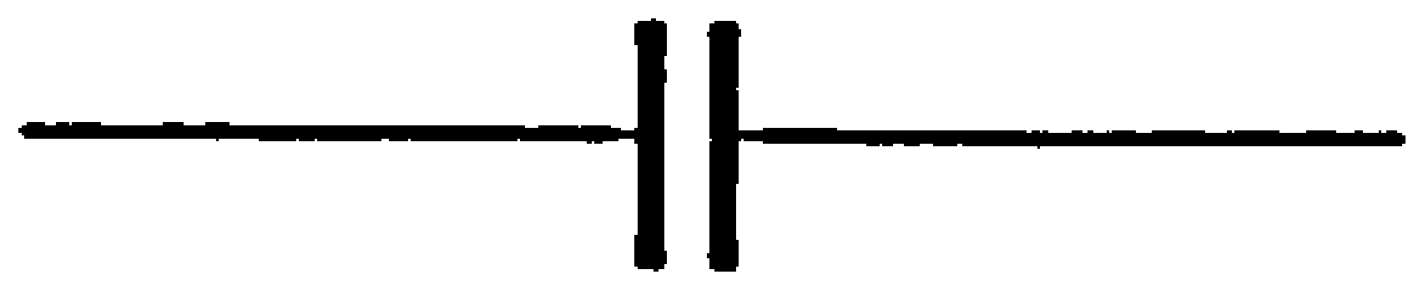


Fig 4.3. <u>Equivalent circuit of an ideal polarised electrode</u>

4.3 Non-Polarised Electrode

An electrode which allows the transfer of charge across the metal/electrolyte interface is termed a non-polarised electrode, and in practice all electrodes are of this type, although over a small range of potential differences some may closely approach the ideal polarised electrode. In terms of an equivalent circuit an electrode allowing charge transfer across the interface may be regarded as a "leaky capacitor" as shown in Fig 4.4, where c_d is the double layer capacity(21) and R_{ct} is the resistance to charge transfer. The current i is the total current being fed to the electrode at any instant, i_c is the portion which is consumed in charging the double layer and i_f is the Faradaic current resulting in oxidation or reduction of species at the electrode surface. The quantity E is the electrode potential.

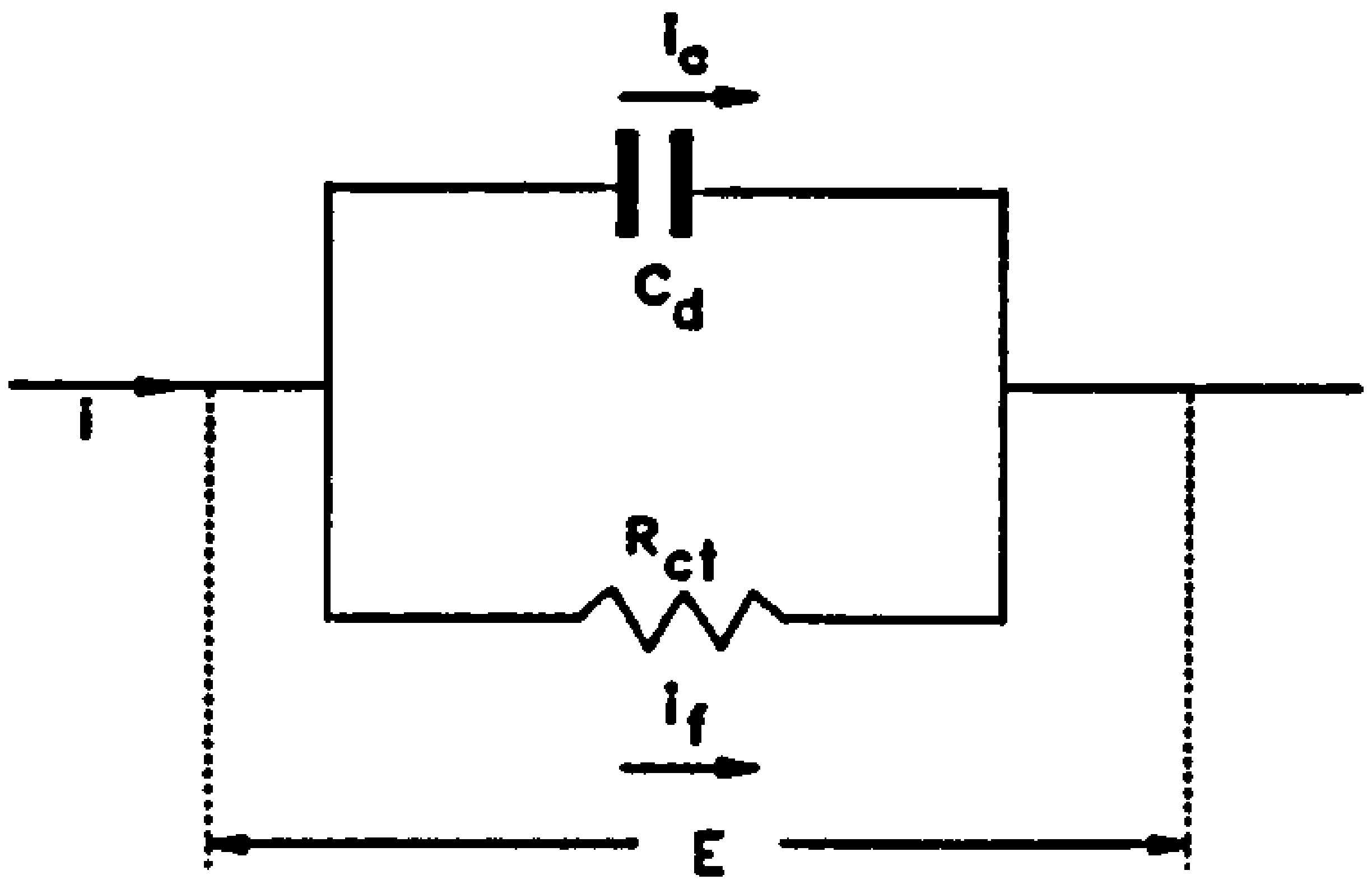


Fig 4.4 Elementary equivalent circuit for an electrode transferring charge

In practice, however, such a picture proves to be oversimplified for the following reasons. Firstly, the measurement of potential, E, is normally carried out using a luggin capillary sited near to, but not directly against, the electrode surface. The electrolyte gap existing between them introduces an ohmic resistance, RΩ, into the circuit which is in series with the metal/electrolyte surface. This modifies the equivalent circuit as shown in Fig 4.5.

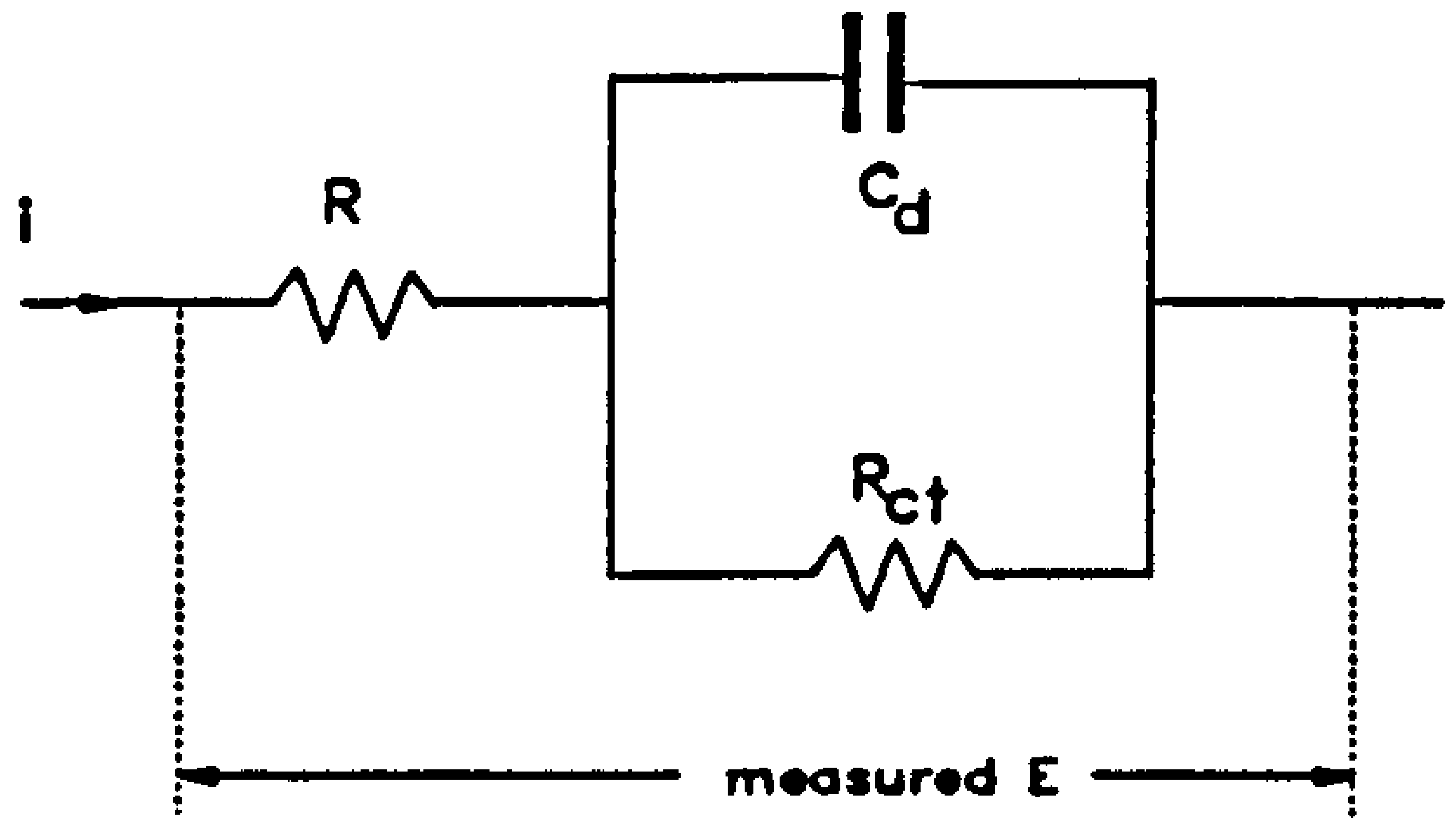


Fig 4.5 Elementary equivalent circuit for an electrode interface including the electrolyte ohmic resistance

Secondly the consumption and/or production of species as a consequence of charge transfer requires the transport of material to and from the electrolyte interphase adjacent to the electrode surface, and the resulting diffusional processes may give rise to further impedance. Since these processes are a direct consequence of charge transfer, it is anticipated that this impedance, Z_W, will be in series with R_{ct}. The final picture for the equivalent circuit therefore takes the form of Fig 4.6.

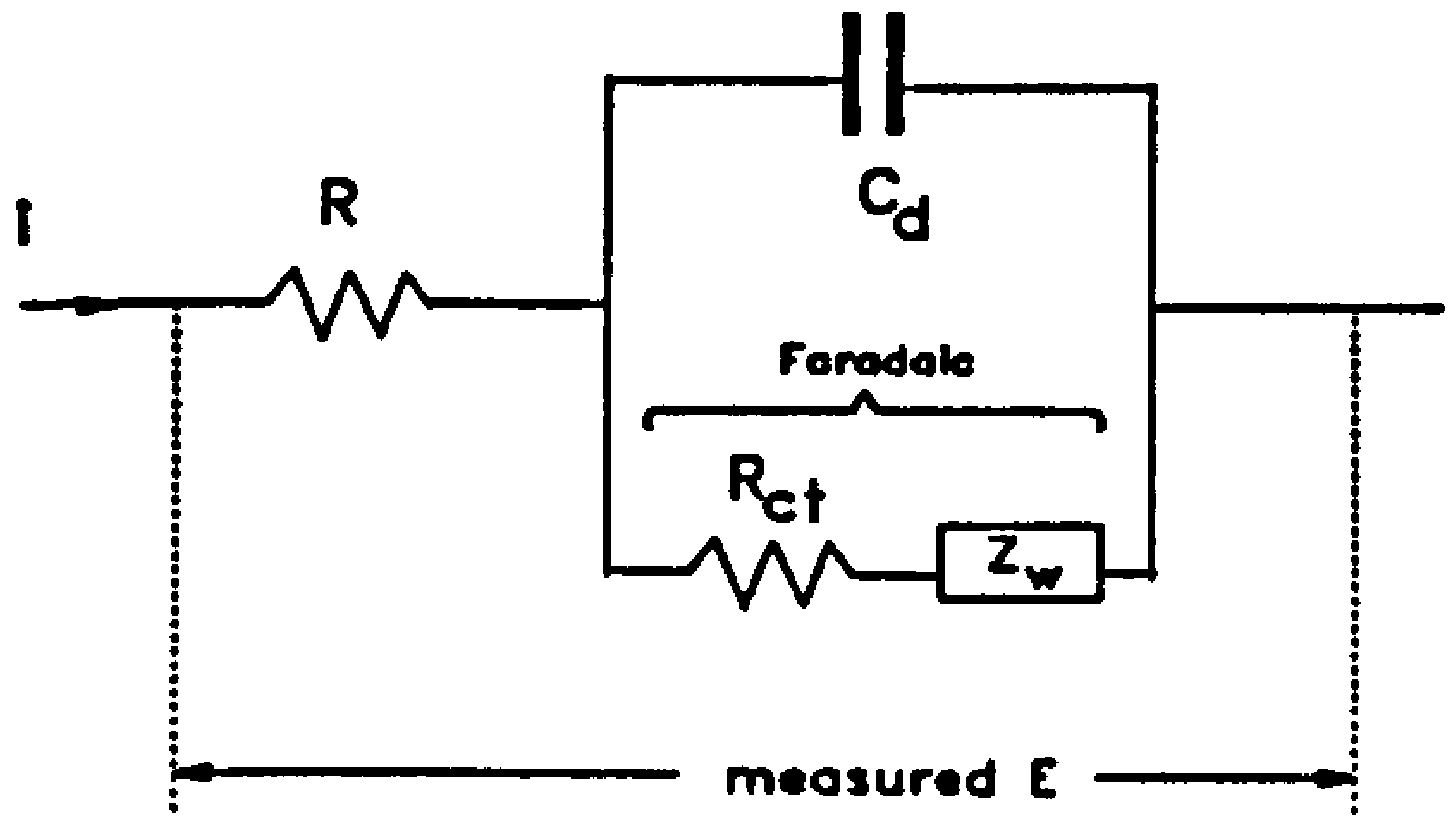


Fig 4.6 Equivalent circuit for an electrode interface

If Z_W is made up of a resistive and a capacitive component the Faradaic impedance of Fig 4.6 can be replaced by the circuit shown in Fig 4.7.

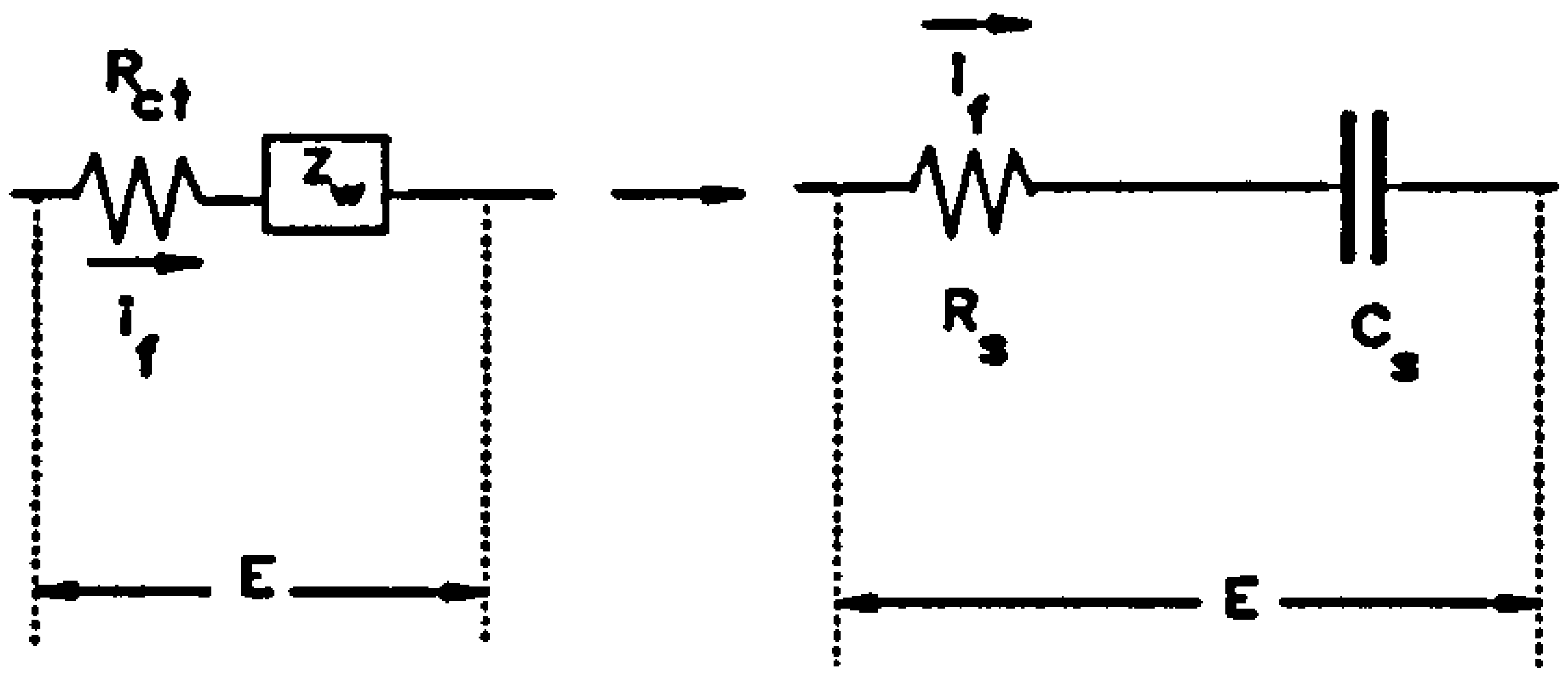


Fig 4.7 **Faradaic Impedance in terms of Resistive and Capacitive components**

The significance of R_S and C_S can be gauged by considering the response of the Faradaic impedance to an imposed small amplitude sinusoidal alternating current. The analysis presented is for an electrode which is perturbed about its equilibrium potential in an unstirred semi-infinite electrolyte after sufficient time has elapsed for a "steady state" to have been reached. Steady state in this context implies that variables relevant to the analysis have attained steady point values when averaged over a timespan which is large compared to the period of perturbation.

The voltage drop, E, across the Faradaic impedance will be given by:

$$E = i_f R_S + \frac{q}{C_S} \qquad - (1)$$

Differentiating with respect to time

$$\frac{dE}{dt} = R_S \frac{di_f}{dt} + \frac{i_f}{C_S} \qquad - (2)$$

Expressing the sinusoidal perturbation by

$$i_f = I \sin wt \qquad - (3)$$

equation (2) becomes

$$\frac{dE}{dt} = Rs\, I.w.\cos wt + \frac{I.\ \sin wt}{C_S} \qquad - (4)$$

However, if the Faradaic reaction is represented by the reduction

$$O + ne \longleftrightarrow R \qquad - (5)$$

the value of E can be functionally represented by

$$E = f(i_f, C^S{}_O, C^S{}_R) \qquad - (6)$$

where $C^S{}_O$ and $C^S{}_R$ are the concentrations of O and R at the electrode surface.

Hence

$$dE = \left[\frac{dE}{dC^S_o}\right]_{C^s_o, C^s_R} . d_{if} + \left[\frac{dE}{dC^S_o}\right]_{i_f, C^s_R} . dC^S_o + \left[\frac{dE}{dC^S_o}\right]_{i_f, C^s_o} . dC^S_R \qquad - (7)$$

or with respect to time,

$$\frac{dE}{dt} = \left[\frac{dE}{dC^S_o}\right]_{i_f, C^s_o} . \frac{d_{if}}{dt} + \left[\frac{dE}{dC^S_o}\right]_{i_f, C^s_o} . \frac{dC^S_o}{dt} + \left[\frac{dE}{dC^S_o}\right]_{i_f, C^s_o} . \frac{dC^S_R}{dt} \qquad - (8)$$

At constant c^s_O and c^s_R equation (6) is the equation of the polarisation curve, and it follows therefore that $(dE/di_f)_{c^s_O c^s_R}$ is equal to the charge transfer resistance, R_{ct}. Denoting the other partial differential coefficients by B_O and B_R, equation (8) becomes

$$\frac{dE}{dt} = R_{ct} \cdot \frac{di_f}{dt} + B_O \cdot \frac{dc^s_O}{dt} + B_R \cdot \frac{dc^s_R}{dt} \qquad - (9)$$

From (3),

$$\frac{di_f}{dt} = I\ w \cos wt \qquad - (10)$$

The quantities B_O and B_R are the rates at which E changes with the surface concentrations of O and R, respectively, and depend upon the specific kinetics of the reaction under consideration.

Expressions for the terms dc^s_O/dt and dc^s_R/dt are determined by solving the diffusion equations(24) in one dimension for semi-infinite space with initial conditions $c_O = c^b_O$ and $c_R = c^b_R$ for $x > 0$ and concentration at $x = 0$ equated to i_f for $t > 0$. The quantities c^b_O and c^b_R are the bulk concentrations of O and R respectively. The results obtained are as follows:

$$\frac{dc^s_O}{dt} = \frac{I}{nFA} \left[\frac{w}{2D_O}\right]^{\frac{1}{2}} [\sin wt + \cos wt] \qquad - (11)$$

$$\frac{dc^s_R}{dt} = \frac{-I}{nFA} \left[\frac{w}{2D_R}\right]^{\frac{1}{2}} [\sin wt + \cos wt] \qquad - (12)$$

Substitution from equations (10), (11), (12) into (9) gives

$$\frac{dE}{dt} = \left[R_{ct} + \frac{\sigma}{\sqrt{w}}\right] Iw\cos wt + I\sigma\sqrt{w}\sin wt \qquad - (13)$$

where

$$\sigma = \frac{1}{nFA\sqrt{2}} \cdot \left[\frac{B_O}{\sqrt{D_O}} - \frac{B_R}{\sqrt{D_R}}\right] \qquad - (14)$$

A comparison of equation (13) with (4) shows R_s and C_s to have the following significance

$$R_s = R_{ct} + \frac{\sigma}{\sqrt{w}} \qquad - (15)$$

$$C_s = \frac{1}{\sigma\sqrt{w}} \qquad - (16)$$

From (15) and (16) it is evident that Z_w is made up of a resistive component $\sigma/\sqrt{w}$ in series with a capacitive component $1/\sigma\sqrt{w}$, both of which are frequency dependant.

An important point which emerges from this analysis is that both, too, are dependant on σ which is intimately associated with the diffusivities of the reactive species i.e with the rates of mass transfer.

The quantity Z_w is referred to as the Warburg impedance(1) and in the present case will be given by

$$Z_w = (R_s - R_{ct}) - \frac{j}{wC_s}$$

or

$$Z_w = \frac{\sigma}{\sqrt{w}} - \frac{j\sigma}{\sqrt{w}} \qquad - (17)$$

The expression given by equation (17) is specific to the case which has been solved, but it is anticipated that a Warburg impedance will always be present and that it will be determined by the mass transfer processes obtaining.

Going back to the case in hand, however, it is seen from equation (17) that at high frequencies Z_W will become unimportant and the circuit of Fig 4.6 will reduce to that of Fig 4.5, with a frequency response similar to that of the semi-circle shown on page 17.

To determine how the system behaves at low frequencies the total impedance Z of the circuit in Fig 4.6 is first established using the standard method, and the expression is split into its real and imaginary components, noting, in doing so, that Z_W is given by equation (17).

The resulting expressions are

$$Z_{Re} = R\Omega + \frac{R_{Ct} + \sigma w^{-\frac{1}{2}}}{(C_d \sigma w^{\frac{1}{2}} + 1)^2 + w^2 C_d^2 (R_{Ct} + \sigma w^{-\frac{1}{2}})^2} \qquad - (18)$$

$$Z_{Im} = \frac{wC_d (R_{Ct} + \sigma w^{-\frac{1}{2}})^2 + \sigma w^{-\frac{1}{2}} (w^{\frac{1}{2}} C_d \sigma + 1)}{(C_d \sigma w^{\frac{1}{2}} + 1)^2 + w^2 C_d^2 (R_{Ct} + \sigma w^{-\frac{1}{2}})^2} \qquad - (19)$$

As w limits to zero the denominators of equations (18) and (19) limit to unity, and so they reduce to

$$Z_{Re} = R\Omega + R_{Ct} + \sigma/\sqrt{w} \qquad - (20)$$

$$Z_{Im} = R_{ct}^2 C_d . w + 2\sigma R_{ct} C_d \sqrt{w} + 2\sigma^2 C_d + \sigma/\sqrt{w} \qquad - (21)$$

As w → 0, however, the first two terms of equation (21) will also limit to zero, and so it reduces to:

$$Z_{Im} = 2\sigma^2 C_d + \sigma/\sqrt{w} \qquad - (22)$$

Eliminating the variable w between (20) and (22) gives an expression relating the complex plane variables Z_{Im} and Z_{Re} as follows

$$Z_{Im} = Z_{Re} - R - R_{ct} + 2\sigma^2 C_d$$

which is a straight line with intercept $(R + R_{ct} - 2\sigma^2 C_d)$ on the Real axis, and slope -1.

Thus combining the behaviour at high frequencies with that at low frequencies a frequency response of the form of Fig 4.8 emerges.

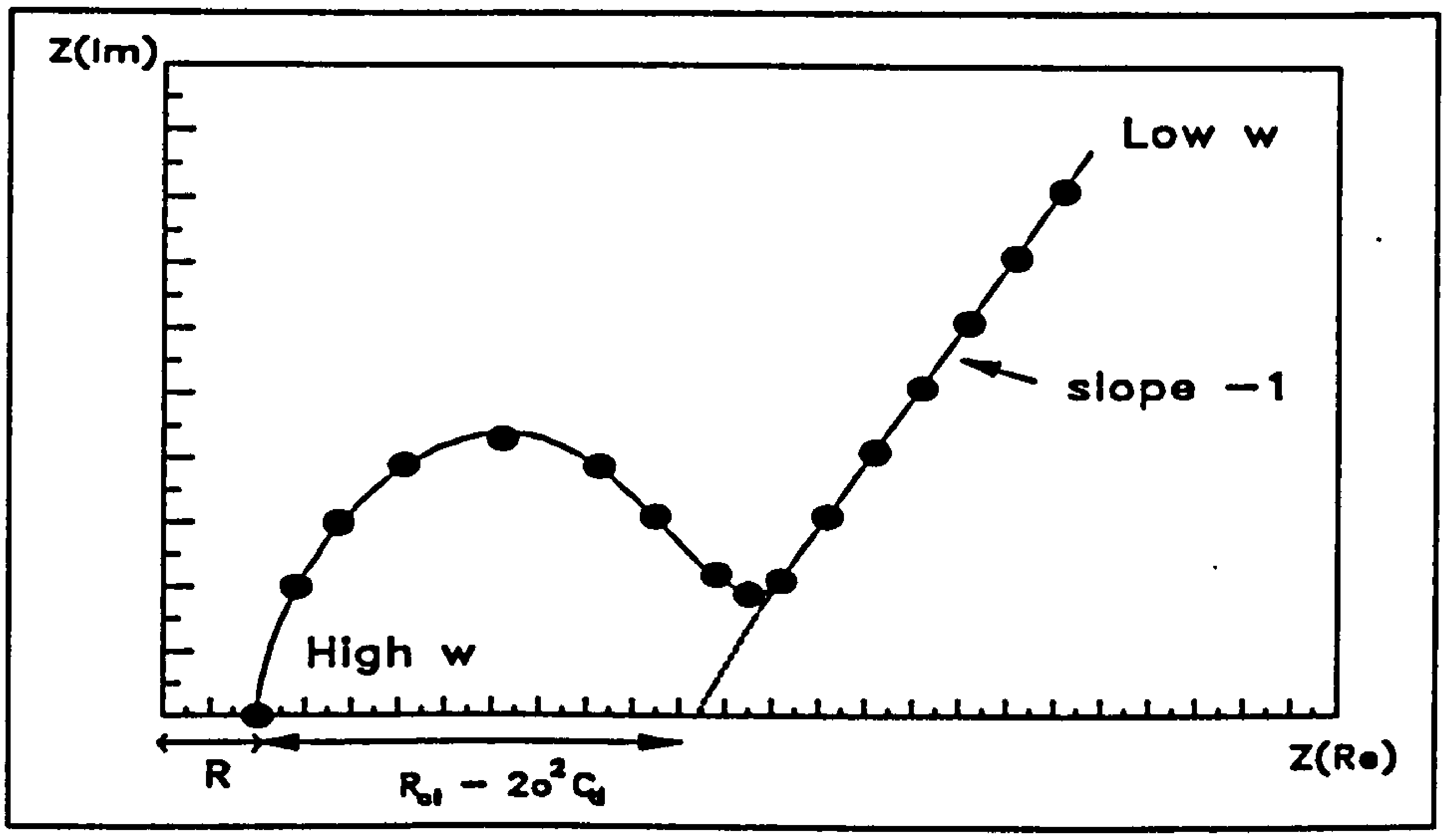


Fig 4.8 Form of the frequency response of a non-polarisable electrode

It is readily seen from equations (20) and (22) that the Warburg impedance term $\sigma/\sqrt{w}$ becomes more and more important as the frequency w falls, implying that diffusional processes are playing an increasingly important rôle.

Under D.C. conditions, when $w = 0$, the impedance rises to infinity and no current is passed. At first sight this may seem at odds with what is expected of the electrode, but it should be remembered that, in the special case for which the above analysis obtains, a steady current would correspond to a "steady state" in which all the depolariser had been converted and no further current could pass i.e no further transfer of reactive material could take place and the Warburg impedance would be infinite.

CHAPTER 5 Equivalent Circuit for a Glass Electrode(2,3,16,17)

As described previously in section 3.4 , a cross section from the external test solution through the membrane to the internal standard solution can be represented as follows, in Fig 5.1.

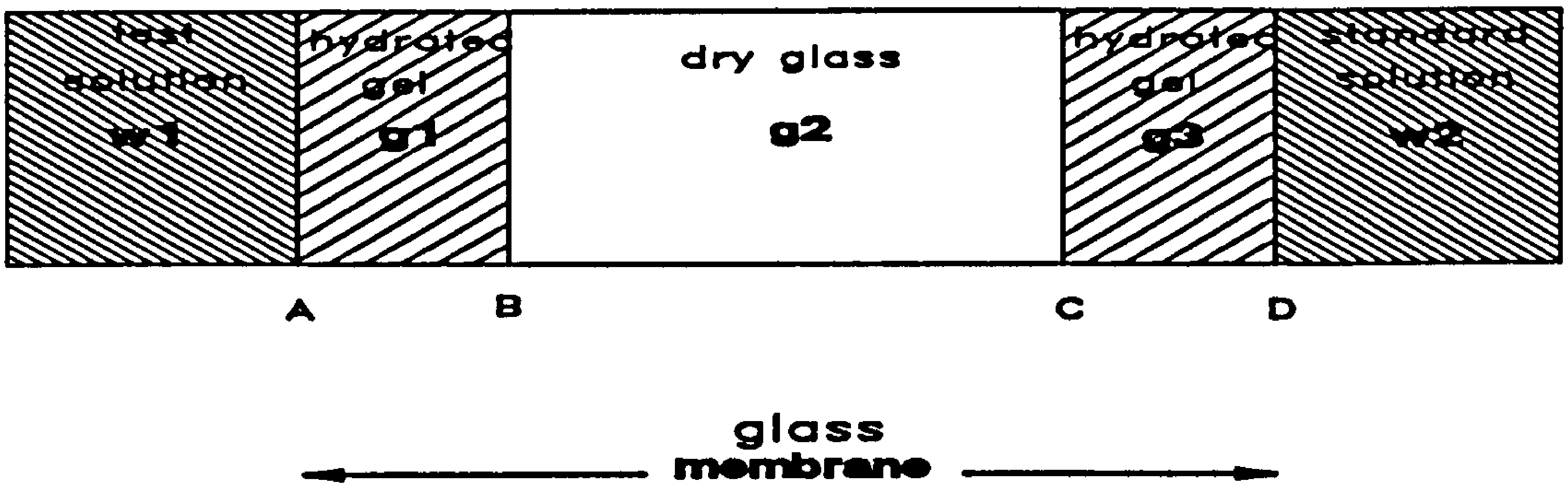


Fig 5.1 Section through a glass membrane

Each phase, as noted before in section 3.4, is at a different potential from those on either side of it as a result of either a Donnan type equilibrium or counter diffusion. Potential differences are the result of charge separation at the phase boundaries, and in consequence each boundary has the nature of a pseudo capacitance. In addition, although there is no oxidative or reductive process due to electron transfer, there will be a resistive component akin to "charge transfer resistance" as ions move across the boundaries A, B, C and D due to changes in solvation and lattice structure. As a result each phase boundary will have the electrical character of a parallel RC circuit, thus giving a combined equivalent circuit as in Fig 5.2.

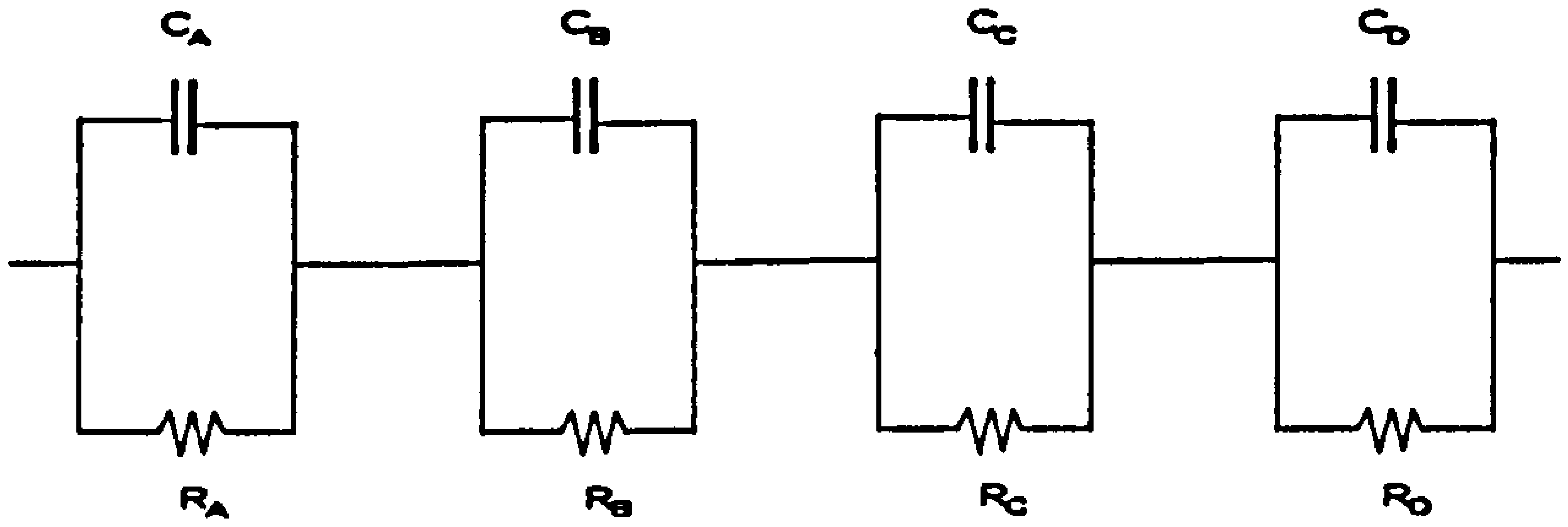


Fig 5.2 Equivalent circuit due to phase boundaries for a glass electrode

However, there are additional elements to take into consideration$^{(19)}$. Firstly, since the processes involved are those of ionic diffusion, there will be a Warburg impedance (W), and secondly each of the solid phases, g_1, g_2 and g_3, will have geometric capacitance C_G, due to their behaviour as dielectrics, and a bulk ohmic resistance, R_∞ . The equivalent circuit therefore expands to that shown in Fig 5.3.

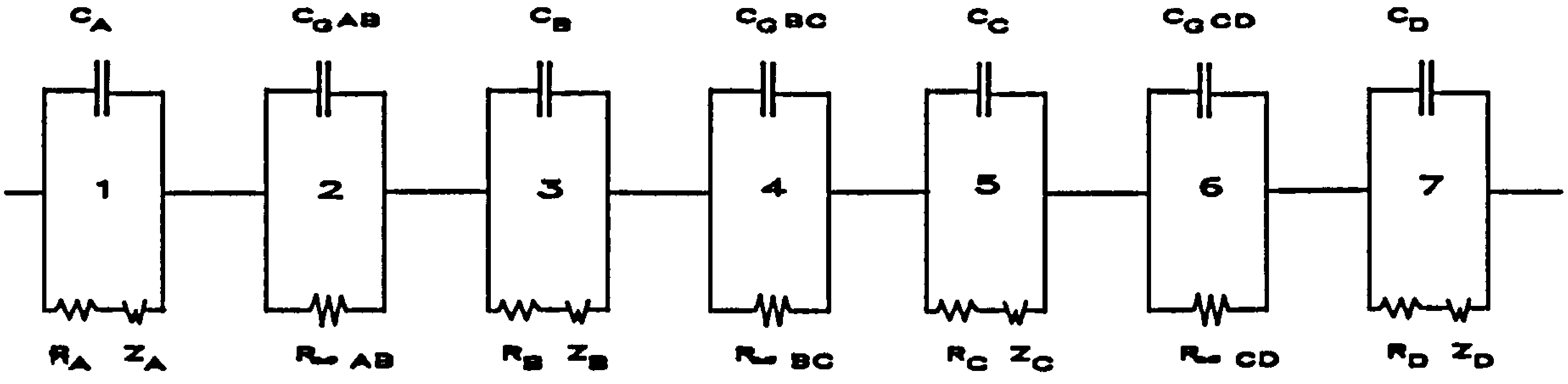


Fig 5.3 Equivalent circuit for a glass electrode

From Fig 5.3 it would appear that the complex plane frequency response curve might well consist of up to seven semicircles with a Warburg element appearing at low frequencies, presupposing of course that all the RC circuits have widely differing time constants. This would almost certainly not be the case, however, because those for RC circuits 1 and 7, 2 and 6, and 3 and 5 are for identical processes and would be roughly similar. At a maximum, therefore, only four semi-circles could be expected.

Buck and Krull$^{(2)}$ and Sandifer and Buck$^{(3)}$ have measured the impedance of Beckman E-2 and General Purpose glass electrodes over a frequency range 0.006 Hz to 100 kHz. Their combined results displayed only two semi-circles, slightly 'flattened', as shown in Fig 5.4 (a)

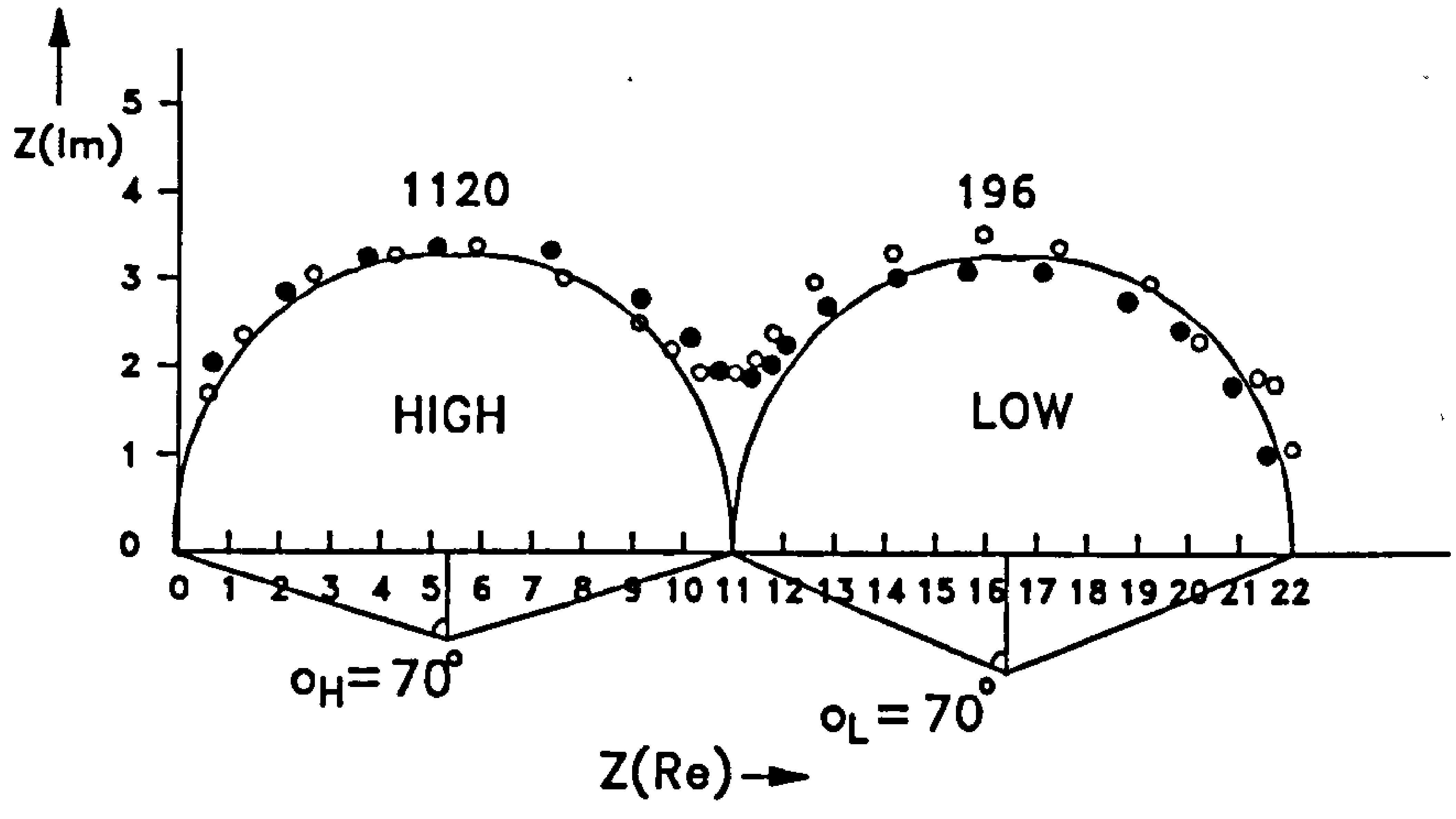


Fig 5.4 (a) Impedance of General Purpose Glass Electrode

- the value of w at peak Z_I is written above each semi-circle

Not surprisingly Sandifer and Buck[3] proposed an equivalent circuit comprising two parallel RC elements in series as in Fig 5.4(b).

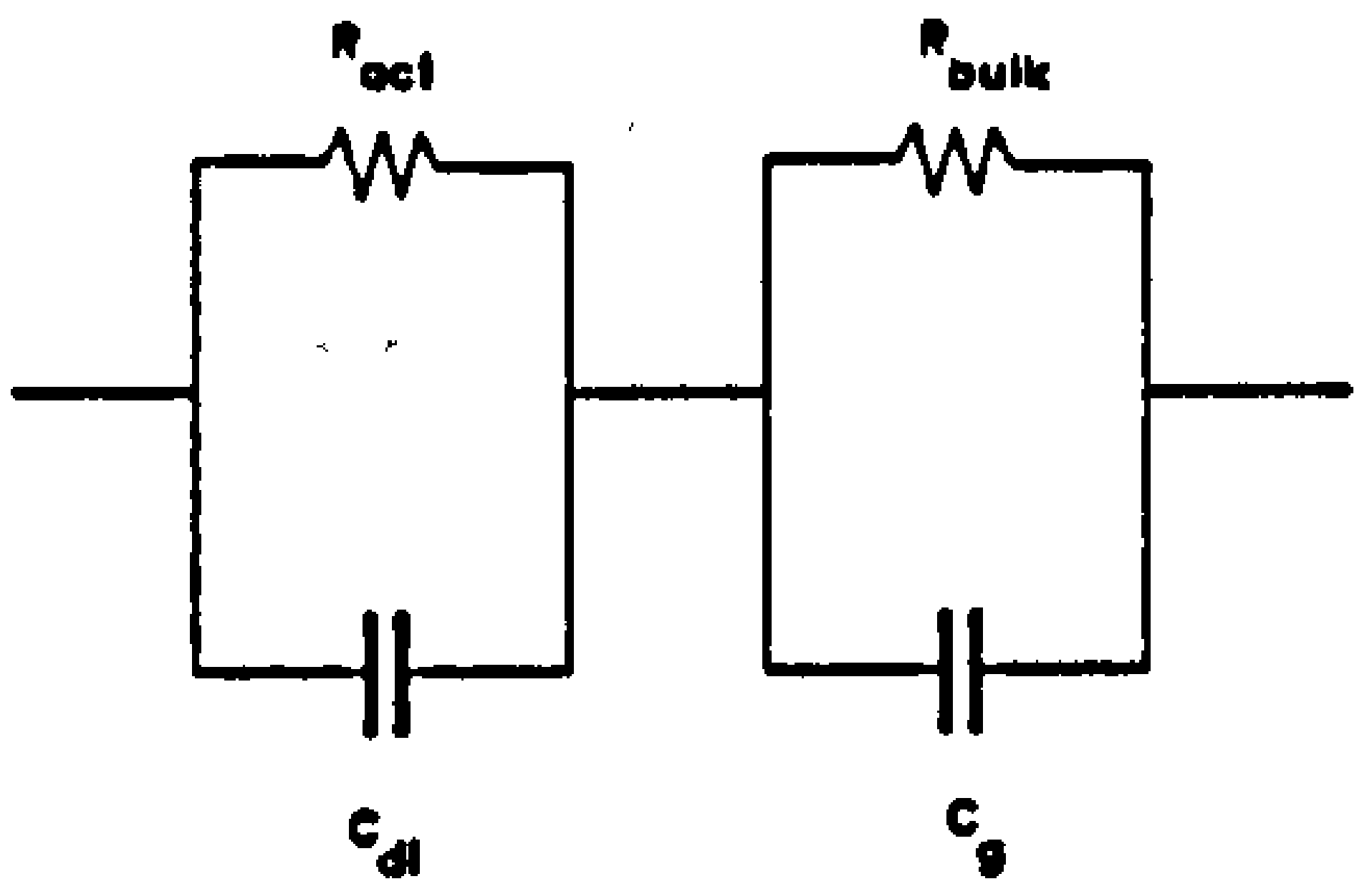


Fig 5.4 (b) <u>**Proposed parallel RC network**</u>

They associated the high frequency semi-circle in Fig 5.4(a) with the bulk resistance, R_{bulk}, and geometric capacitance, C_g, of the glass membrane, and the lower frequency semi-circle with the membrane surfaces where an activation resistance for ion exchange, R_{act}, combines with a comparatively large double layer capacitance, C_{dl}. In terms of Fig 5.1 this implies that conditions at the interfaces A and D and the bulk properties of the intervening solid are taken into consideration, but not the conditions at interfaces B and C. The results were correlated by an empirical fit to the equation

$$Z = \frac{R_{act}}{1 + (jwR_{act}C_{dl})^{\alpha_L}} + \frac{R_{bulk}}{1 + (jwR_{bulk}C_g)^{\alpha_H}} \qquad - (1)$$

This approach was necessitated by the flattened nature of the semi-circles, which are looked upon as segments of circles the centres of which are empirically located below the real axis as shown in Fig 5.4(a). The values of α_L and α_H are related to ϕ_L and ϕ_H by $\phi = (\pi/2)\alpha$.(See Figure 5.4(a))

Sandifer and Buck claimed to demonstrate that the low frequency semi-circle was linked to surface properties as opposed to the bulk properties of the glass by carrying out the following experiments. Firstly, they immersed a glass electrode in mercury so that the ion exchange process on the outer surface was effectively stifled. Under these conditions the low frequency semi-circle contracted but the high frequency semi-circle remained virtually unchanged. Secondly, by repeating the experiment after etching the glass surface with 10% HF, further contraction was observed. These results are summarised in Fig 5.5, where the evidence appears to be more convincing in the case of etching than in that of mercury immersion.

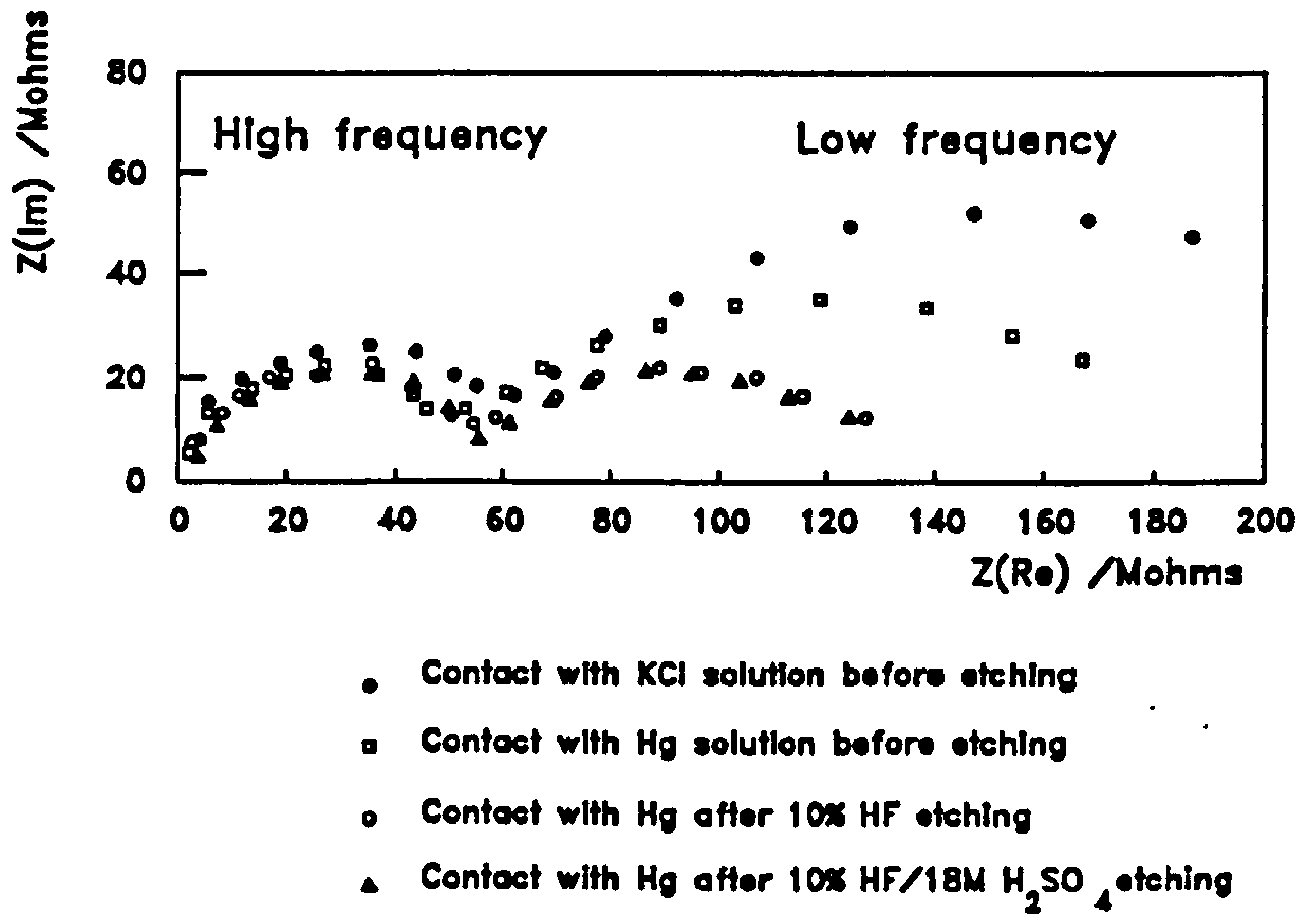


Fig 5.5 <u>Effect of etching and mercury blocking on the impedance of a glass membrane</u>

From the values of R_{act} which they obtained at three different temperatures, Sandifer and Buck determined the activation energies for the low frequency processes in both mercury and KCl solution and found that they were virtually the same in both cases. They concluded that mercury, contrary to their expectations had poor blocking properties and was apparently capable of providing an "ionic" contact with the glass.

The fact that only two semi-circles of a possible four were observed may indicate that some of the parallel RC circuits have a much lower impedance than others. Accepting the thesis of Sandifer and Buck that the two semicircles observed correspond to surface processes and membrane bulk properties, these circuits, referring to Fig 5.3, would be 2, 3, 5 and 6.

CHAPTER 6.0 EXPERIMENTAL EQUIPMENT

6.1 Introduction

Experimental measurements were made both to determine the frequency response of the glass electrodes supplied for the present studies and their Nernstian slopes. The latter were measured using conventional techniques which need no further description but the frequency response measurements required both equipment and procedural development and these will be described in some detail.

6.2 Cell and Electrode Assembly

The equipment was designed and built as shown in Fig 6.1 and 6.1(a). Essentially it comprised a glass vessel seated on a metal platform and closed by a polypropylene lid which was pierced by five holes, three of which received, respectively, the glass electrode , the saturated calomel electrode and a stirring leg and the remaining two allowed the addition of reagents from a burette and the venting of the air space to the atmosphere.

The stirring leg could be connected either to a piston and cylinder to provide pulse stirring or to a nitrogen gas cylinder for bubble stirring and in some cases it was removed and replaced by a rotary mechanical stirrer.

When the glass vessel was in place the equipment was electrically screened by raising a cylindrical metal curtain. This curtain was held in place in the raised position by pins attached to the inside of the base of the curtain which mated in bayonet fashion with slots in the mild steel skirt running around the metal platform . The screening was completed by a metal skin attached to the upper surface of the polypropylene lid and by metal sleeves placed around the protruding parts of the glass and calomel electrodes. When in place all the component parts of the screen were wired together and one of them was connected to earth.

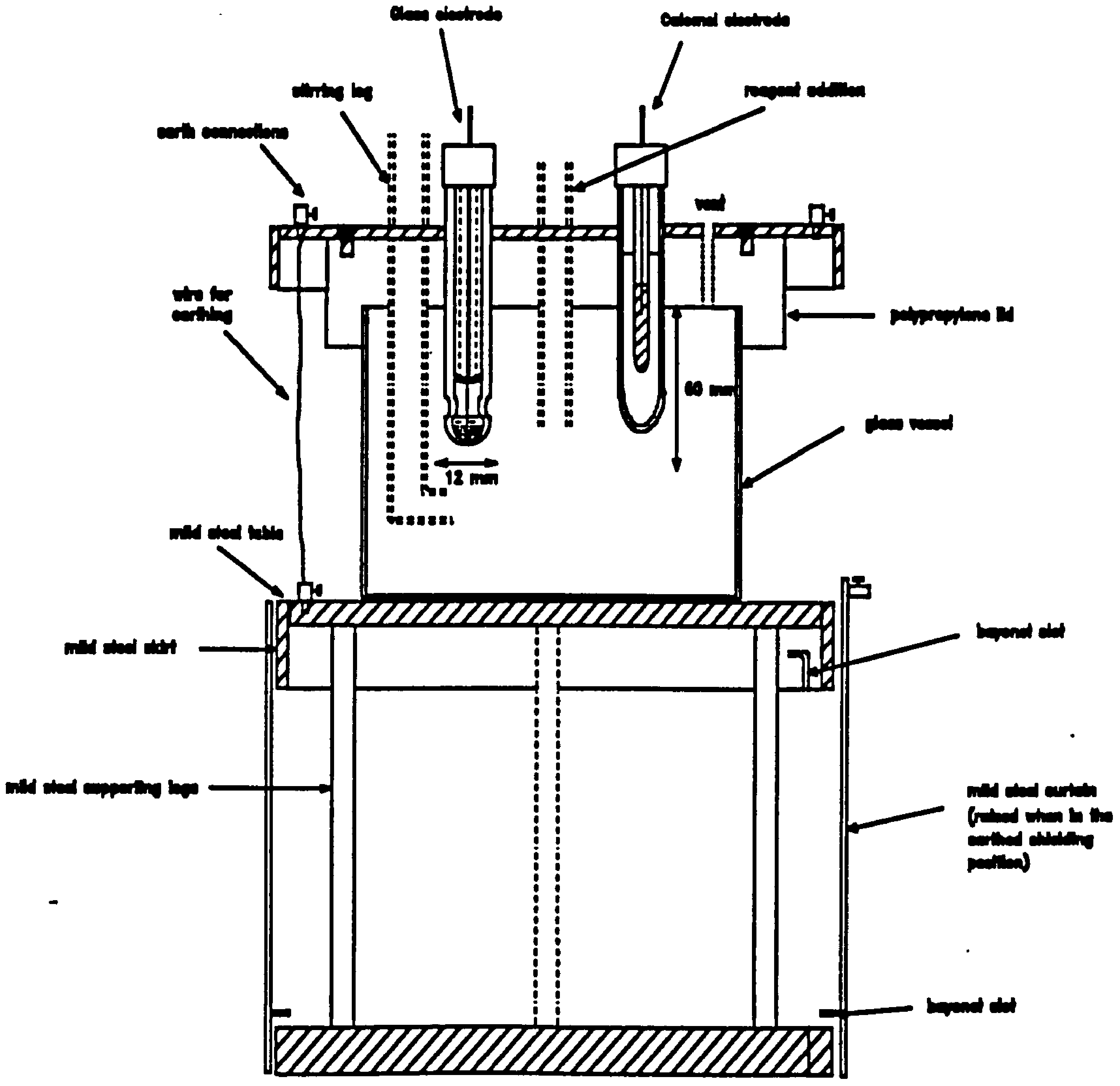


Figure 6.1 <u>Experimental equipment</u>

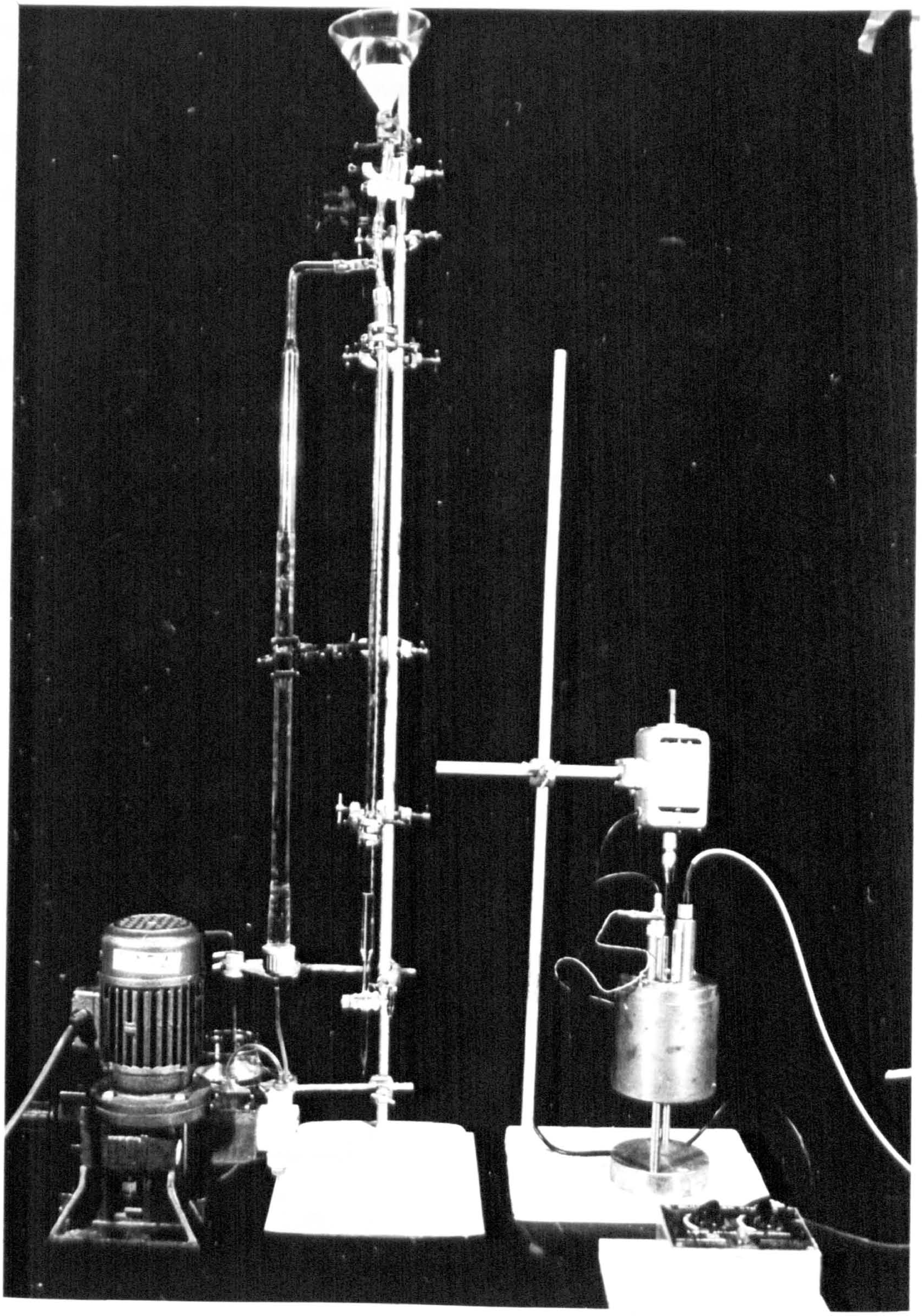


Figure 6.1(a) Experimental equipment

This design was eventually chosen as it allowed both measurements and reagent addition to be made without the inconvenience of disturbing the equipment, which in earlier designs had been found to introduce inaccuracies in the observations.

The capacity of the glass vessel was approximately 0.5 dm^3. Other salient dimensions are provided in Fig 6.1.

Reagents were added to the contents of the glass vessel, when required, by means of a displacement method using a micrometering pump and water. The system is shown in Fig 6.2,

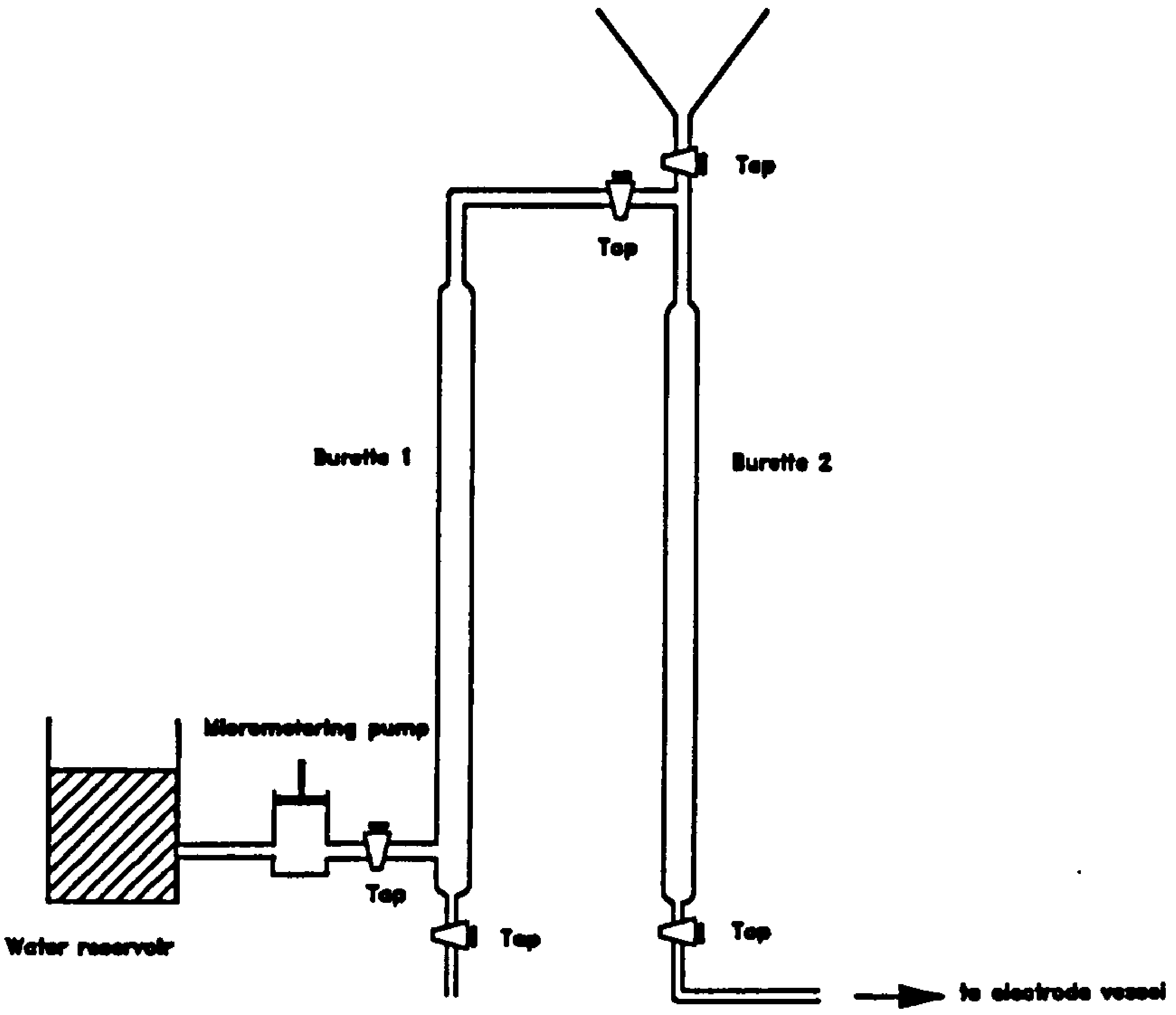


Figure 6.2 System for Reagant Addition

and comprised two burettes, 1 and 2, with their upper ends connected by polythene tubing. A side arm at the lower end of burette 1 was connected to the delivery port of the metering pump, the inlet port of which was connected to a water reservoir. When necessary burette 1 could be emptied by means of the nozzle at its lower extremity.

Burette 2 was fitted with a T-piece at its upper end, the stem of which made the connection with burette 1 and the remaining arm a connection with a funnel by means of which it could be charged with the required reagent. The nozzle at the lower end of the burette was attached to a length of small bore polythene tubing which dipped into the electrode vessel through one of the orifices noted previously. By opening and closing appropriate taps and starting the pump water was transferred to burette 1 and reagent was displaced from burette 2 into the vessel. By this device the pump was isolated from the reagent and corrosion problems thereby avoided .

6.3 ELECTRODES

(a) Glass Electrode

The glass electrodes used were supplied by Polymetron AG, CH-8617 Monchaltorf, Switzerland, of types distinguished by the proprietary numbers 8400B and 8404S. They were of conventional form as shown in Figure 6.3, but of robust construction suitable for commercial application.

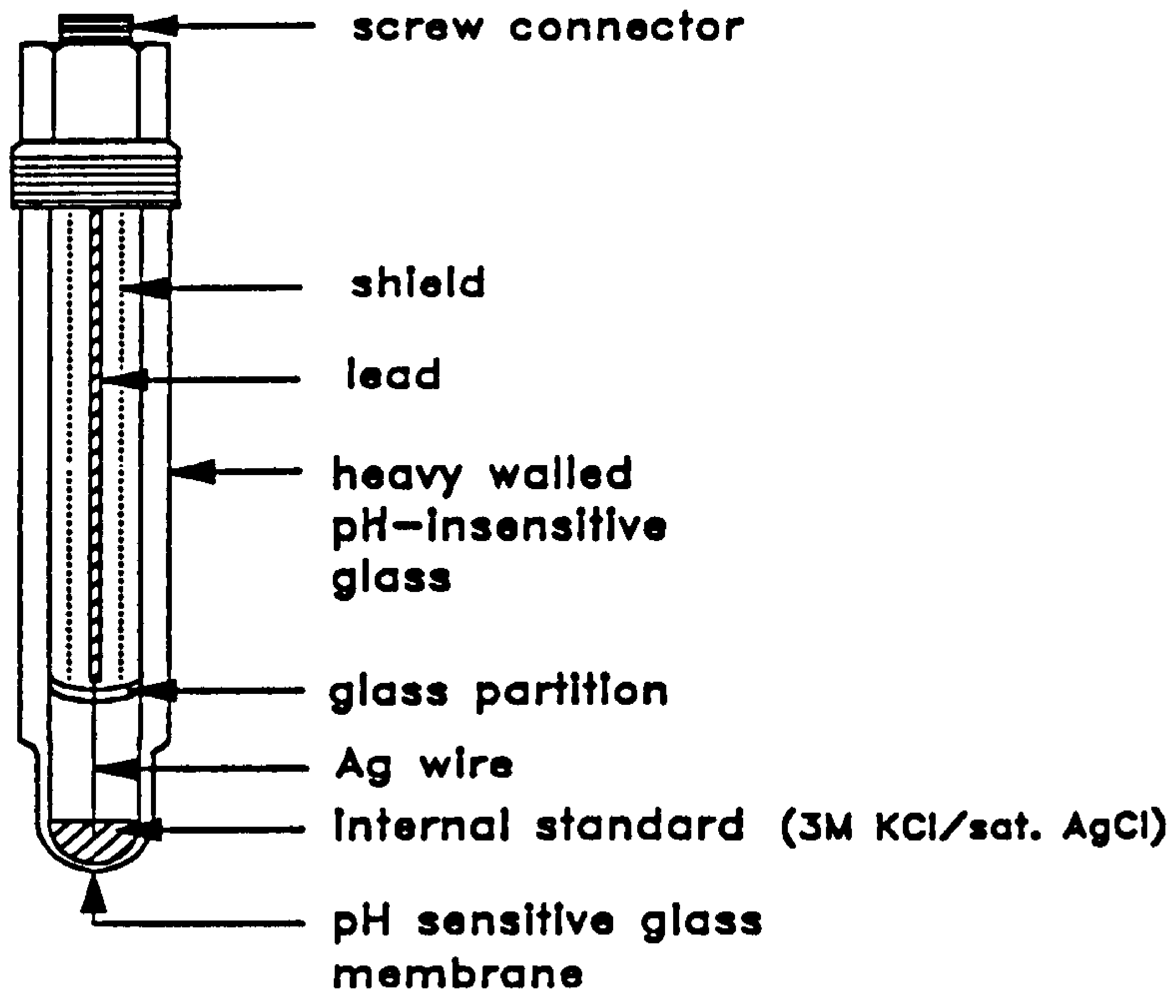


Figure 6.3 Glass Electrode

The internal standard comprised a solution of 3M KCl, saturated with AgCl. Each electrode was closed by a plastic cap which was threaded for "on-line" fitting and carried a proprietary screw connector for making electrical connection to an external circuit.

Although the appearance of the electrodes was very similar the specifications were somewhat different, due mainly to the difference in composition and thickness of the glass membranes. In particular the D.C. impedance varied from 150 to 600Mohms in the case of the type 8400B electrodes to around 300Mohms with the type 8404S electrode. The use of two types of electrode gave a broader base to the investigations.

(b) Reference Electrode

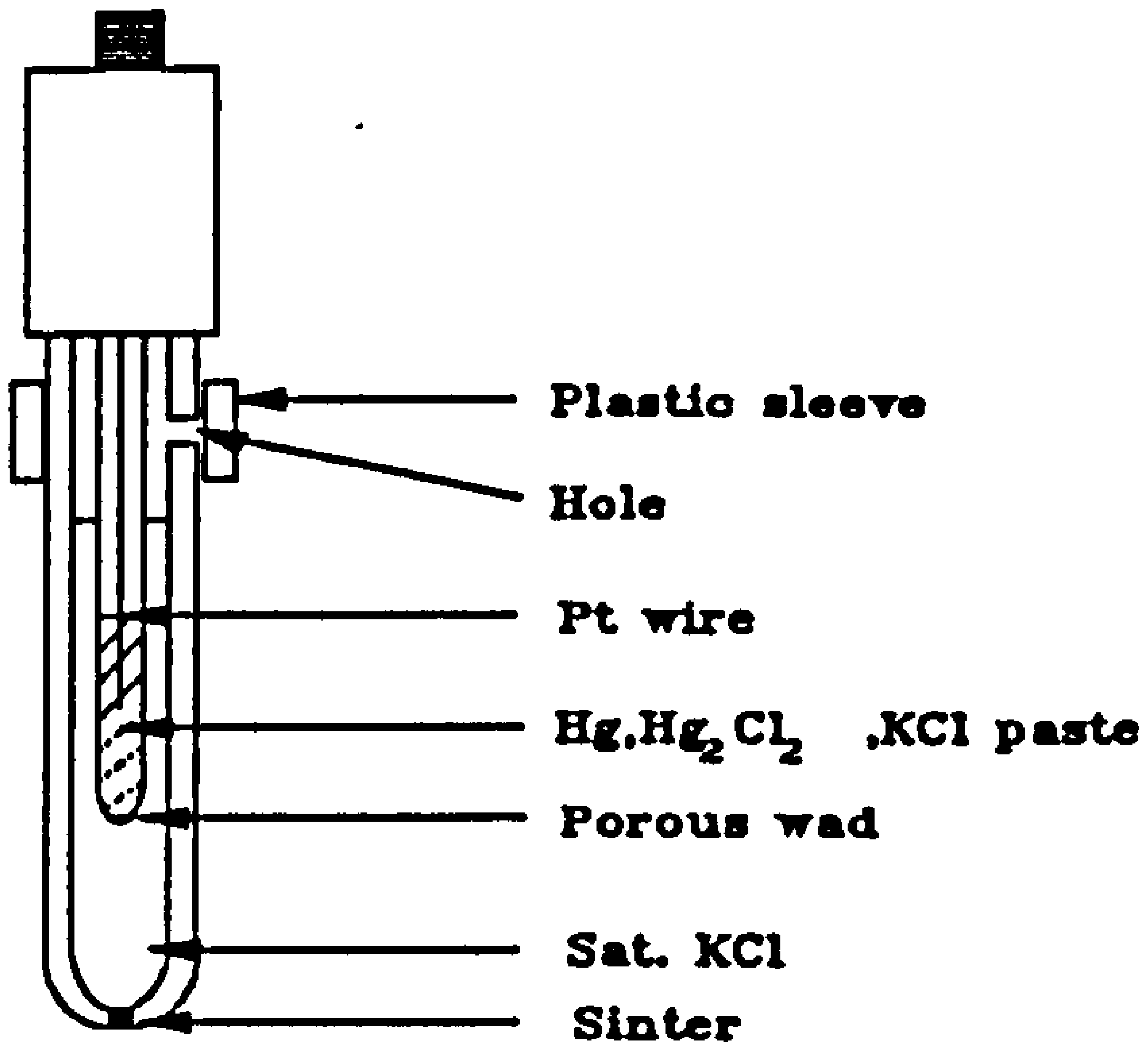


Figure 6.4 Reference Electrode

The reference was a commercial, but conventional, saturated calomel electrode. It basically comprised a small bore glass tube located concentrically in a wider bore tube. The small bore tube contained a paste of $Hg/Hg_2Cl_2/KCl$ and was closed at the bottom by a porous wad. A Pt wire dipped into the paste and was connected by a wire to a metal terminal attached to a plastic cap which sealed the upper end of both tubes. The bottom of the outer tube was closed by a sinter, which retained the saturated KCl solution while allowing it to form a current conducting liquid junction with an electrolyte outside the tube. A hole in the upper half of the outer tube allowed the KCl solution to be replenished when necessary. When the electrode was in use this hole was closed by a plastic sleeve. Electrical contact to an external circuit was made via the terminal attached to the cap.

The electrode potential of the reference with respect to the hydrogen electrode was +244mV (25°C), and it could be used reliably in the range 0 - 60°C.

6.4 Instrumentation and Circuitry

The cell comprising the glass and reference electrodes was connected to the instrumentation and circuitry shown in Fig 6.5. which was designed to determine both the frequency response of the glass electrode and the open circuit potential developed between the electrodes.

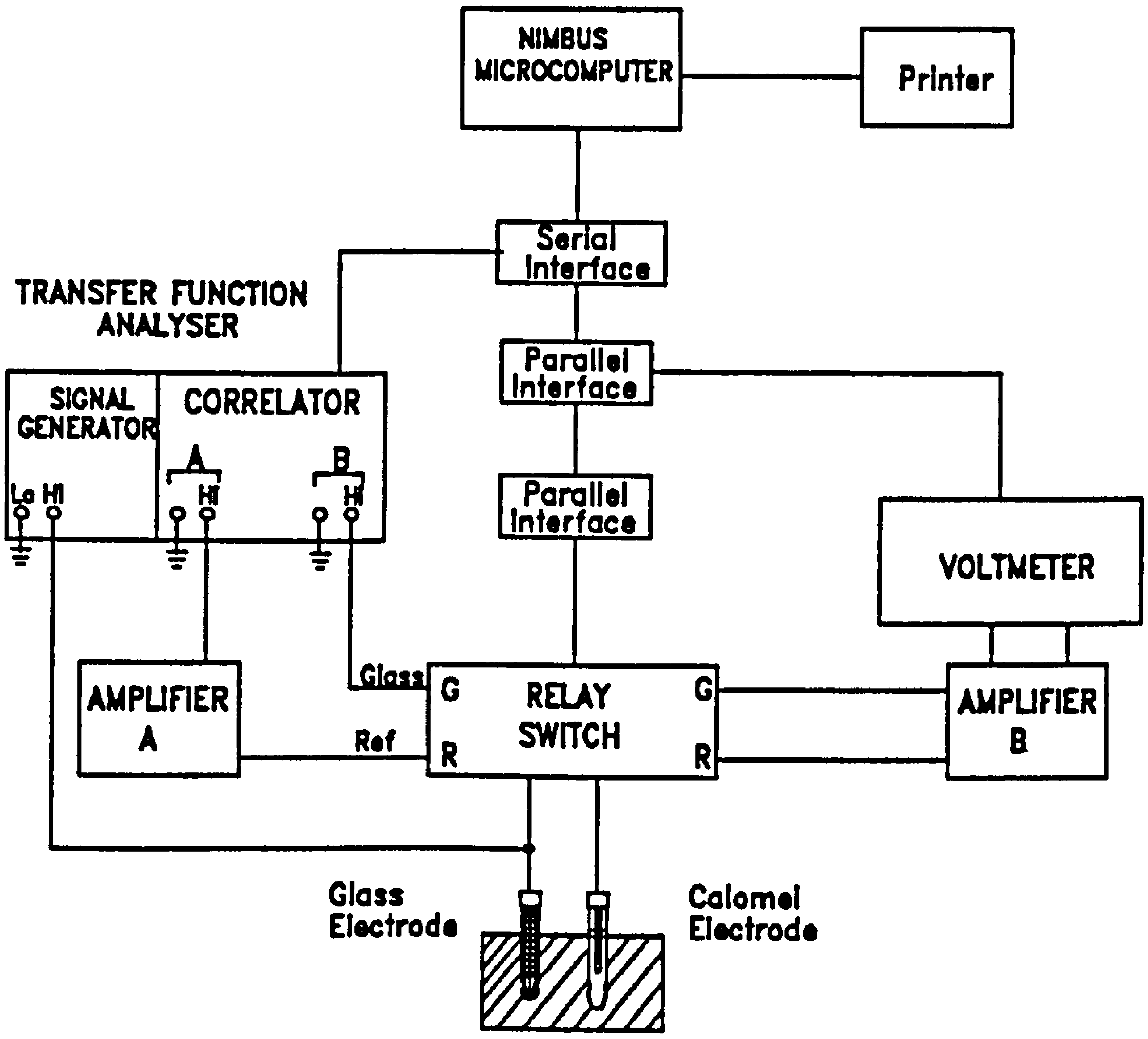


Figure 6.5 Instrumentation and Circuitry

Software was developed so that the system could be driven by an RM Nimbus microcomputer, which was linked via serial and parallel interfaces to a Transfer Function Analyser, a relay switch and a voltmeter.

At the request of the microcomputer the relay switch linked the cell either to the transfer function analyser via amplifier A for frequency response measurements or to the voltmeter via amplifier B for D.C potential measurements.
In the frequency response mode the calomel electrode was earthed and an A.C voltage of a few hundred millivolts amplitude was applied to the glass electrode from the signal generator. The resulting current was passed through amplifier A, which was a current to voltage converter, and the output from the amplifier was fed to the "hi" terminal of the correlator's A input. The potential on the glass electrode was fed to the "hi" terminal of the correlator's B input. The two inputs were processed and then scaled, as described later, to give the frequency response in terms of real and imaginary components, or im terms of the resultant and phase angle .

Fig 6.5 shows the experimental equipment in its final form, which was the end product of numerous modifications made in the light of experience as the work progressed. Each item in the circuit will now be taken in turn.

6.4.1 TRANSFER FUNCTION ANALYSER (TFA)

The TFA was an EMI instrument type SE 2450/00 and comprised a correlator and a signal generator with the following specifications.

FREQUENCY RANGE : 0.0001Hz - 9999Hz
RESOLUTION : 1:9999
AMPLITUDE RANGE : 1mV - 9.99 V r.m.s or peak
WAVESHAPES : a) Sinewave
b) Squarewave
c) Triangular Wave
OUTPUT IMPEDANCE : 0.5 ohm

Control of the TFA is simplified by the provision of a keyboard, CRT display and RS232C link enabling remote signalling to/from the analyser. Digital techniques are used throughout the instrument.

A sine, square or triangular waveform can be selected as the input to excite the system under test, and this together with the resulting output from the system are fed to the correlator(terminal sets A and B in Fig 6.5) which uses the data to compute the impedance, the phase angle and the real and imaginary components of the impedance. The correlation technique employed has the property of integrating out any noise that may be present in the system.

Correlation technique:

The correlator operates on the input signal to the system under test and the resulting output, and for the purposes of this discussion these will be referred to as the "generator output" and "correlator input" respectively.

The correlation technique primarily resolves the signals it receives into real and imaginary components or parts, and then uses this information for deriving the amplitude, phase angle, etc, as required by the user.

It can be shown that

$$Xa = \frac{1}{nT} \int Vmax \sin(wt + \phi) \sin wt \, dt$$

$$Ya = \frac{1}{nT} \int Vmax \sin(wt + \phi) \cos wt \, dt \qquad - (6.1)$$

where

Xa = real part in volts

Ya = imaginary part in volts

Vmax = peak of correlator input signal

ϕ = phase shift of correlator input signal relative to generator output

t = time

n = no of cycles over which the integration is carried out

T = period of the a.c signal

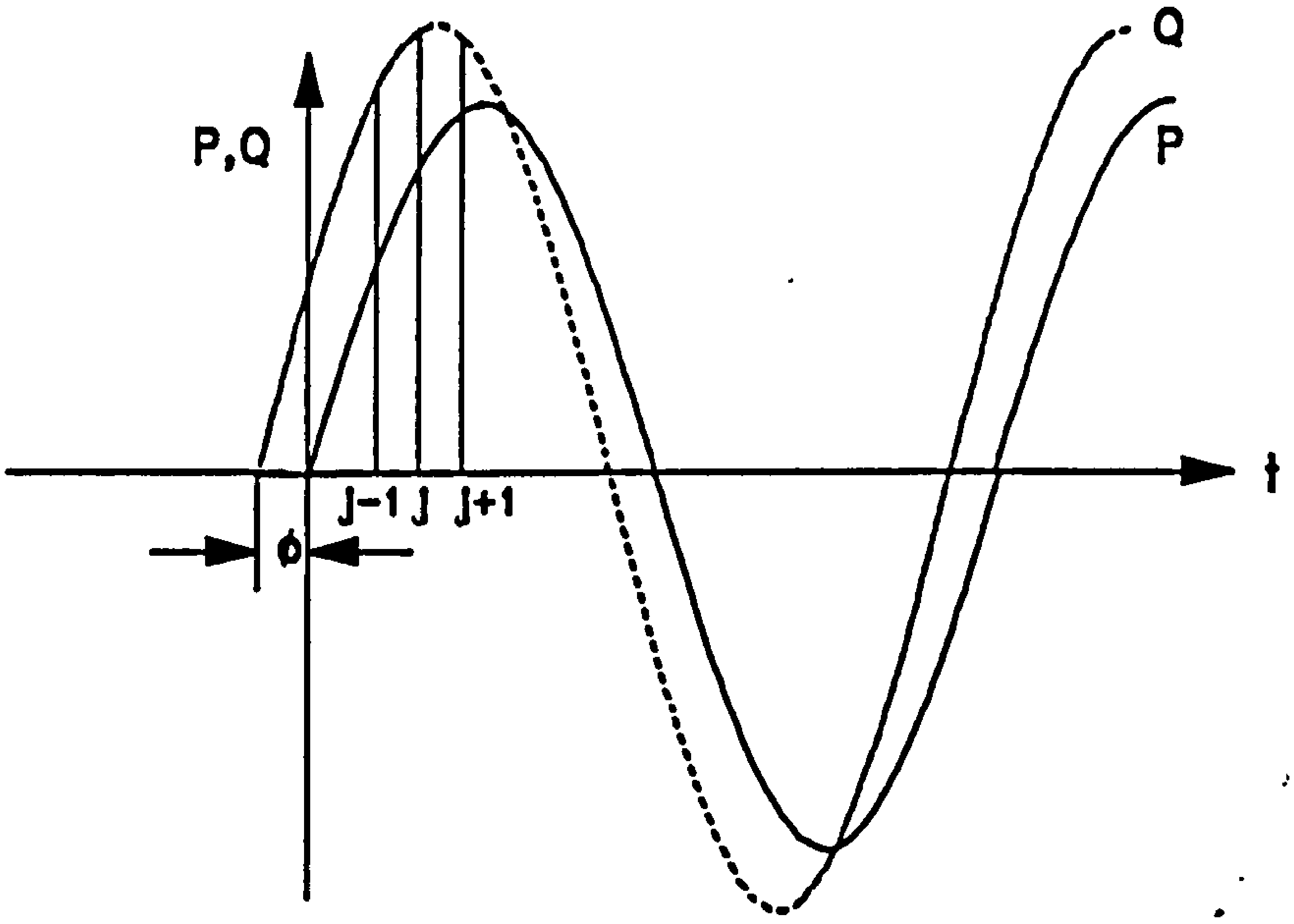
The correlator input is clearly the voltage output from the current to voltage converter and in order to convert X_A and Y_A

into impedances the inclusion of a scaling factor is necessary which will be returned to later. In finite difference terms the above equation become

$$Xa = \frac{1}{nT} \Sigma \quad Vmax \sin(wt_j + \phi) \sin wt_j$$

$$Ya = \frac{1}{nT} \Sigma \quad Vmax \sin(wt_j + \phi) \cos wt_j \qquad - (6.2)$$

The quantity Vmax $\sin(wt_j + \phi)$ is the value of the correlator input at time t_j, and $\sin wt_j$ is the normalised value of the generator output. To ensure that the summations provide an accurate evaluation of the integrations it was necessary to select a fast rate of sampling, 48kHz. This meant that in order to carry out the above summations it was necessary to compute both Vmax $\sin(wt_j + \phi)$.$\sin wt_j$ and Vmax $\sin(wt_j + \phi)$.$\cos wt_j$ and add them to the sum of the previous results within a time interval $t_{j+1} - t_j$ of roughly 0.02ms. This is was too fast for the software to handle and therefore computations were performed by hardware, the results of 256 samples (a block) being added together, as illustrated in Fig 6.6, and stored in a register. The software then retrieved the result of this block and added it to the sum of the previous block. When the required number of blocks had accumulated, the software calculated the real and imaginary parts by dividing the results by a constant.



Normalised generator output $P = \sin wt$

Correlator Input $Q = V_{max} \sin(wt + \phi)$

$$\text{Real part} = \sum_{j=1}^{256} P(t_j).Q(t_j) \text{ with } t_{j+1} - t_j = 0.02\text{ms}$$

Figure 6.6 Hardware Sampling and Computation

In cases where the number of samples required was not directly divisible by a block, it was necessary to select part of the block. This was computed by the software at the outset of the run and loaded into the register which controlled the number of samples to be performed in the incomplete block .

6.4.2 VOLTMETER

The voltmeter was a Thurlby type 1905 intelligent multimeter with the following specifications

- Voltage range - 1microV to 1100V
- 5.5 digit manual ranging
- Keyboard programmable and datalogging facility

Voltages between 1microV and 2.1V could be measured at an input impedance in excess of 1000Mohms thus reducing loading errors occasioned by very high impedance circuitry.

6.4.3 Amplifier A

Since the correlator of the TFA only accepted signals in the form of potential differences it was necessary to convert cell current values to this form before they could be sampled and processed. Since these currents were in the order of nanoamps and the signal for the correlator was to be in the order of mV's, the simple method of placing a resistor in the path of the current was not feasible because its magnitude would need to be in the region of 100 MΩ, which is comparable to that of the electrode. The necessary conversion was therefore carried out using a current to voltage converter designed using the good offices of the Department of Electrical and Electronic Engineering, the University of Newcastle upon Tyne, who were also responsibile for Amplifier B and the Relay Switch.

The circuit diagram for Amplifier A is shown in Fig 6.7. It consists of a Radiospares OPA111 current-to-voltage converter

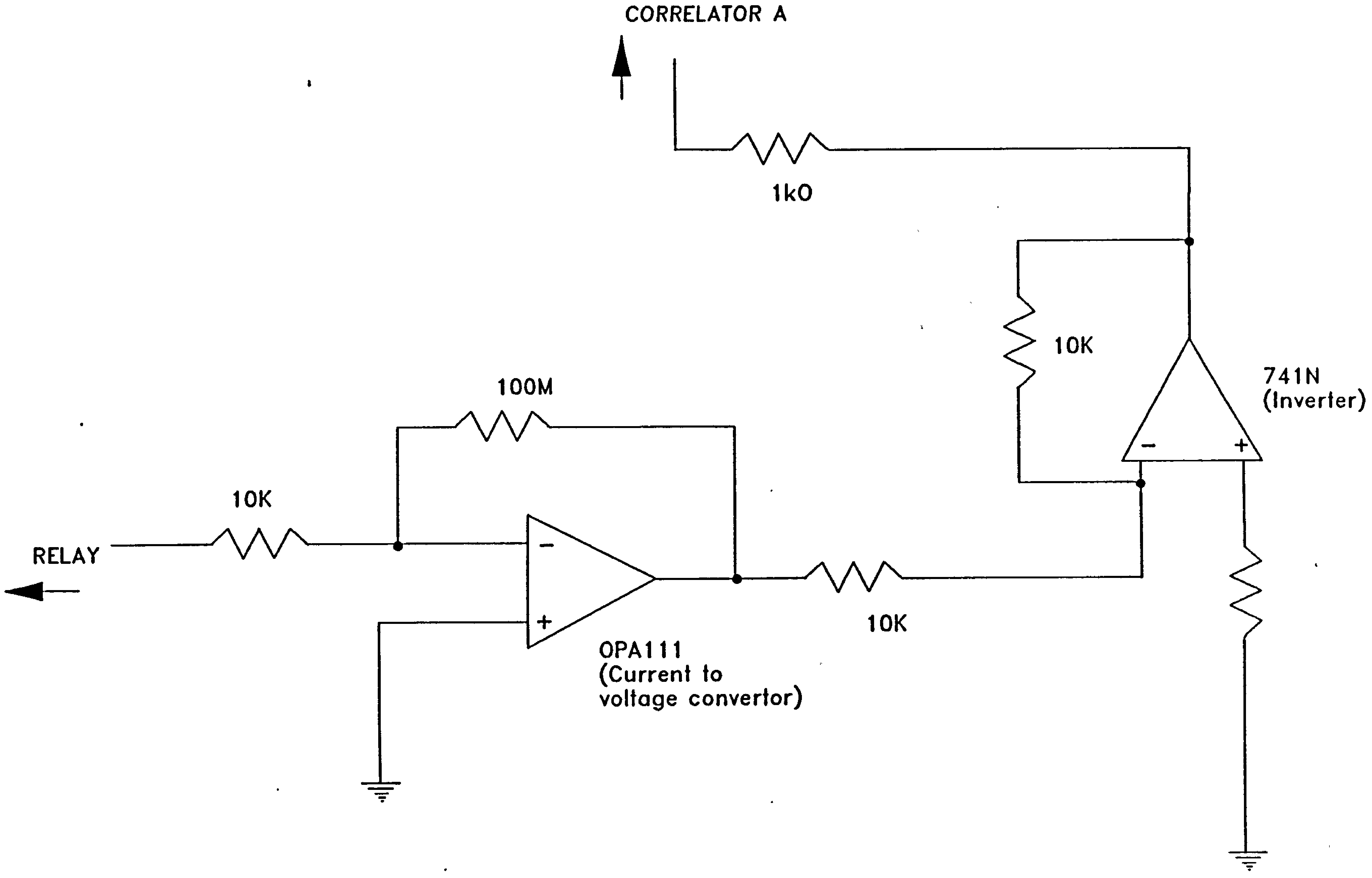


Figure 6.7 Amplifier A

with a 100 MΩ feedback resistor. In view of the very small currents involved it was necessary that all components and insulation be of the highest quality to eliminate leakage currents.

The ratio of input current to output voltage was 1μA to 100mV.

6.4.4 Amplifier B

Although the Thurlby multimeter was a high impedance instrument in voltage measurement mode it was nevertheless of comparable impedance to the glass electrode system and in consequence was isolated from it by Amplifier B. This consisted of two high impedance buffer amplifiers connected to a very high impedance operational amplifier, as shown in the circuit diagram Fig 6.8. A virtual earth is created at the negative terminal of the operational amplifier, causing the input current to flow through the 1M0 resistor, and giving a gain of -10.

6.3.5 Relay Switch

As a methodology for testing the integrity of the electrode began to develop it became increasingly important to be able to measure cell voltage or electrode impedance at random intervals and have the facility to be able to switch from one to the other. For this purpose a relay switch was utilised, controlled by the Nimbus microcomputer via a parallel interface module (Analogue mode). A circuit diagram of the switch is shown in Fig 6.9. It consisted of two half LM319 operational amplifiers the output from which was either

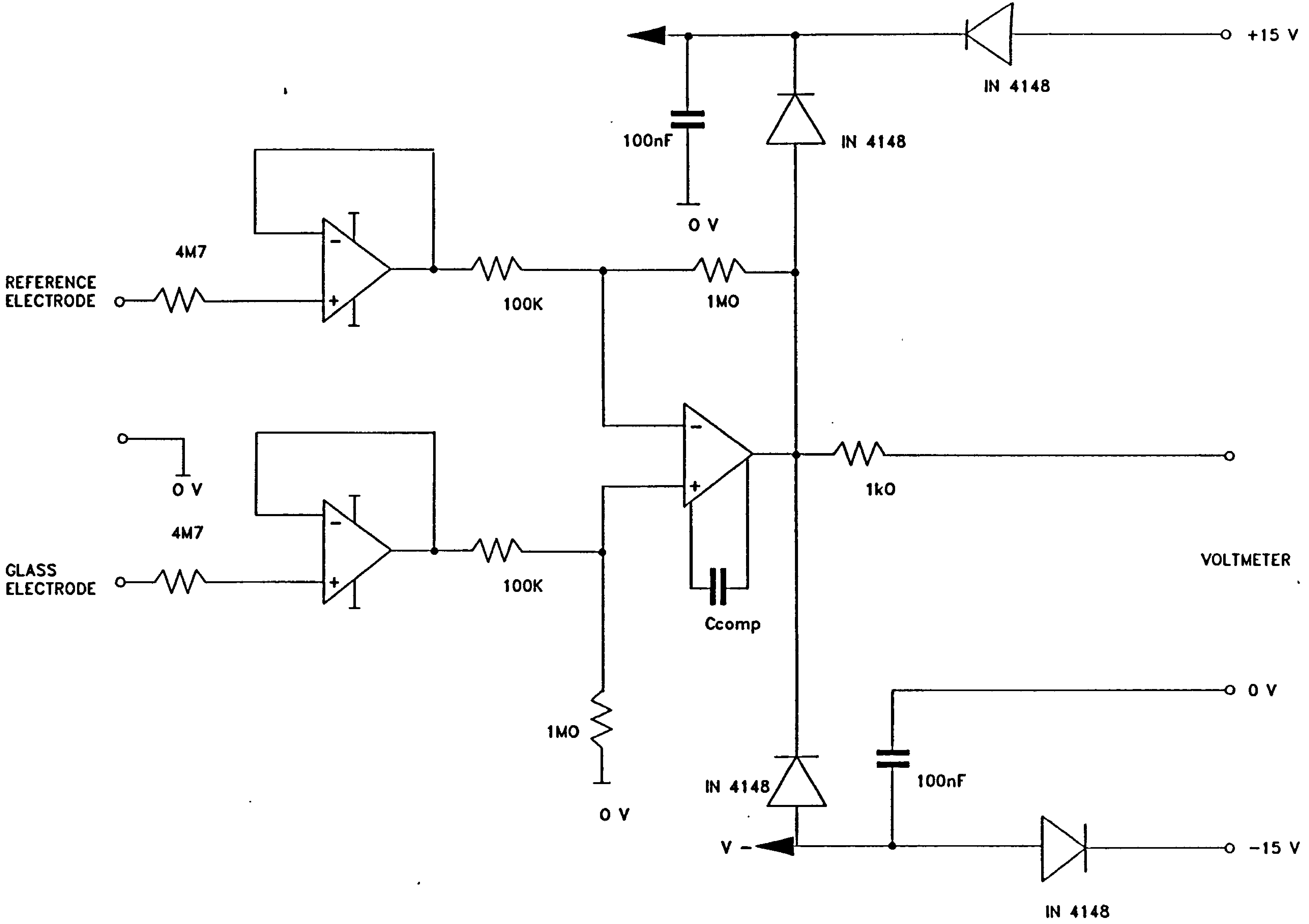
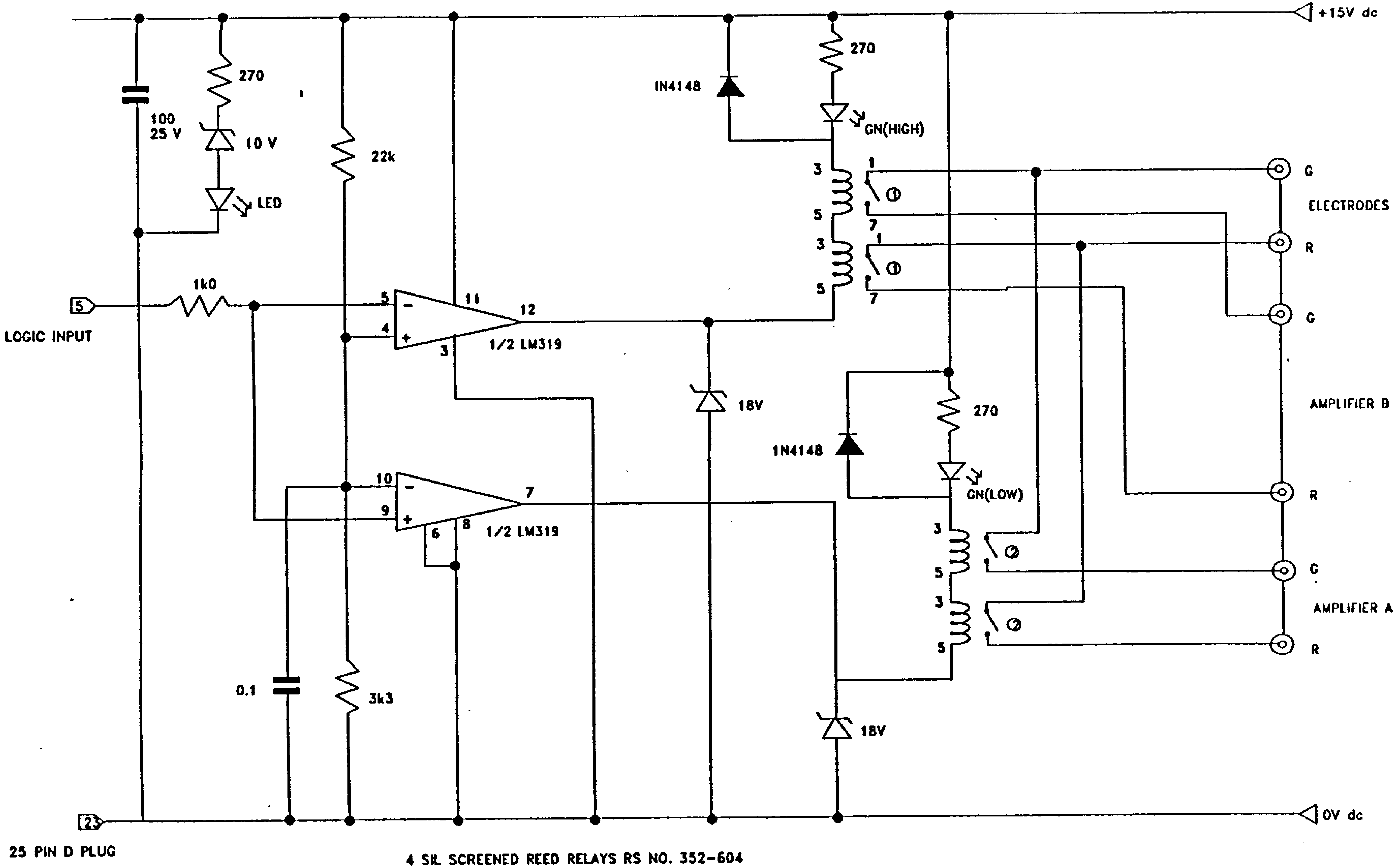


Figure 6.8 Amplifier B



4 SIL SCREENED REED RELAYS RS NO. 352-604
(PINS 1 AND 7 SOLDERED TO PTFE LEAD THROUGH
INSULATORS RS NO. 433-882, WIRED DIRECT TO
BNC SOCKETS)
BNC SOCKETS INSULATED FRON CASE. SHELLS WIRED
TOGETHER)

Figure 6.9

Relay Switch

high(+15V) or low(0V). A high output backed off the power supply and deactivated the relays, whereas a low output activated them. By operating the amplifiers out of phase one pair of relays could be brought in while the other pair were cut out. The status of the switch was indicated by an LED which was powered to signal "switch on".

6.4.6 Computer Hardware

The hardware used comprised the following

- RM NIMBUS MICROCOMPUTER
- EPSON LX-86 PRINTER
- RM NIMBUS PICONET SERIAL INTERFACE MODULE
- RM NIMBUS PICONET PARALLEL INTERFACE MODULE

The microcomputer was used to run the software developed for the project, and to control the voltmeter, TFA and relay switch, via the use of the Piconet interface modules.

Piconet is an expansion network for Nimbus peripherals . It provides a relatively cheap and simple to use method of connecting up to 30 peripheral devices simultaneously and controlling them from either the operating system or a program.

Data transfer between the Nimbus and each peripheral device is handled by a separate intelligent Piconet module. Two types, the serial and parallel modules will accommodate most devices. Further details of the system are given in Appendix 1.

The Epson LX-86 Printer was used to plot out the impedance graphs and to provide hard copy of test and input data.

CHAPTER 7 SOFTWARE

7.1 Introduction

The EMI Transfer Function Analyser could be used as a "stand alone" instrument and comprised a keyboard and VDU for this purpose. The required experimental conditions concerning frequency range, signal amplitude and so on, could be keyed in and the selected values were displayed as exemplified below in Figure 7.1.

```
Start Frequency                          [0.01]    Hz
Final Frequency                          [100]     Hz
Harmonic                                [ 1 ]
Gen. Amplitude                      [0.15]    V RMS
Gen. BIAS                           [  0 ]    V
Correlator range                         Auto      [*]
Channel              A [500] V           B  [500] V
Integration                              [10  ]    CYCLES
Delay                                 [ .1 ]    SECONDS
Intervals                           [ 10 ]
Interval Mode        LINEAR  [    ]         LOG [ *  ]
Channel             A [    ]   B [    ]   B/A [ *  ]
Coordinates                           CARTESIAN
```

Figure 7.1 Input Parameters to the Transfer Function Analyser

The first two inputs define the frequency range and the fourth and fifth the RMS amplitude of the A.C signal required of the signal generator and the D.C bias it should be given. The output from the system is broken down into harmonics for the purpose of correlation, and the third input specifies which of these is to be used. In the present work harmonics higher than the first were virtually nonexistent. The sixth input, when "starred" instructed the TFA to scan the frequency range over a number of equal intervals, the number being specified as the tenth input. The equality of the intervals could either be on a linear or log scale as selected in the eleventh input. The number of cycles over which integration is to be carried out and the delay before integration commences is selected in inputs eight and nine. The function to be integrated, in this case B/A, is selected by input twelve and the co-ordinates for data presentation by input thirteen. The maximum values of the signals to be sent to channels A (which receives the output signal from the system under test) and B (which receives the generator signal fed to the system) are set by input seven.

When the instructions to commence the experimentation are keyed in the input data page is deleted from the screen and is replaced by a page showing the output as exemplified below in Figure 7.2.

```
No      FREQ       REAL        IMAG
        Hz          A           jB

 1       .0100     8.8507     -2.9742
 2       .0263     5.9833     -3.3304
 3       .0695     3.9974     -2.3459
 4       .1832     2.8543     -1.3998
 5       .4832     2.4039     -.77173
 6      1.274      2.2087     -.59382
 7      3.359      2.0531     -.48212
 8      8.858      1.6526     -.69202
 12     100.0      .14687     -.41001
                READY
```

Figure 7.2 <u>Output of results on T.F.A</u>

When the experiment has been completed the input data page can be recalled and a further set of conditions keyed in and investigated. In doing this, however, the record of the conditions of the previous experiment and its results are lost because the instrument has no means of data storage. For this reason it was decided to interface the TFA with a RM Nimbus and run the experiments under computer control with computer data management. In the present chapter a brief description of the software developed for this purpose is described. Program listings are supplied in Appendix 2.

In the final stages of the project the software was refined so that the glass electrode system could be transferred at pre-selected intervals from pH measurement to frequency response mode and thereby simulate on-line testing of integrity. For this type of experimentation there was no alternative to computer control.

7.2 Software Tasks

Software for the project was developed over a period of eighteen months and was designed to undertake the following tasks.

- **Interface with Input / Output devices**
- **Data management**
- **Data output in a tabulated or graphical form**

Each of these tasks will now be treated separately in the sections which follow.

7.3 Interfacing

The input/output devices were

i) Transfer Function Analyser (T.F.A)
  - for impedance measurement

ii) Multimeter
  - for measuring the voltage developed across the glass and calomel electrodes(i.e pH measurement)

and later on, as the process of testing the integrity of the system began to take shape,

iii) Relay switch
  - to transfer electrodes from voltage to impedance measurement and vica versa.

Interface to these devices was provided through the serial and parallel piconet modules, as discussed earlier in section 6.4.6, and the duty of the software with respect to each device will be taken in turn.

7.3.1 Transfer Function Analyser

Information transferred to and fro between the Transfer Function Analyser and Nimbus comprised the input data defining the required experimental conditions, the start and stop signals and the results which emerged from the impedance measurements. These tasks were sequenced in three steps as follows.

STEP 1 : In step 1 the input page of the TFA (Fig 7.1) was mirrored on the computer and the experimental conditions typed in on the computer keyboard, the final instruction being that to start the experiment.

These instructions were sent along a line to the TFA via the serial piconet module. To do this a simple program was devised based on the logic of a 'simple terminal emulator' shown in block diagram form in Fig 7.3.

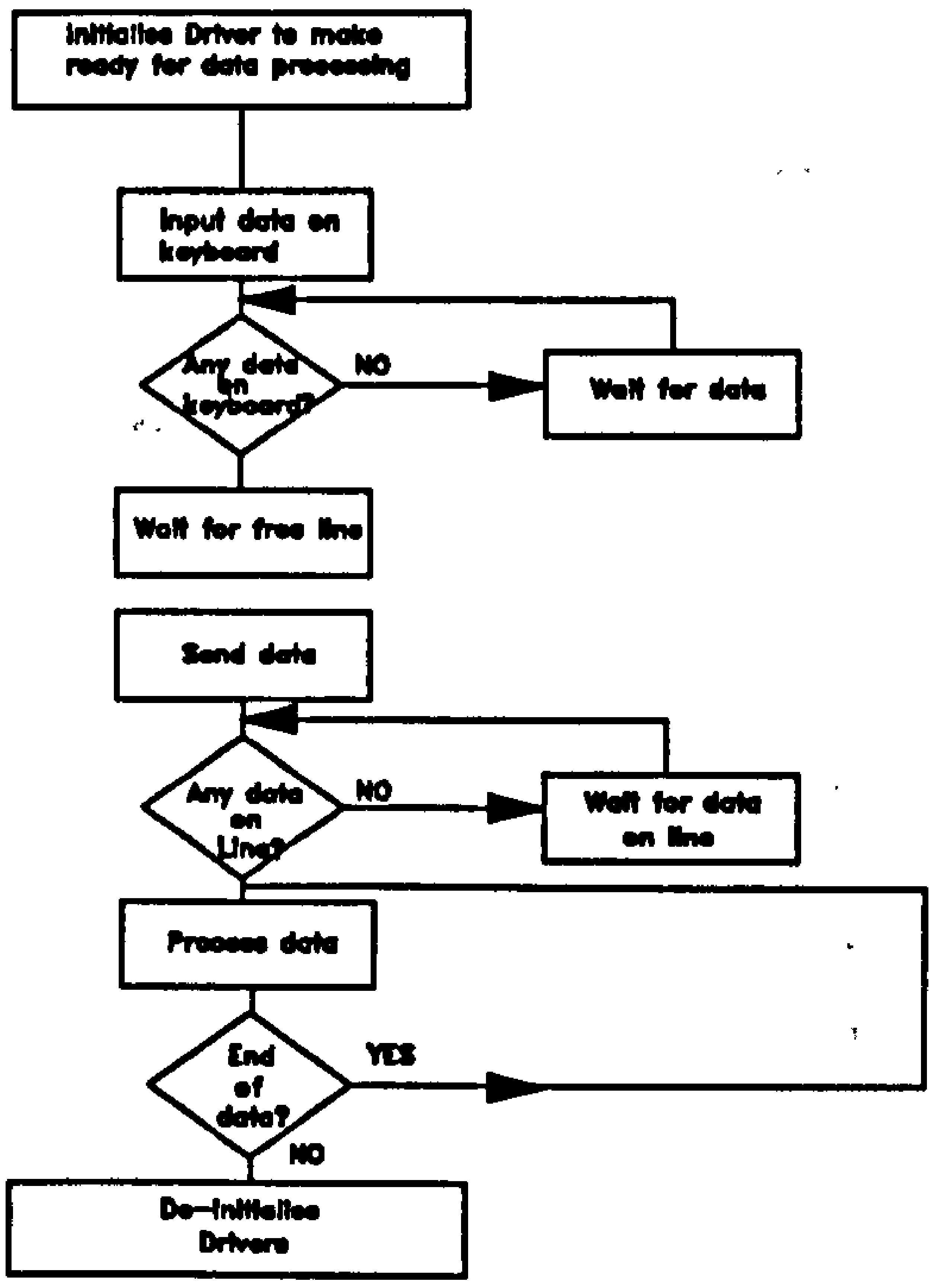


Figure 7.3 Flow chart for a "Simple Terminal Emulator"

The Transfer Function Analyser is an intelligent machine and can be instructed to expect data by means of control signals, sent to it by the Nimbus, which take the form:-

CONTROL SIGNAL followed by **COMMA**

For instance the signal %2, instructs the TFA to display the input data page(i.e Data entry Form 2 illustrated in Fig 7.1). The available control signals are listed below

FREQUENCY RESPONSE CONTROL SIGNALS

COMMAND	SIGNAL
Data Entry Form 1	%1
Data Entry Form 2	%2
Cartesian Coordinates	!1
Show results page	/3
Show input data	/2
Roll data to next page	/1
Dump results to Nimbus	T]4
Dump input data to Nimbus	T]2
Autobias on	B]*
RMS sine wave	V*_*
Echo off	DYO
Start measurement	^

Numerical data to the TFA, such as the initialisation values specifying the required experimental conditions, are sent in a similar format i.e NUMERICAL INPUT DATA followed by a COMMA.

The logic for Step 1 is shown in block diagram form in Fig 7.4.

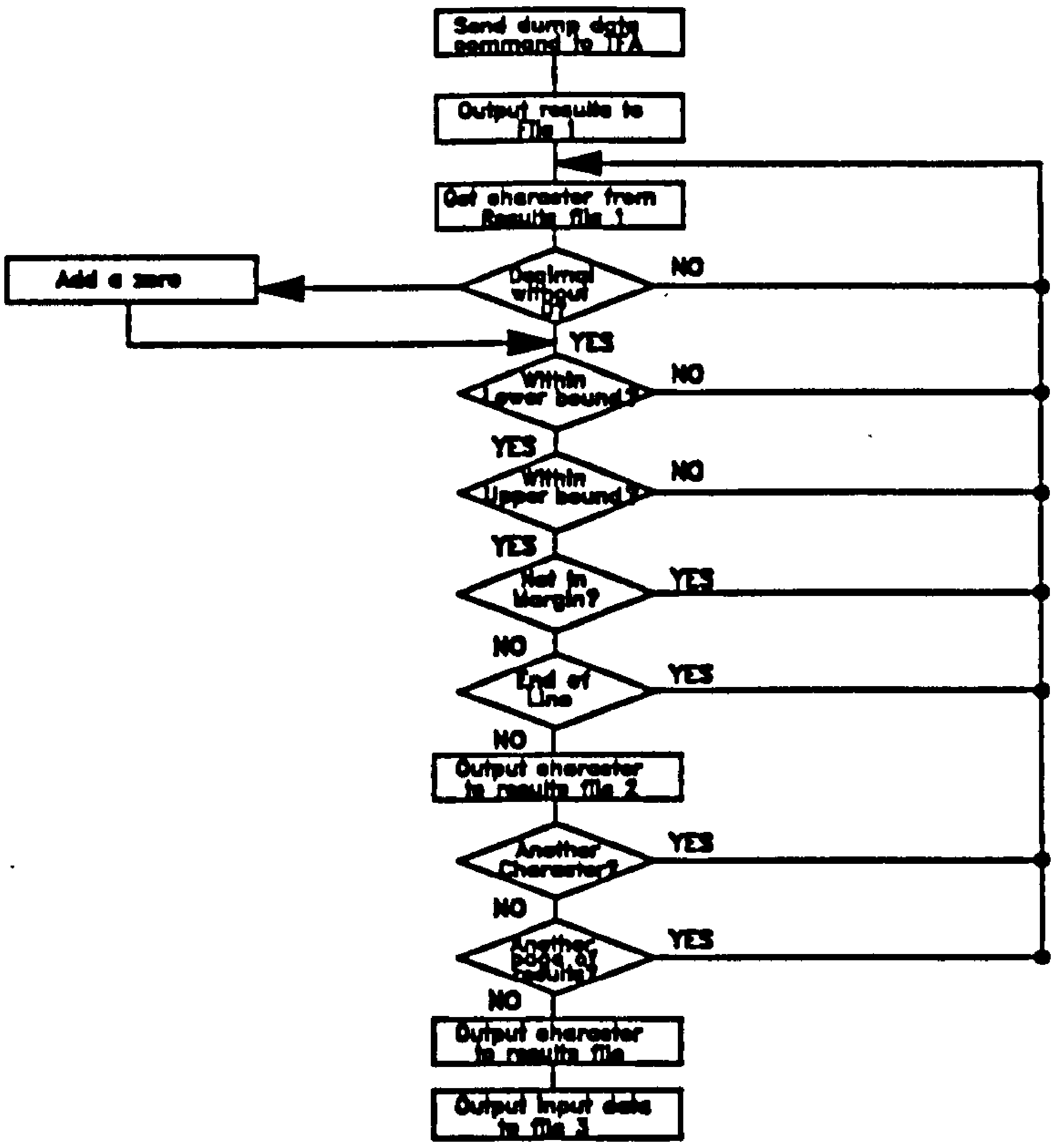


Figure 7.4 Data Transfer to/from TFA

STEP 2 : Whilst the impedance measurements were taking place the software had to remain dormant, and prevented from implementing Step 3 until the experiment had been completed. The length of time over which the software was inactive depended upon the frequency range covered, the number of integration cycles, the delay and the number of intervals in the frequency scan, and was estimated for each run from past experience. Dormancy was provided by asking the program to build up a number from zero by the repetitive addition of one. The number selected was large enough for the operation to bridge the period required.

STEP 3 : In this step data are retrieved from the TFA. To do this the data were first mirrored on the output screen of the TFA and then dumped to the Nimbus screen, whence they were stored on a hard disc in a file specified at the outset of the run. The logic of the software followed the flow chart of Fig 7.5 which was designed to transfer one or more pages of results and the corresponding experimental conditions (the "input" data) from TFA to hard disc, a function which was labelled "Receive Signal Back".

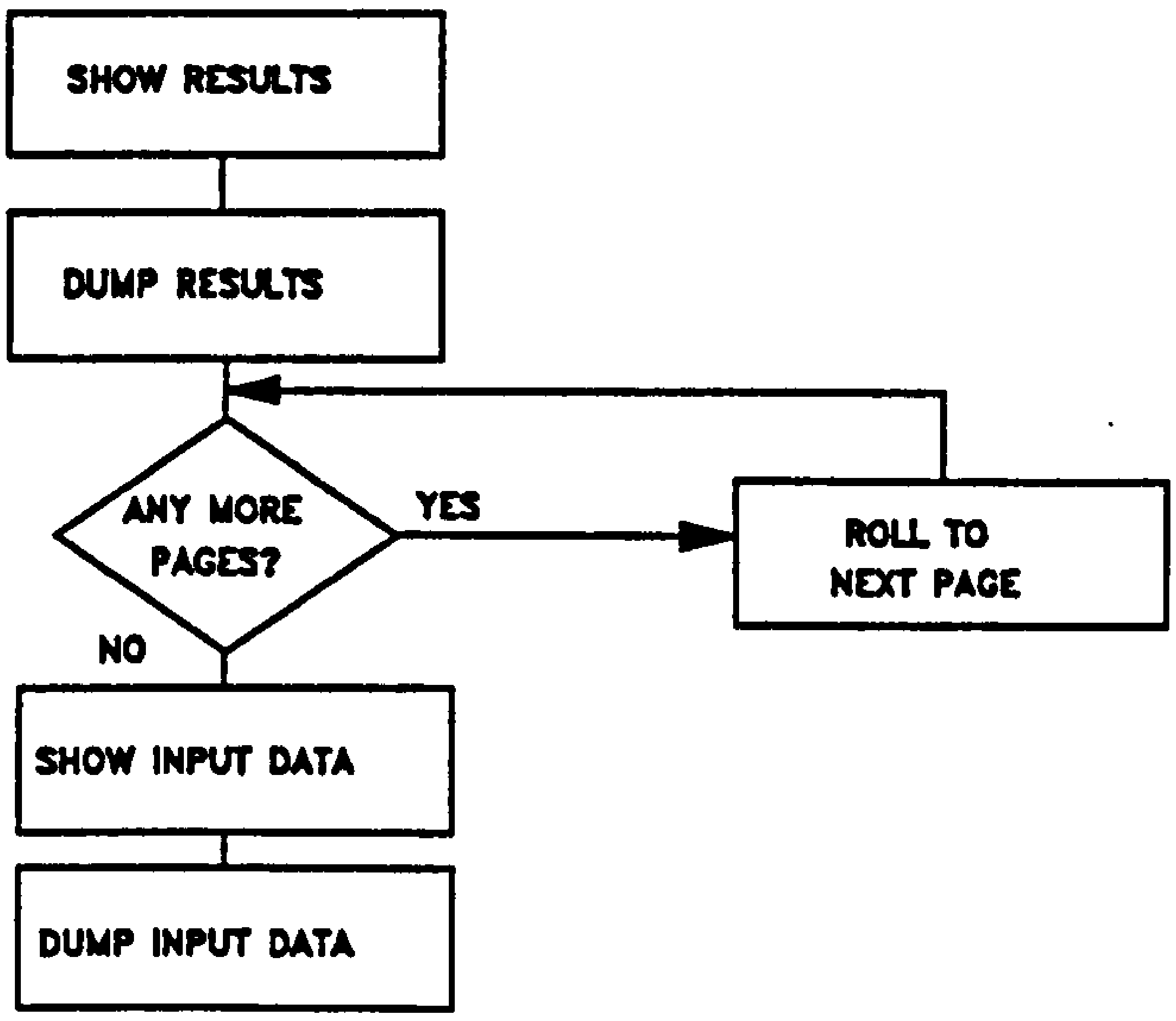


Figure 7.5 Flow chart for function 'Receive Signal Back'

7.3.2 Multimeter

Signals from the 'intelligent' multimeter appear as an 8 bit pattern of characters specifying a number in binary form lying between the values -256 and +256 which represent the lower (zero) and the upper limit of the voltage range. For the

Nimbus to make use of these signals they had to be converted to a decimal form, a facility which is provided by the analogue to digital converter residing in the RM Nimbus Parallel Module. The analogue driver is designed to start a new conversion in response to a change in the analogue channel and so in order to measure a continuous voltage the logic shown in the flow chart 7.6 was followed, where the channel was changed repeatedly from 0 to 1 and back again.

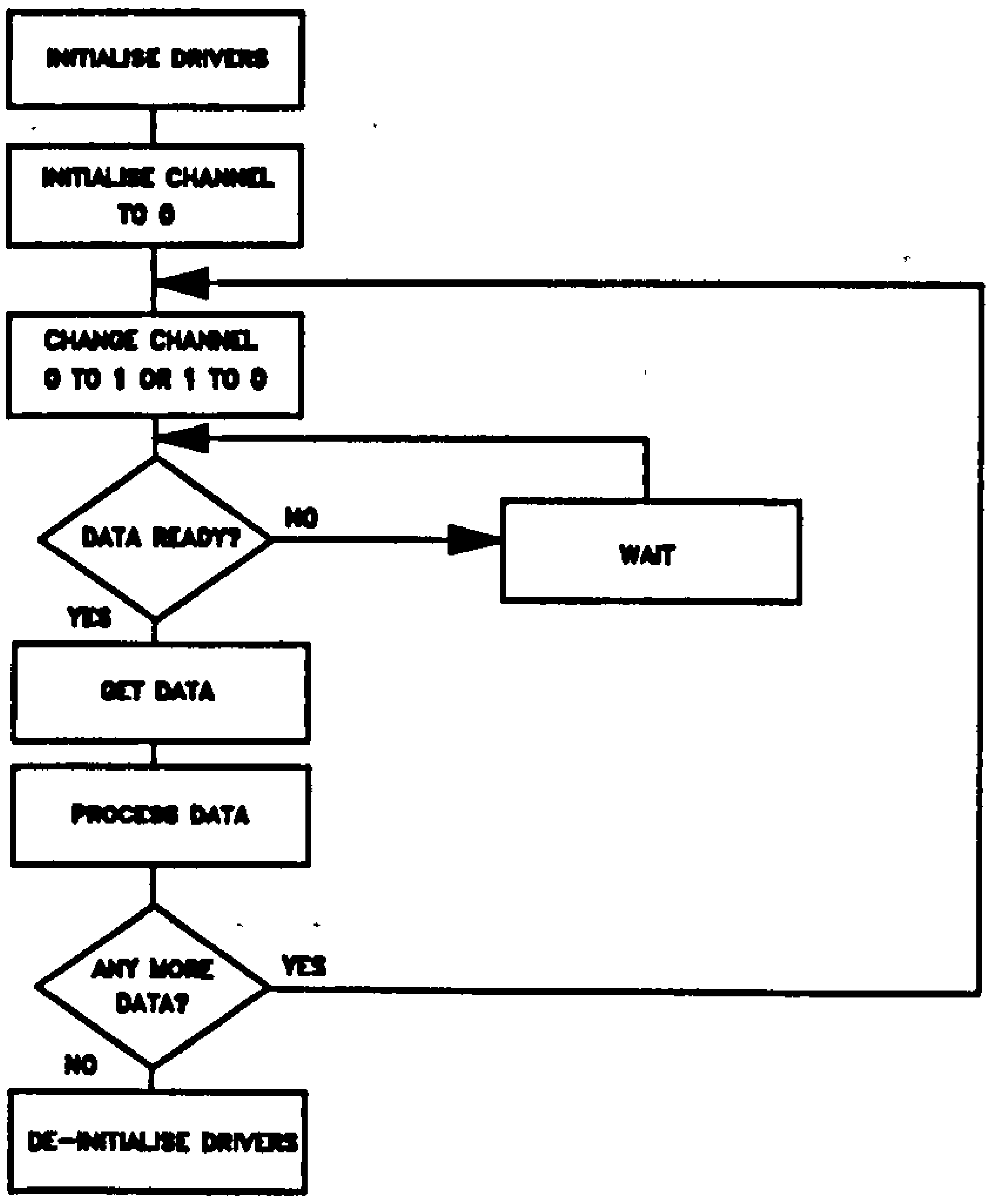


Figure 7.6 Flow chart for voltage measurement

7.3.3 Relay Switch

The control of the relay switch was exercised through the second parallel interface module, which was employed in the 'Analogue Interface mode' using the 15-way d-type connector (see Appendix 1). The control of the relay switch was possible via the output status register, 25H.

Assigning an odd number to 25H resulted in pin 5 in the d-type connection being forced "high". Referring to the relay switch circuit Fig 6.10, this resulted in a "high" output at point 12 which backed off the 15V D.C supply and in consequence relays 1,1 remained open. At the same time a "low" output occurred at point 7, and so the 15V D.C supply was able to pass current and the relays 2,2 closed. In consequence the electrodes were connected to Amplifier A but not to B. When an even number was assigned to 25H the opposite was the case. The change from one to the other was clearly accomplished by adding unity to whatever number existed in status register 25H.

The flow charts for function "Switch On" (directs signals to amplifier A) and "Switch Off" are shown in Figs 7.7 and 7.8.

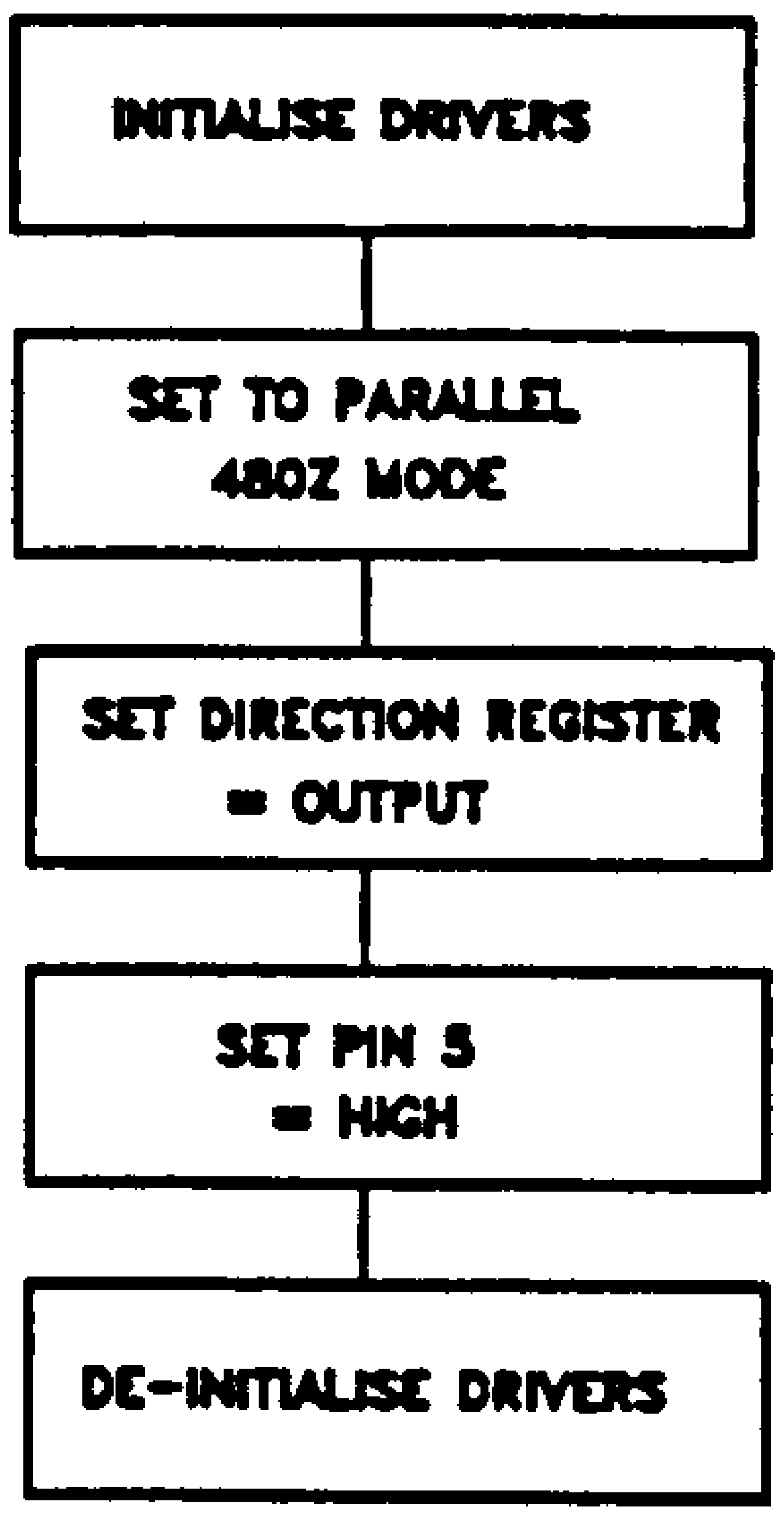


Figure 7.7 Flow chart for function 'Switch On'

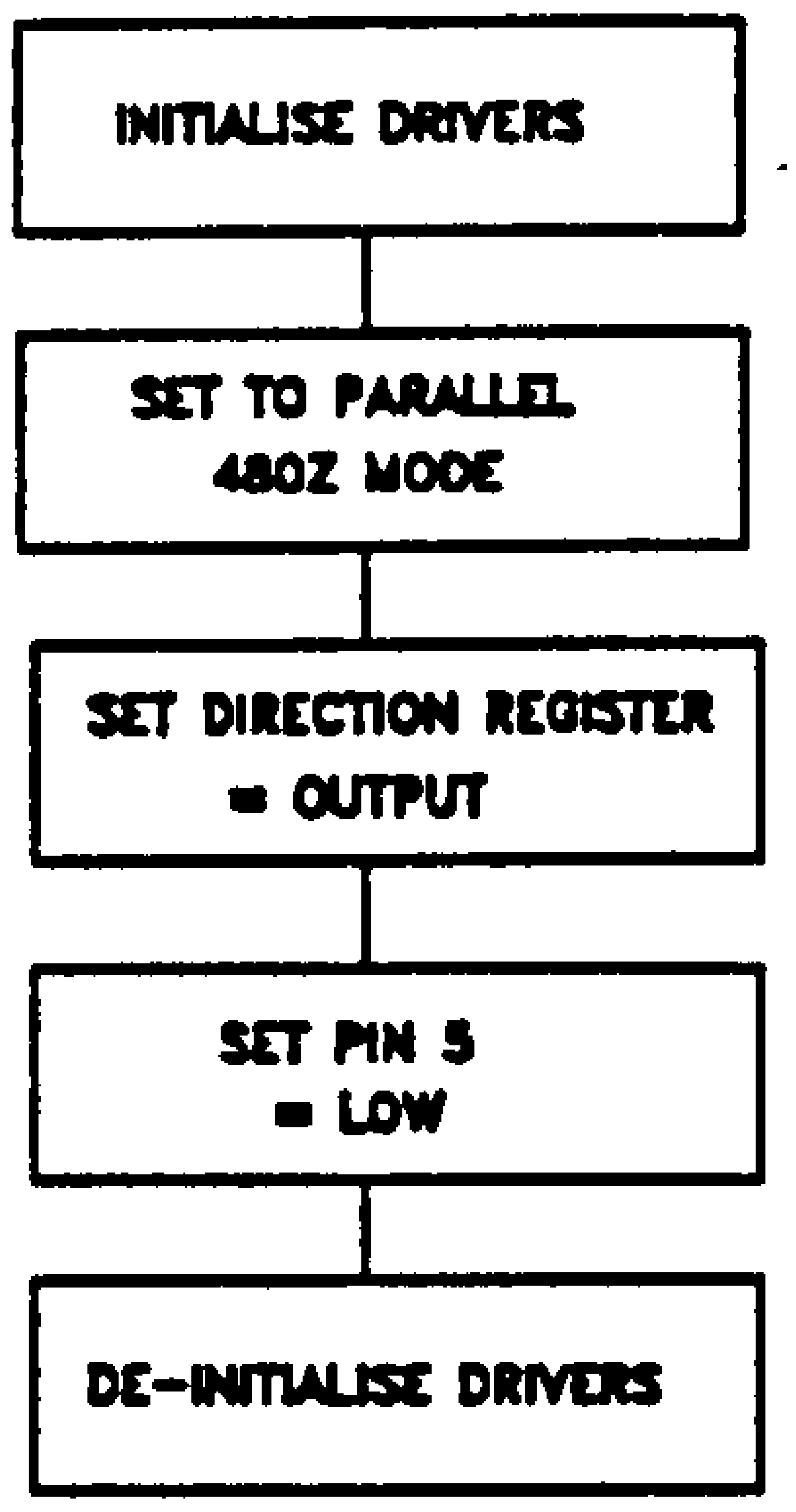


Figure 7.8 Flow chart for function 'Switch Off'

7.4 Data Management

As well as allowing the RM Nimbus to communicate with the interface devices, the software had also to carry out the important task of organising and managing the data arising from this activity, whether it be input data entered by the user or results obtained from a run.

Management of data fell into the following categories.

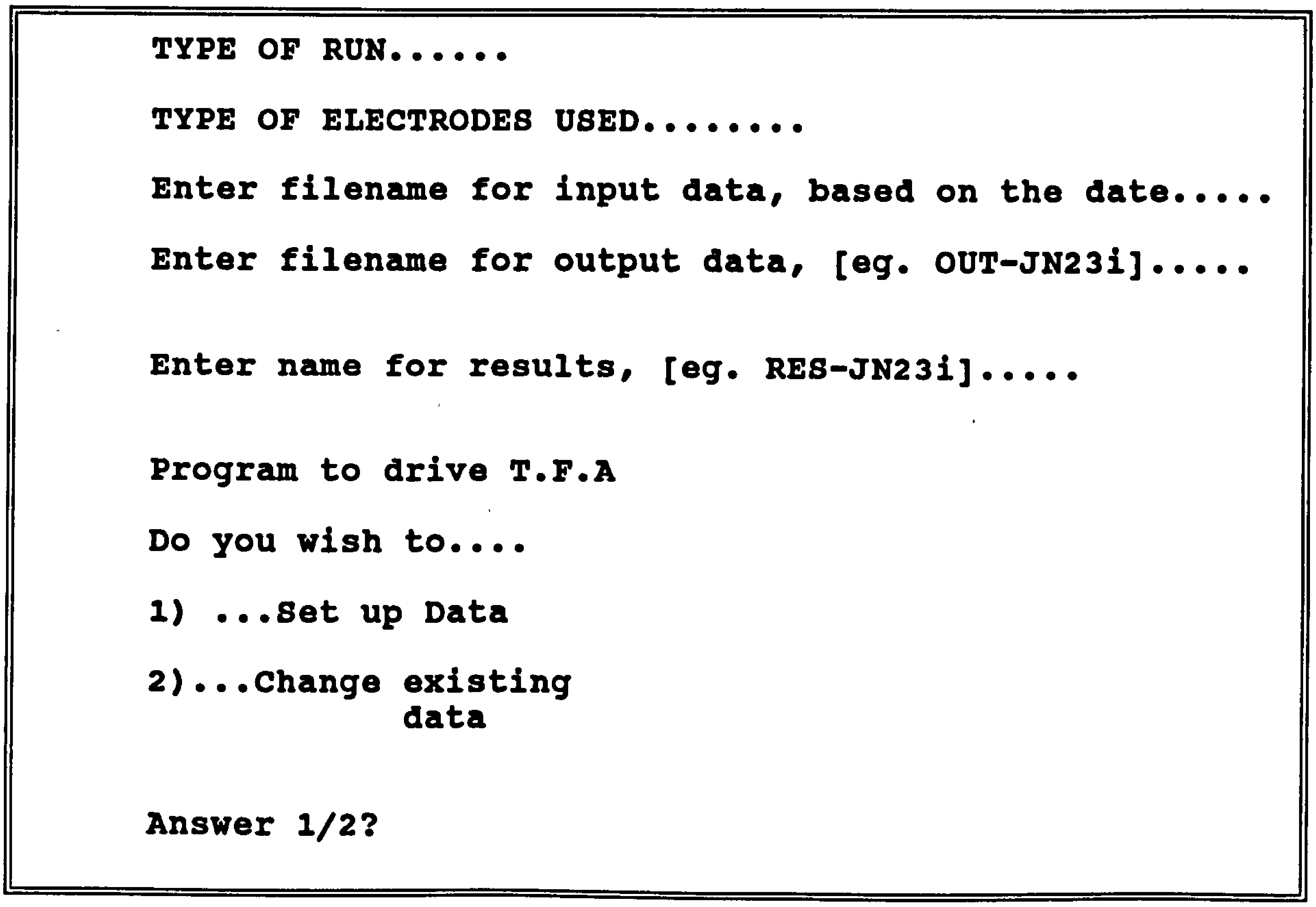
- **Initialisation**
- **Manipulation of results**
- **Storage of data**

7.4.1 Initialisation

Initialisation refers to the data which must be fed into the system at the start of a run, and in this case it comprised not only entering the required experimental conditions but also, and equally important, creating a file to receive all data relevant to an experiment, both input and output, so that it could be stored and recalled for future reference.

The program was designed to be menu driven, the screens available being shown sequentially in Figures 7.9, 7.10, 7.11 and 7.12. The first menu Fig 7.9, allowed the user to enter a brief statement describing the type of run, to record the type of electrode being used and to create files for the storage of input data, output data and results. By choosing between alternatives 1 and 2 the user was then passed either to menu 7.10 which allowed the complete complement of experimental conditions to be set up, or to menu Fig 7.11 which allowed minor changes to be made if an experiment not much different from the previous one was to be carried out. Depressing the "send" button then passed the user to the final menu Fig 7.12, which allowed the voltage across the cell(measured manually prior to connection to the TFA) to be keyed in and recorded, together with the number of intervals required over the frequency range, and the pH of the buffer used in the experiment. A run time was also keyed in which informed the computer of the "wait" time between starting the experiment and calling for the results. The number of intervals was keyed in again because it was required in the data handling procedure and was not easily recovered for this purpose from the input data. Finally the menu allowed a choice of graphical presentation and whether or not hard copy was required. Depression of "send" at the end of this menu started the run and put the software in "wait" mode.

Some initialisations were carried out internally by the software, in particular the initialisation of the drivers and the number of pages of data the output would generate. The latter was calculated by the software from the number of intervals used in scanning the required frequency range.



```
TYPE OF RUN......

TYPE OF ELECTRODES USED........

Enter filename for input data, based on the date.....

Enter filename for output data, [eg. OUT-JN23i].....


Enter name for results, [eg. RES-JN23i].....


Program to drive T.F.A

Do you wish to....

1) ...Set up Data

2)...Change existing
           data


Answer 1/2?
```

Fig 7.9 Initial screen to enable the user to choose run

<ANSWER = 1>

```
read in start FREQUENCY and a comma, Ctrl-T to stop...
read in end FREQUENCY and a comma, Ctrl-T to stop...
read in HARMONIC and a comma, Ctrl-T to stop...
read in AMPLITUDE/VOLTS and a comma, Ctrl-T to stop...
read in BIAS/VOLTS and a comma, Ctrl-T to stop...
read in INTEGRATION CYCLES and a comma, Ctrl-T to stop...
read in DELAY and a comma, Ctrl-T to stop...
read in INTERVALS and a comma, Ctrl-T to stop...
```

Fig 7.10 Enter data to be sent to the TFA

<ANSWER = 2>

```
Data to be changed..........

  1; Start Frequency
  2; End Frequency
  3; Harmonic
  4; Amplitude / Volts
  5; Bias / Volts
  6; Integration Cycles
  7; Delay
  8; Intervals
  9; RUN + STORE DATA
```

Fig 7.11 Amendment of existing data

<SEND>

```
Approx voltage of the run....

No of intervals to be taken....

pH of the run....

RUN TIME

Hours....

Minutes....


Do you want graphs of

1) REAL against IMAGINARY

2) LOG FREQ against REAL

3) BOTH

4) NO GRAPHS


Do you require a printout of the graphs

1) ...YES

2) ... NO
```

Fig 7.12 Runtime options available to the user

7.4.2 Manipulation of results

Results from the Frequency Response Analyser were dumped down the line character by character and appeared on the Nimbus as shown in Fig 7.13.

In this form they were not easily plotted by the computer for the following reasons. Firstly, the computer cannot inherently distinguish between text and numerical data. Secondly, the data were not in any consistent numerical sequence (i.e largest number at the top or bottom, say) making a decision on scaling difficult. Thirdly, figures less than unity were represented without a leading zero, and finally imaginary values required inversion.

```
  No        FREQ          REAL          IMAG
            Hz             A             jB
   1         .0100        8.8507       -2.9742
   2         .0263        5.9833       -3.3304
   3         .0695        3.9974       -2.3459
   4         .1832        2.8543       -1.3998
   5         .4832        2.4039       -.77173
   6        1.274         2.2087       -.59382
   7        3.359         2.0531       -.48212
   8        8.858         1.6526       -.69202
   9        14.38         .85919       -.97196
   10       37.92         .50378       -.78979
   11       61.58         .27675       -.59111
   12       100.0         .14687       -.41001
                     READY
```

Fig 7.13 Typical results transferred from Analyser

In order to deal with these problems the data were manipulated according to the logic of Fig 7.14.

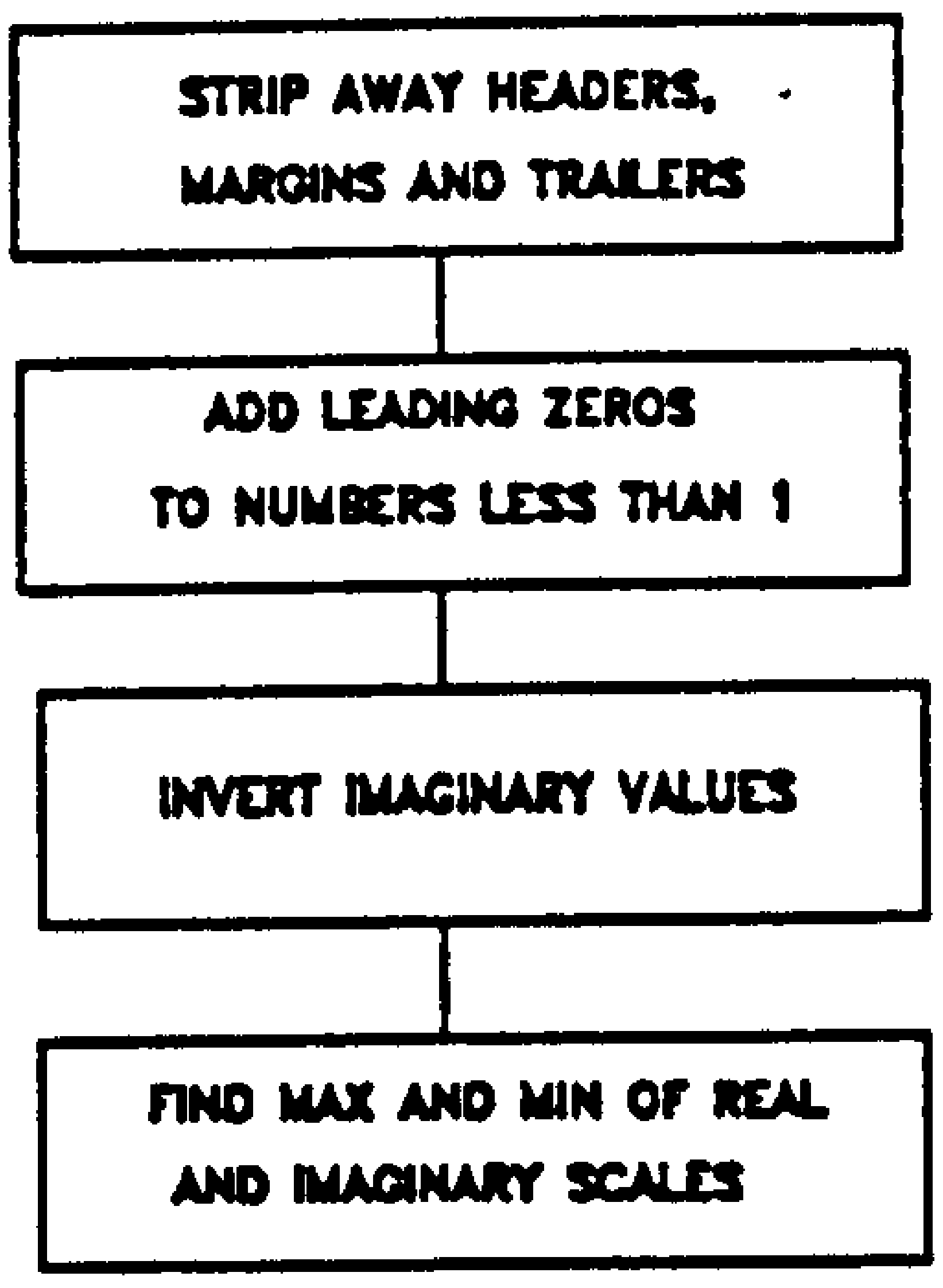


Figure 7.14 Flow chart for data manipulation

7.4.3 <u>Storage of data</u>

Data were stored in files named during the initiallisation procedure prior to a run. These files were:

Input file	- contained all the input data for a run, as well as electrode type, buffer pH value, pH value indicated by the glass electrode, the date of the run
Output file	- a mirror of the data dumped from the Frequency Response Analyser (TFA).
Results file	- bare data after stripping away unwanted text and adding leading zeros.

7.5 Output of data/graphics

Once the data had been sorted and minimum and maximum values had been calculated for the real and imaginary components, the representation of the data in a graphical form was possible.

This was achieved by following the logic shown in Fig 7.15, which resulted in a graphical representation of the form shown in Fig 7.16.

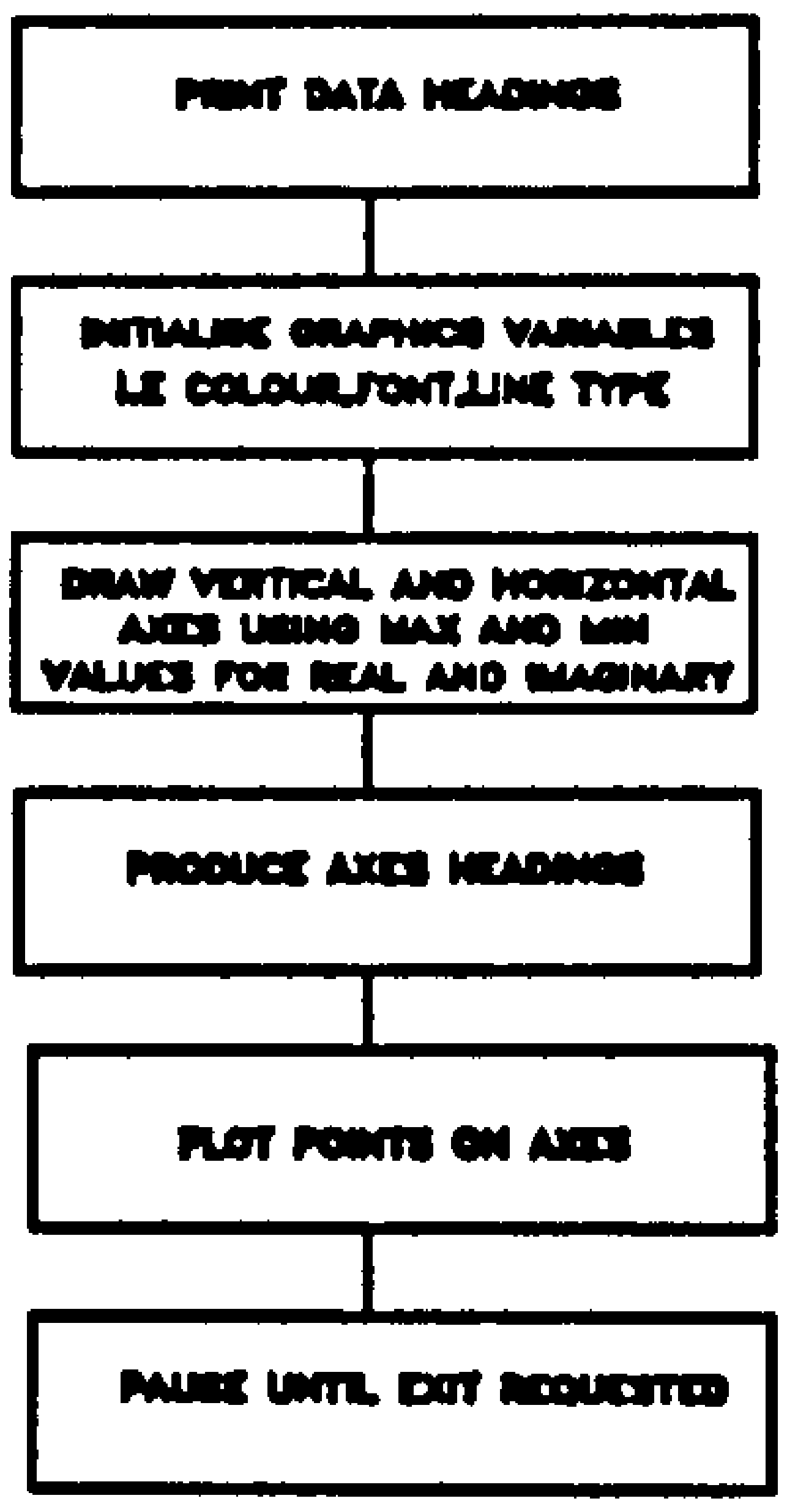


Figure 7.15 Flow chart for data graphics

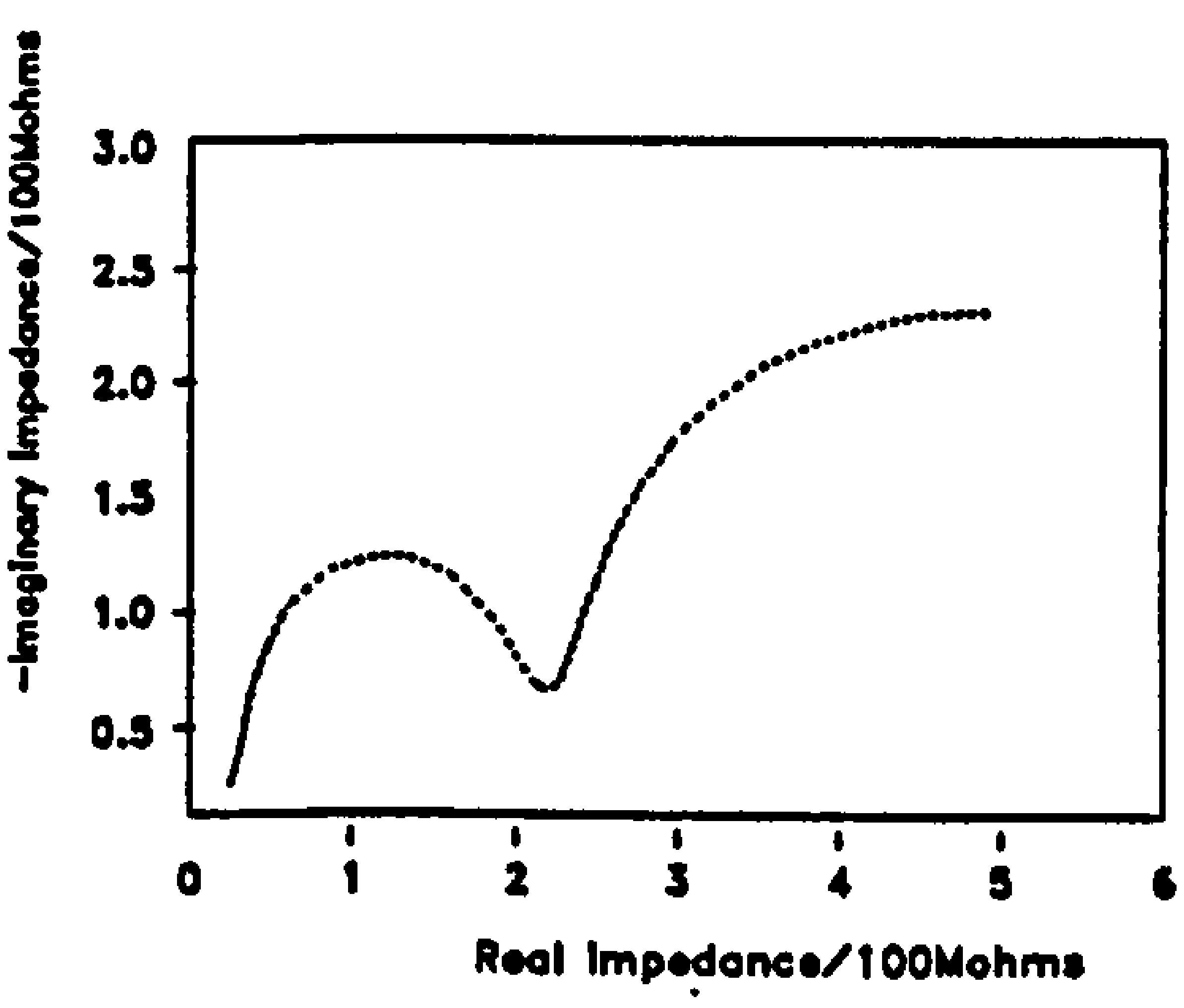


Fig 7.16 Typical impedance plot

7.6 Resulting Software

The final resulting software 'FINAL' and 'ETEST' are a concatenation of the ideas developed and the result of many smaller units of code being joined together.

FINAL

Final was a menu driven program designed specifically to measure frequency response, store the results and also present them graphically in the complex plane. It comprised the procedures referred to in previous sections as "Single Terminal Emulator", "Data Transfer to/from TFA", "Receive Signal Back", "Data Manipulation" and "Data Graphics"

Before performing a frequency sweep the program required the user to select the desired test conditions from a number of options . Graphical representation of the data both visually (on screen) and physically (on printer) was an option to the user. All data, both input and output, were stored in logical sequential files for future reference.

ETEST

ETEST was designed to test the integrity of a glass electrode, and essentially divided time between frequency response measurement and pH measurement. It comprised all the procedures employed in FINAL together with "Voltage Measurement", "Function.'Switch On'" and "Function 'Switch Off'".

After calling for electrode input data and an initial measurement of the impedance data via the frequency response analyser, the software switched to monitor the pH of the system for a pre-determined time chosen by the user. Upon completion of this time further impedance measurements were performed, and cross-checked with the historical record of the given electrode. If the deviation between the two fell outside selected limits an alarm was signalled, otherwise pH measurement was continued.

The logic of the resulting program is shown below in Fig 7.17.

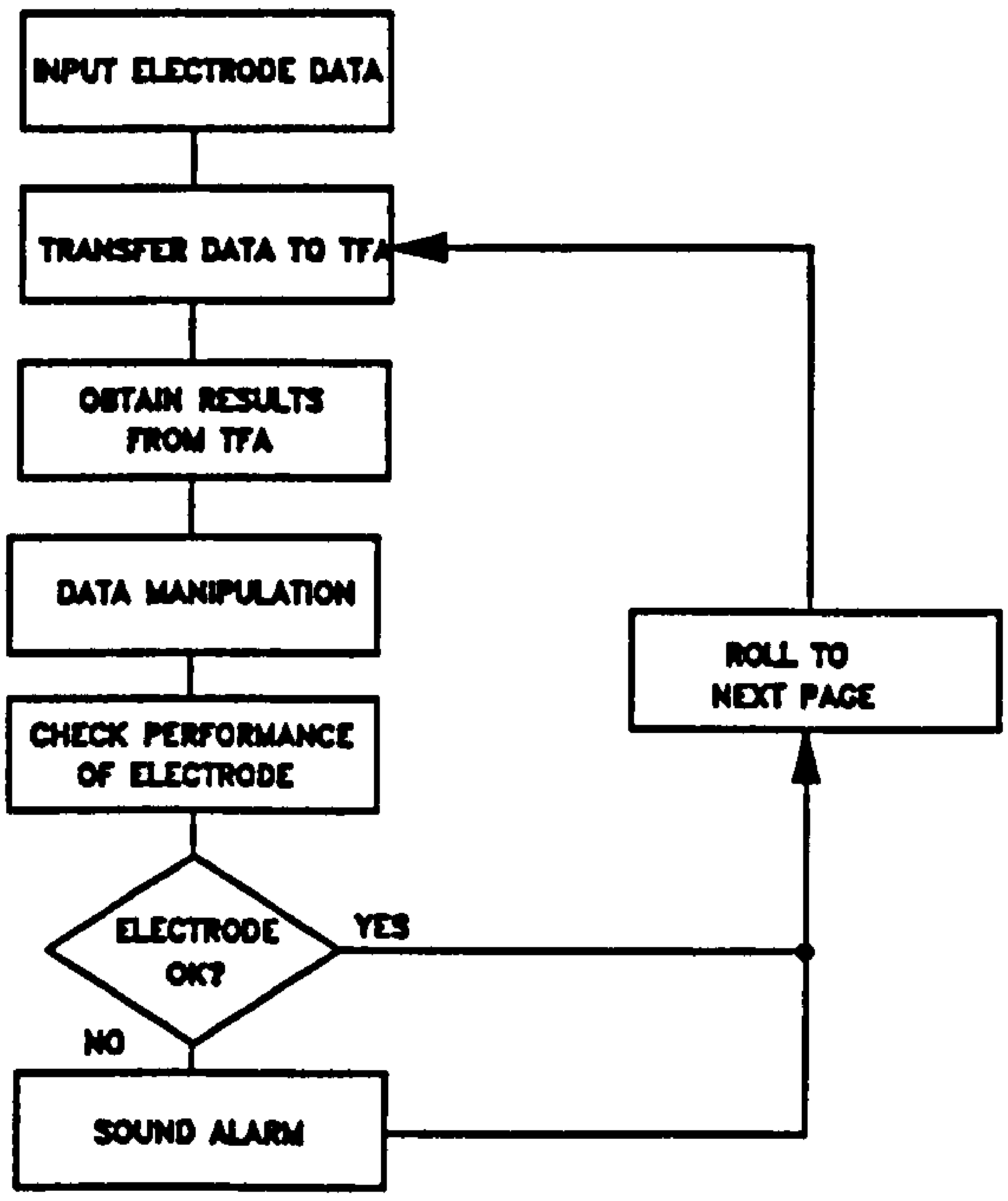


Figure 7.17 Flow chart for integrity testing

The program is again menu driven and the input by the user is shown in Figure 7.18.

```
Give date ....

Give electrode no ....


Give time for pH measurements (in mins) ....
```

Figure 7.18 Input to the program "ETEST"

CHAPTER 8 EXPERIMENTAL PROCEDURE

8.1 Introduction

Experiments were carried out to determine the frequency response, the Nernstian slope and the integrity of a number of glass electrodes both in clean environments and in environments which it was thought might adversely affect the glass membrane surface. Prior to these experiments a number of tests were carried out to establish a reliable experimental methodology.

8.2 Methodology for Frequency Response

In carrying out an experiment the equipment was assembled as already described in Section 6.1., with the solution to be used residing in the glass vessel and the glass and calomel electrodes fitted into the lid.

After the mild steel curtain had been raised the earthing of all the screening components was checked and the appropriate connections made between the electrodes and the measuring circuitry. Stirring was then commenced by allowing nitrogen to bubble into the solution, and the instrumentation was switched on to "warm up". Instructions for the required sequence of operations were then keyed into the Nimbus and the experiment allowed to proceed.

The procedure to this point and the equipment employed was the result of a long process of development in which instabilities, probably due to leakage currents and external electric fields, were painstakingly eliminated from the system until it was capable of providing reproducible and reliable results. In describing the equipment and electronics in earlier sections these development stages have been omitted.

All experiments were carried out at or near 25°C.
The use of bubbling as a stirring agent was quickly abandoned because some of the bubbles adhered to the glass membrane and although they may not have affected the integrity of the electrode they did affect the impedance by partially blanking off the surface. It was replaced by mechanical stirring. A glass rod with a butterfly end passed through the lid of the vessel and connected to an overhead motor which rotated at a rate of 4 revs/s. The butterfly rotated immediately below the glass electrode bulb.

The accuracy of the impedance measurements would clearly depend upon the number of cycles over which the summations of equations 6.1 and 6.2 were carried out and on the amplitude of the A.C signal fed to the cell from the TFA signal generator. These variables were therefore tested prior to any other experiments. Several electrodes of both types, 8400B and 8404S, were investigated using the following buffered solutions.

pH 2 All buffers were based on a 0.05M
pH 4 Potassium hydrogen phthalate solution
pH 7 containing 20pmm Mercury as Mercuric
pH 9 potassium iodide

(i) Time interval: Experiments were performed in which the summations were carried out over one, two, five and ten cycles for each electrode and over a frequency range of 0.01 to 100 Hz. The results were obtained as a sequence of impedance plots for ease of comparison.

(ii) Signal amplitude: Using the same frequency range, signal amplitudes of 10, 50, 150 and 600 mV were investigated and as before the results were obtained in the form of impedance plots.

As a result of these experiments, for reasons which will become clear in the next Chapter, all subsequent experiments were carried out using summations over ten cycles and amplitudes of 150mV. The spread of frequency, 0.01 to 100 Hz, was arbitrary, but the lower limit was selected for practical reasons. For regular on-line monitoring a ten-cycle summation at a frequency of 0.01 Hz would require the electrode to be out of service for regular periods of twenty minutes or so. This may be acceptable if the electrode is twinned, but even so twenty minutes off-line in chemical processing is sufficiently long for a malfunction to develop in the on-line electrode, with consequences which might well be serious.

The use of frequency response behaviour at less than 0.01 Hz was felt therefore to be impractical in the context of on-line integrity testing, and was not therefore investigated. The upper limit at this stage, however, remained open.

8.3 Frequency Response Experimentation

The method described in section 8.2 above was used to obtain frequency response data under the conditions described below.

8.3.1 Clean Environment

Both types of electrode were submitted to a number of experiments to test the following:

- Reproducibility
- Effect of pH
- Effect of ageing
- High and low frequency characteristics

These experiments also served the function of building up a file of data on normal behaviour which could be used as a standard against which behaviour in other environments could be compared.

i) Reproducibility:

Ten electrodes of each type were tested in buffer pH 7 at 25°C over the standard frequency range 0.01 to 100 Hz. After washing in distilled water they were tested again, a process which was repeated three times.

ii) Effect of pH(23):

Ten electrodes of each type were tested in the buffer solutions pH2, pH7, and pH9. After testing, each electrode was washed in distilled water and the test repeated. This was done three times for each electrode.

iii) Effect of Ageing:

The effect of ageing was investigated by leaving an electrode in a buffer solution over an extended period of time and measuring its impedance after 0, 1 and 2 months. Both types of electrode were examined in this way, and were allowed to age in buffer solutions of pH 2, 7 and 9.

iv) High and Low Frequency Characteristics:

These characteristics were determined largely to acquire data which might prove to be useful outside the immediate aims of the present work, as for instance in off-line testing or quality testing at the manufacturing stage. Measurements in buffer pH 7 were made on both types of electrodes. The frequency ranges investigated were 0.1 to 1000 Hz and 0.0001 to 100 Hz.

8.3.2 Adverse Environments

Both types of electrode were exposed to environments which affected the glass membrane surface and might possibly therefore have an adverse effect on their integrity. Impedance characteristics were obtained, in each case, over the frequency range 0.01 - 100 Hz with the intention of comparing them with those for normal behaviour and thereby indentifying aspects which could be used as tell-tales for malfunction.
The adverse environments investigated were as follows:

i) Precipitation

When glass electrodes are used to monitor a process involving precipitation some of the precipitate may form over the surface of the glass membrane causing it to malfunction. One such precipiate is hydrated aluminium oxide and this was used in the present work to typify the effect.

Hydrated aluminium oxide is precipitated when aqueous NaOH is titrated into an aqueous solution of HCl, AlCl3(anhydrous). The first equilibrium to be established is

$$NaOH + HCl + AlCl_3 \longleftrightarrow NaCl + H_2O + AlCl_3 \qquad (1)$$

but with increased amounts of NaOH the reaction changes to

$$3NaOH + HCl + AlCl_3 \longleftrightarrow Al(OH)_3 + Na_3HCl_4 \qquad (2)$$

The experimental procedure was as follows. Two solutions, one containing 1.39 mol of HCl per litre and the other 200g of $AlCl_3$ per litre, were made up and 300ml of each of these solutions were then mixed together. 100ml of this mixture was measured out and transferred to the experimental vessel, which was then set up as described in Section 6.2.

A solution of 4M NaOH was poured into the right hand burette of the displacement system (see Section 6.2) and the vessel positioned under it so that it could receive the reagent. Distilled water was pumped into the left hand burette at the rate of 5 ml/s, thereby displacing NaOH from the right hand burette at the same rate.

When the required amount of NaOH had been added to the vessel in this way the impedance characteristics were determined over the range 0.01 - 100 Hz. The glass and reference electrodes were then removed, cleaned with 0.1M HF solution and washed with distilled water. The experiment was repeated with the amount of NaOH added to the system as the variable. Both types of glass electrode were tested.

ii) Oil:

The presence a dispersed oil phase in a process stream may result in the membrane being partially coated by it and therefore blanked off. This condition was simulated by smearing "Vaseline" petroleum jelly over approximately half of the membrane. Both types of electrode were treated in this way and their impedance characteristics measured in buffer pH7.

iii) Abrasion:

The membranes of both types of electrode were severely scratched by abrading with emery board (No 2) to simulate the type of mechanical damage which might be inflicted by suspended solids in a process stream. Impedances were again measured in buffer pH 7 over the standard frequency range.

8.3.3 On-line Intermittent Frequency Response

As will be shown in the next Chapter, the results of the frequency response measurements identified a *modus operandi* for on-line integrity assessment which was put to the test using hydrated aluminium oxide precipitate as the adverse environment. For this purpose the experiment was set up as in 8.3.2(i), and the experimentation programmed so that the relay switch transferred connection of the electrodes from the TFA to the multimeter and back to the TFA at prescribed intervals. When attached to the TFA information on the impedance of the glass electrode was provided, and when attached to the multimeter the pH of the $AlCl_3/HCl$ solution was measured. Meanwhile, at intervals, aliquots of NaOH solution were added from the burette by switching the metering pump on and off and this was continued until a point was reached at which the glass electrode malfunctioned, the success of the system being qualitatively determined by its ability to detect malfunction and activate the alarm.

These experiments simulated on-line conditions, and the time spent attached to the TFA for impedance measurements was only a tiny fraction of that spent attached to the multimeter for pH measurement.

8.4 Measurement of Nernstian Slope

The Nernstian slope was determined by dipping the electrode under test into the a series of buffers (pH2, 7 and 9) and in each case determining the E.M.F generated against the calomel reference electrode by connecting to the multimeter via a unit gain high impedance operational amplifier. This method was employed for electrodes as supplied and which had been treated with Vaseline or abraded.

In the case of precipitation the procedure was slightly modified, the electrode being removed from the solution and dipped into pH 3.5 and 4.5 buffers. Determination of the slope was limited to this relatively narrow range because over a wider range any coating of precipitate on the electrode would re-dissolve.

CHAPTER 9 RESULTS AND DISCUSSIONS

9.1 Introduction

The first phase of the experimentation was aimed at identifying effects which were attributable to the methodology, and adjust it accordingly. For this purpose frequency response measurements were made in the benign and reproducible environment of standard buffer solutions. Having established a satisfactory methodology experimentation was continued in standard buffers to provide frequency response data on ten of both type 8400B and 8404S glass. These data were used as a reference against which the behaviour of the electrodes in adverse environments was compared for the purpose of establishing a protocol for testing their integrity. In the final stage of the work the proposed protocol was tested under simulated on-line conditions. The results for each of these stages will now be taken in turn.

9.2 Methodology

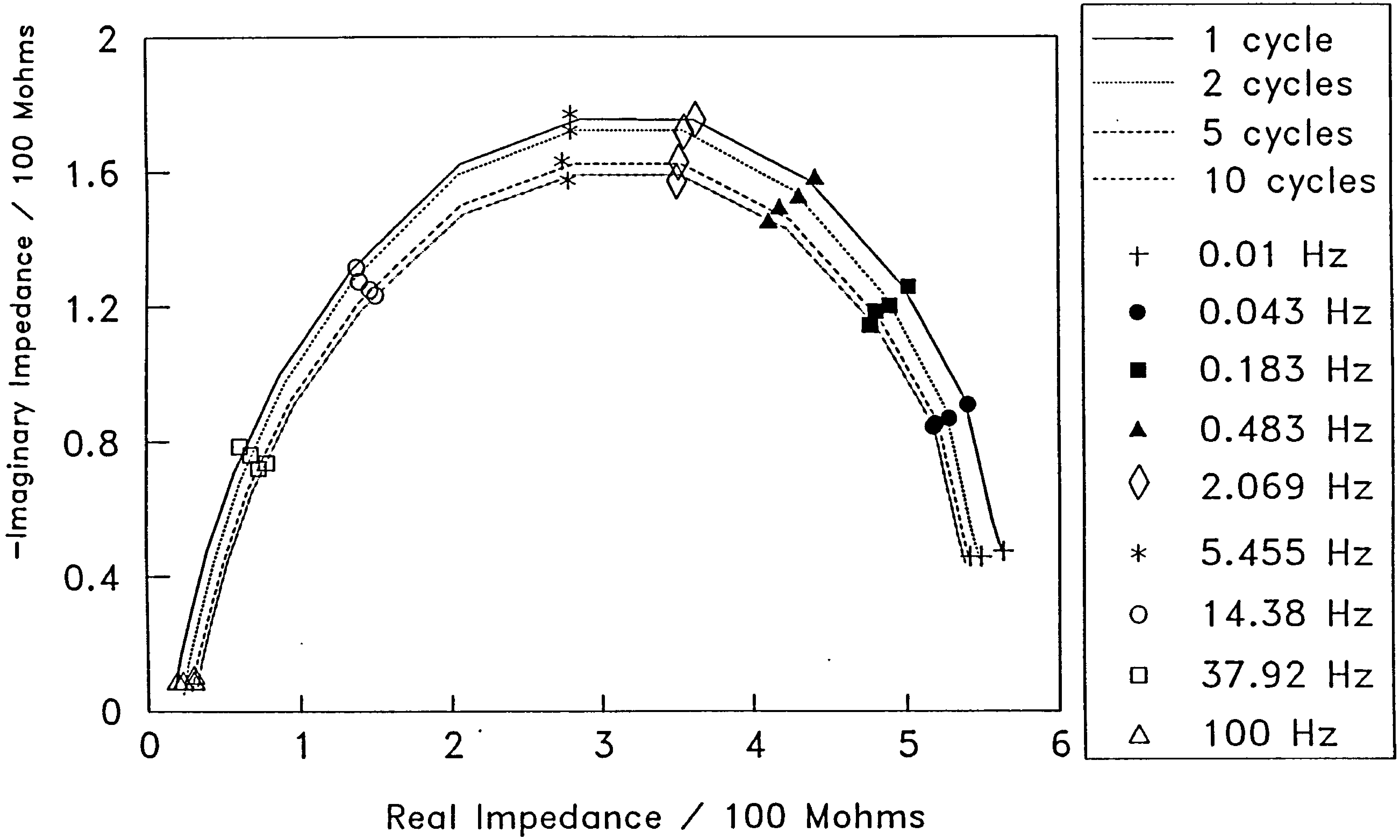
The variables which were tested were the number of cycles over which integration was carried out by the TFA correlator, the amplitude of the signal from the signal generator and the mode of stirring the contents of the vessel in which the electrodes were immersed.

(i) Integration cycles

The effect of varying the number of integration cycles on the form of the frequency response curve, 0.01 - 100 Hz, for a type 8400B electrode at pH 7 is shown in Fig 9.1,

Figure 9.1 Effect of no. of Integration Cycles

Electrode type 8400B / pH 7



where the imaginary and real components of the impedance are plotted against one another for integration cycles ranging from 1 to 10. From the resulting curves it can be seen that the number of integration cycles is a significant factor, the impedance being displaced by roughly 7% at 100 Hz as it increases from 1 to 10. This shift fell to less than 1% from 5 to 10 cycles, and it was concluded therefore that inaccuracies from this source, over the frequency range of interest, were to all intents and purposes eliminated at ten cycles, the figure which was employed for all subsequent experimentation.

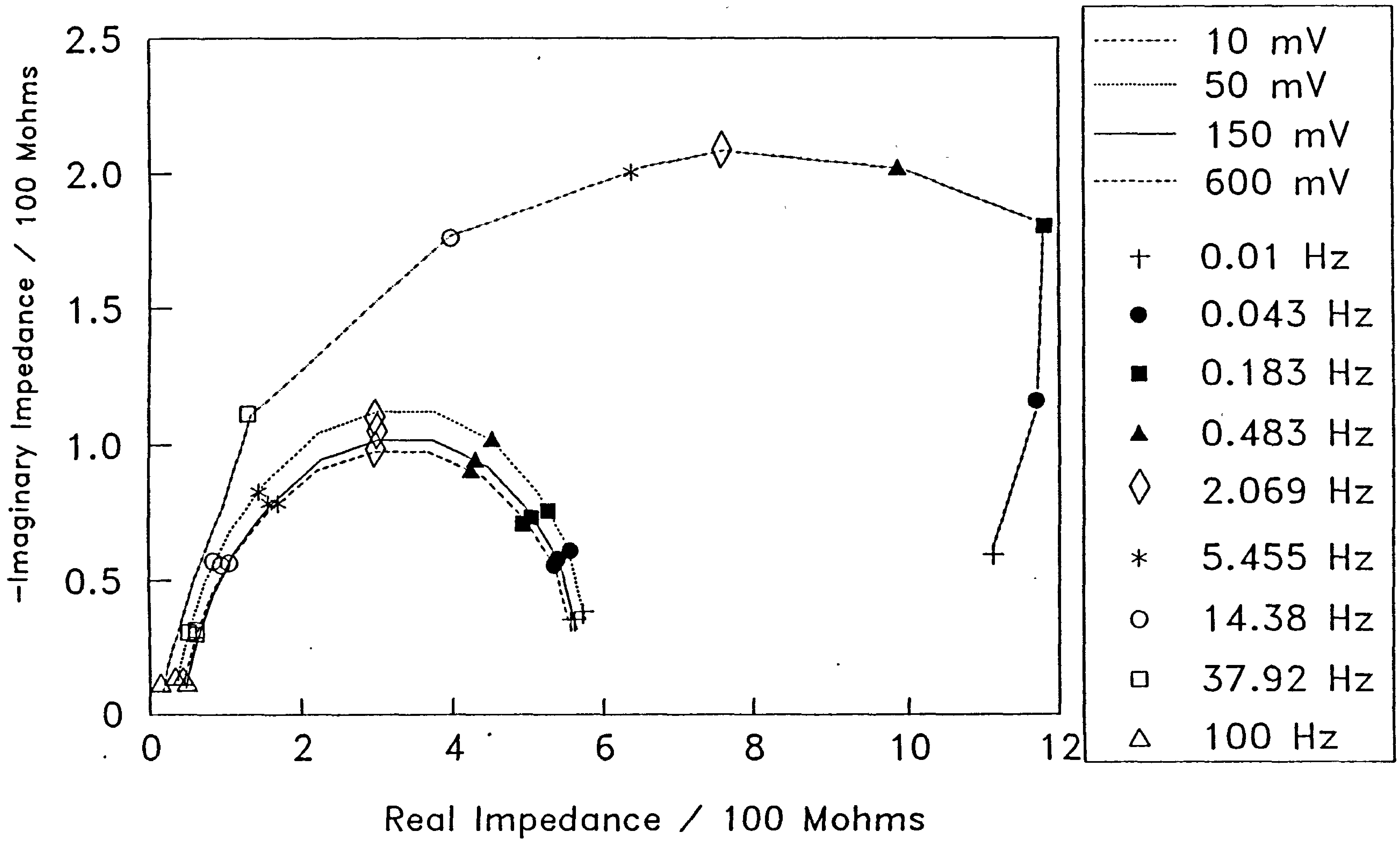
The number of cycles employed affects the experimentation time. At 10 cycles, for instance, an impedance value corresponding to a signal frequency of 0.01 Hz would take 1000 seconds for the integration to be completed. In the interests of shortening the time of experimentation it is therefore important that the number of cycles is kept as low as possible, but this clearly must not be pursued at the expense of accuracy. These considerations become even more important in the context of the on-line monitoring of an electrode; for under these circumstances the time spent in a frequency response mode is time not spent in measuring pH, and it should therefore be kept as short as possible.

(ii) Signal Amplitude

The effect of varying the signal amplitude from 10 to 600 mV on the frequency response observed for a type 8400B glass electrode in buffer pH 7 is shown in Fig 9.2 over a frequency range 0.01 to 100 Hz. Using mutual consistency

Figure 9.2 Effect of Signal Amplitude

Electrode type 8400B / pH 7



as a criterion, it is seen from this figure that with an increase in signal amplitude there comes an apparent increase in accuracy of the data produced. At very low amplitudes, in the region of 10 mV, the A.C currents generated against the high impedance of the glass electrode will be very small, less than 10^{-11}A at the lower frequencies, and perhaps comparable to possible leakage currents. This effect will become progressively less evident as the signal amplitude widens and possibly accounts for the effects observed.

With increasing amplitude non-linearities in the system will become more and more apparent, and for this reason investigations of this nature usually employ the lowest amplitude which is commensurate with acceptable levels of accuracy. In the present work it was decided from the observations that an amplitude of 150 mV provided a good compromise.

(iii) Mode of stirring

The results of investigations into the effect of bubble stirring, mechanical stirring and no stirring on the impedance of electrode type 8400B at pH 7 are shown in Fig 9.3.

From this figure it is seen that the impedance observed in the presence of bubble stirring is strikingly different from that for mechanical and no stirring, which are in fact in close agreement. The reason for this

Figure 9.3

Effect of stirring

Electrode type 8400B / pH 7

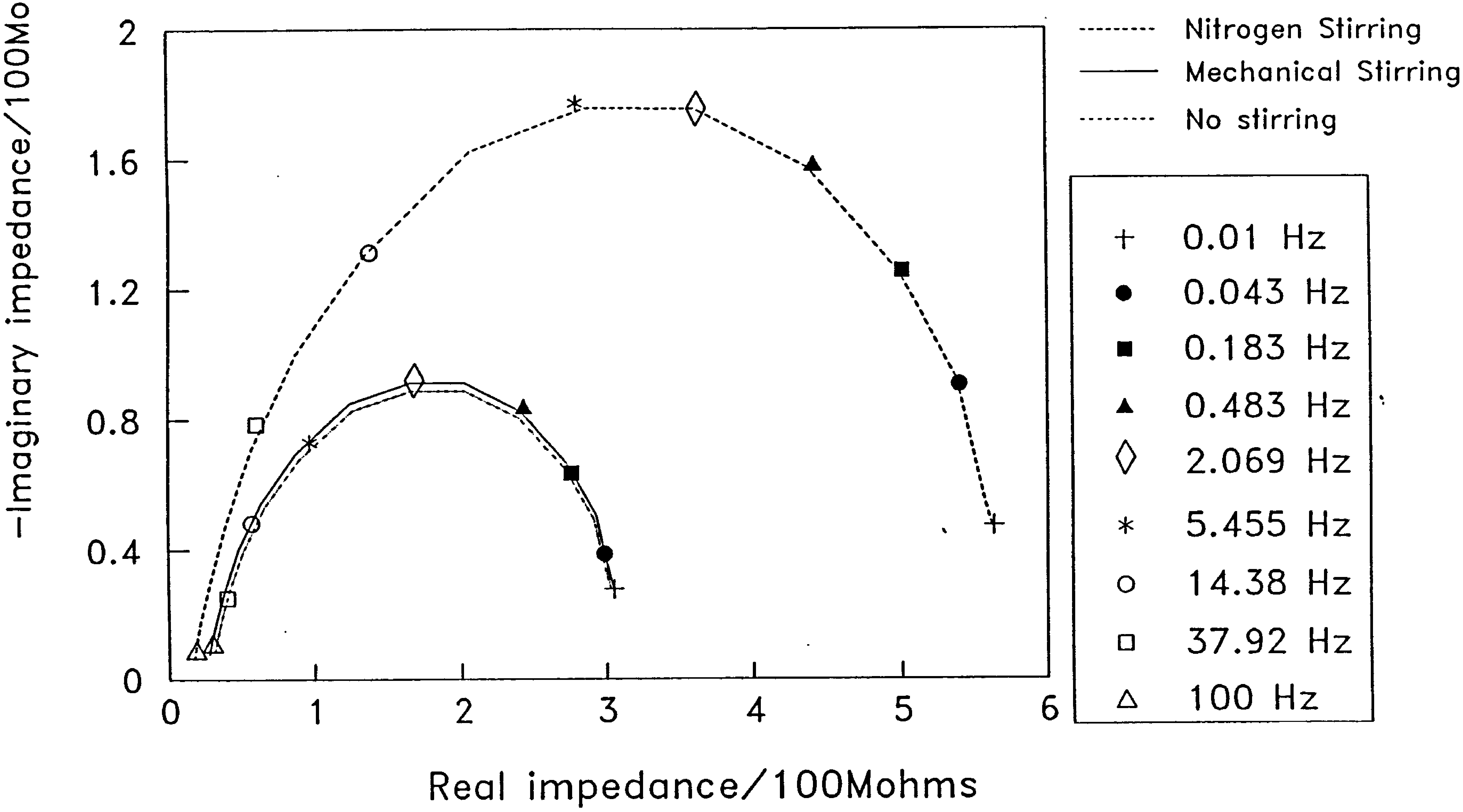
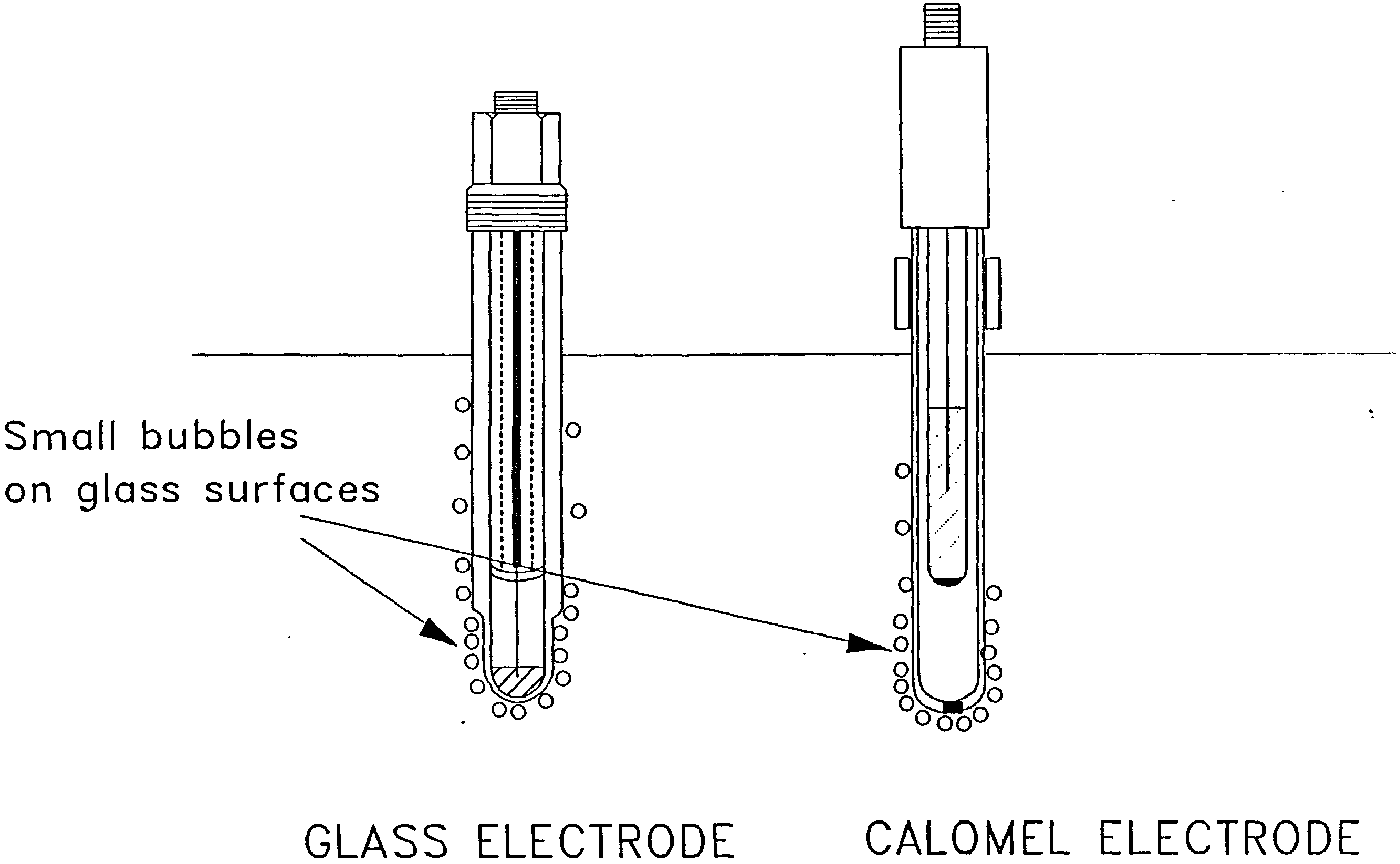


Figure 9.4 Bubble Adhesion to the electrode surface during bubble stirring



became clear when visual inspection showed that with bubble stirring the glass and reference electrodes took on the appearance illustrated in Fig 9.4. This shows small bubbles adhering to the surface of both electrodes, which with regard to the glass electrode has a blanking off effect thereby raising its impedance. It is clear that this effect would be variable from one run to another and in the interests of producing consistent data bubble stirring was abandoned in favour of mechanical stirring.

It is also evident from Fig 9.3 that in a standard buffer reliable impedance measurements can be made in the complete absence of stirring. This, however was not an option in the present studies because in later stages of the work stirring was required to ensure that reagants added to the system were rapidly and uniformly dispersed.

9.3 Frequency Response in Standard Buffers

Frequency response was measured in standard buffers of pH 2, 4, 7 and 9 (see Section 8.3.1) to obtain information on the reproducibility of the data, the consistency between electrodes of the same proprietary type, the effect of pH and the effect of ageing. Nernstian slopes were also measured. The results are discussed under the relevant headings below.

(i) Reproducibility

Impedance data for ten electrodes of type 8404S and six of 8400B in buffer pH7 were obtained over a frequency range 0.01 to 100 Hz, three runs being carried out for each one. Typical results are shown in Figs 9.5, 9.6, 9.7, and 9.8, and it is plain from these figures that the data for any particular electrode are reproducible to within approximately 1%.

Over the frequency range employed the form of the curves from the two types of electrode is quite different. For the type 8404S the frequency response would appear to be represented by a small "semi-circle" at high frequencies preceded by a much larger "semi-circle" at low frequencies. The term "semi-circle" is used somewhat loosely, because they are clearly flatter than this description would suggest. If they had been true semi-circles it would have implied that these electrodes could have been represented by an equivalent circuit comprising two parallel R-C circuits in series with significantly different time constants (c.f Section 2.2). The fact that they are not true semi-circles suggests that the equivalent circuitry is more complex, a point that has already been discussed in Section 5.

The form of the type 8404S frequency response was not surprising and does no more than echo the findings of Sandifer and Buck, described in Section . Recalling their work they suggested that the two "semi-circles" implied that the behaviour of the electrode was dominated by two RC circuits in series, one corresponding to the ohmic resistance and geometric capacitance of the glass

Figure 9.5 Reproducibilty

Electrode type 8404S / pH7

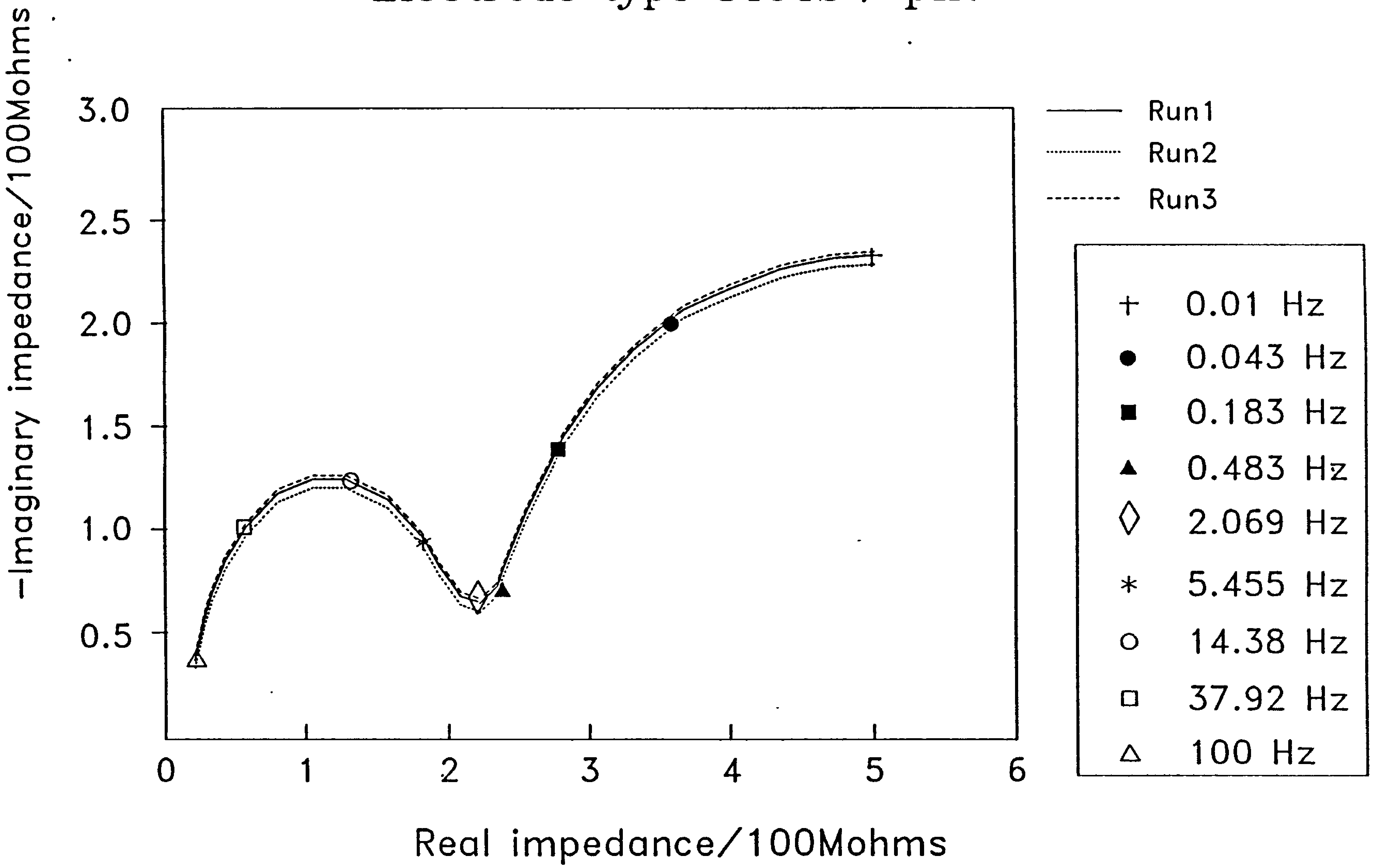


Figure 9.6 Reproducibilty

Electrode type 8404S / pH7

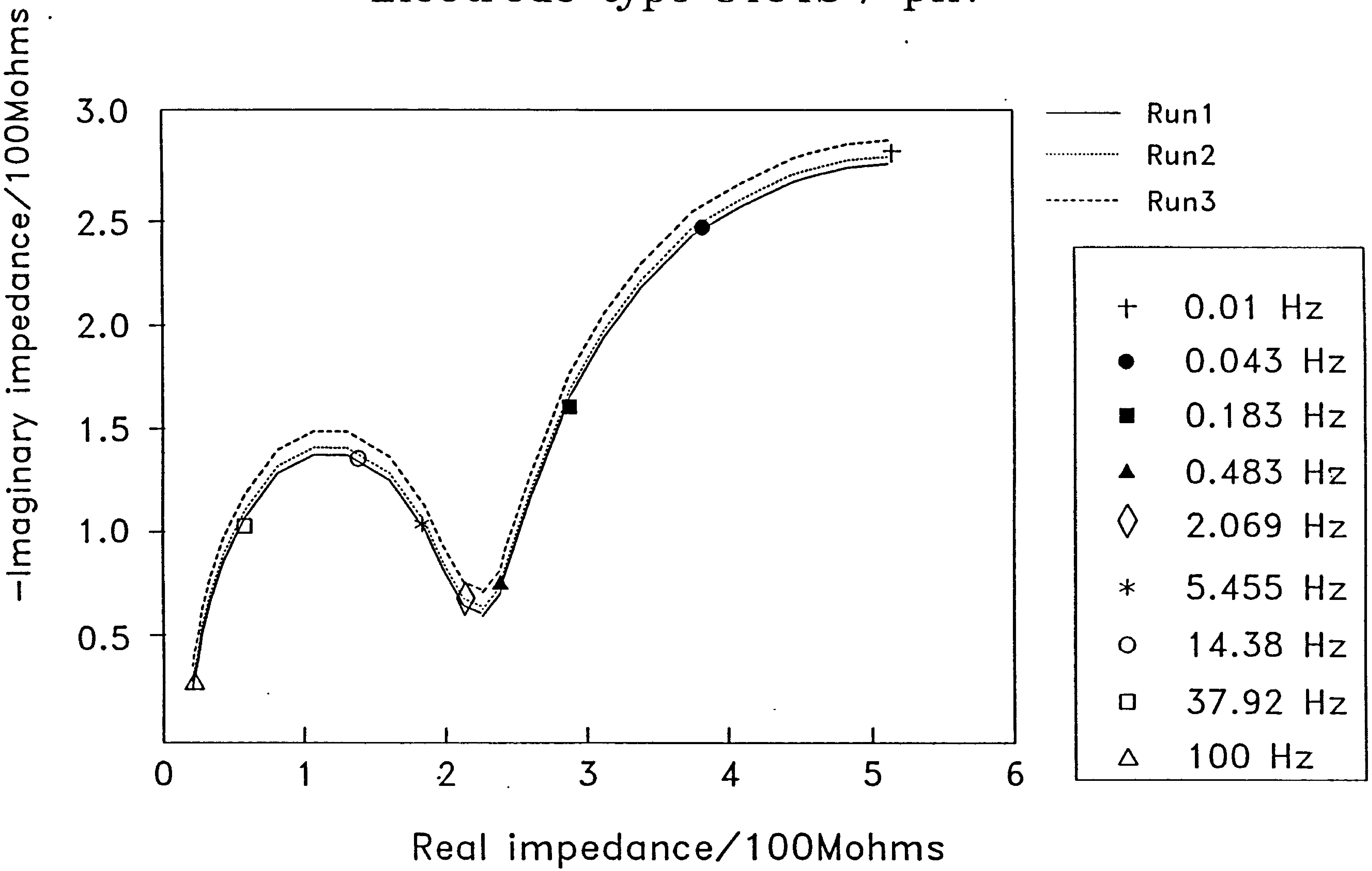


Figure 9.7 Reproducibility

Electrode type 8400B/pH7

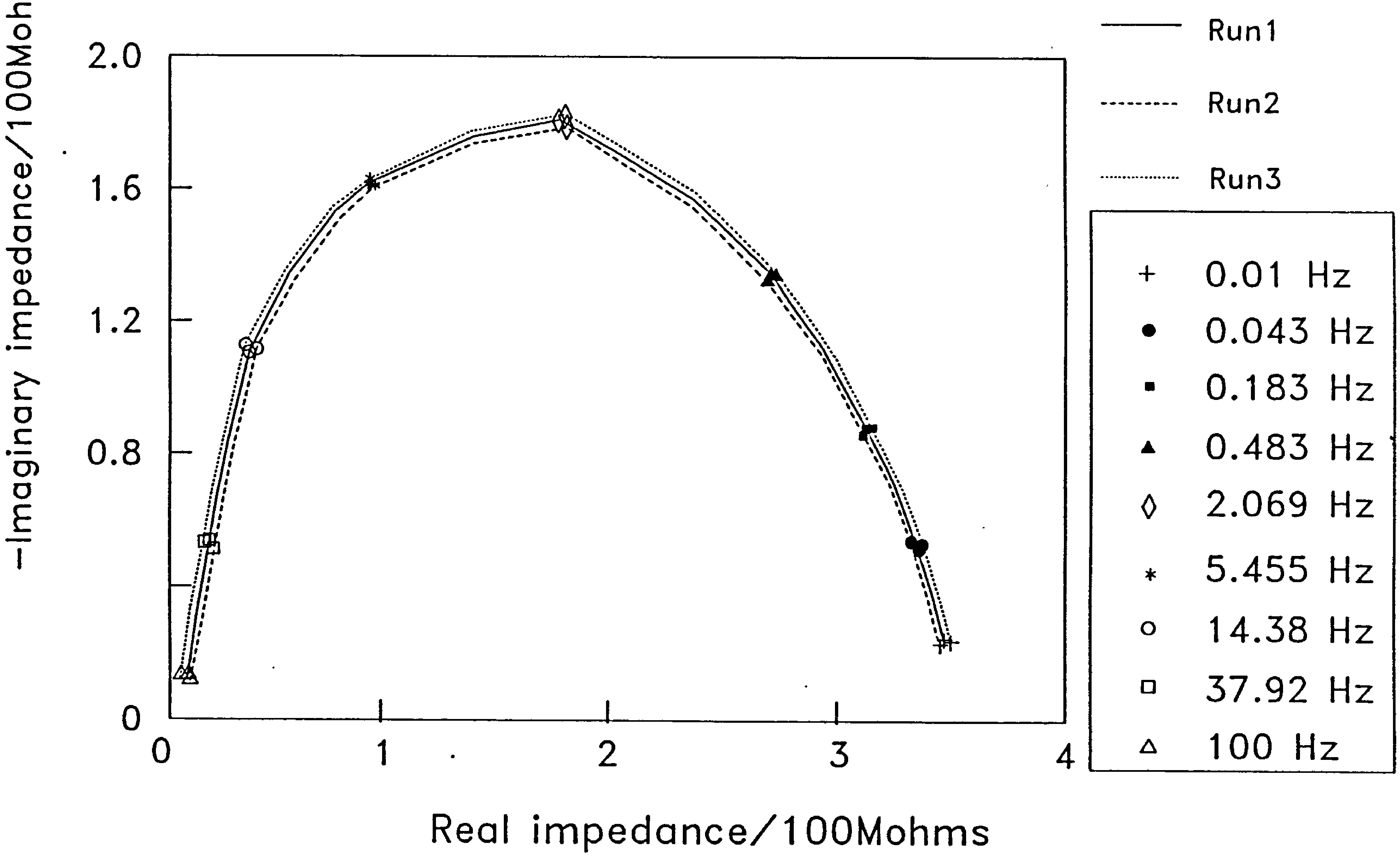
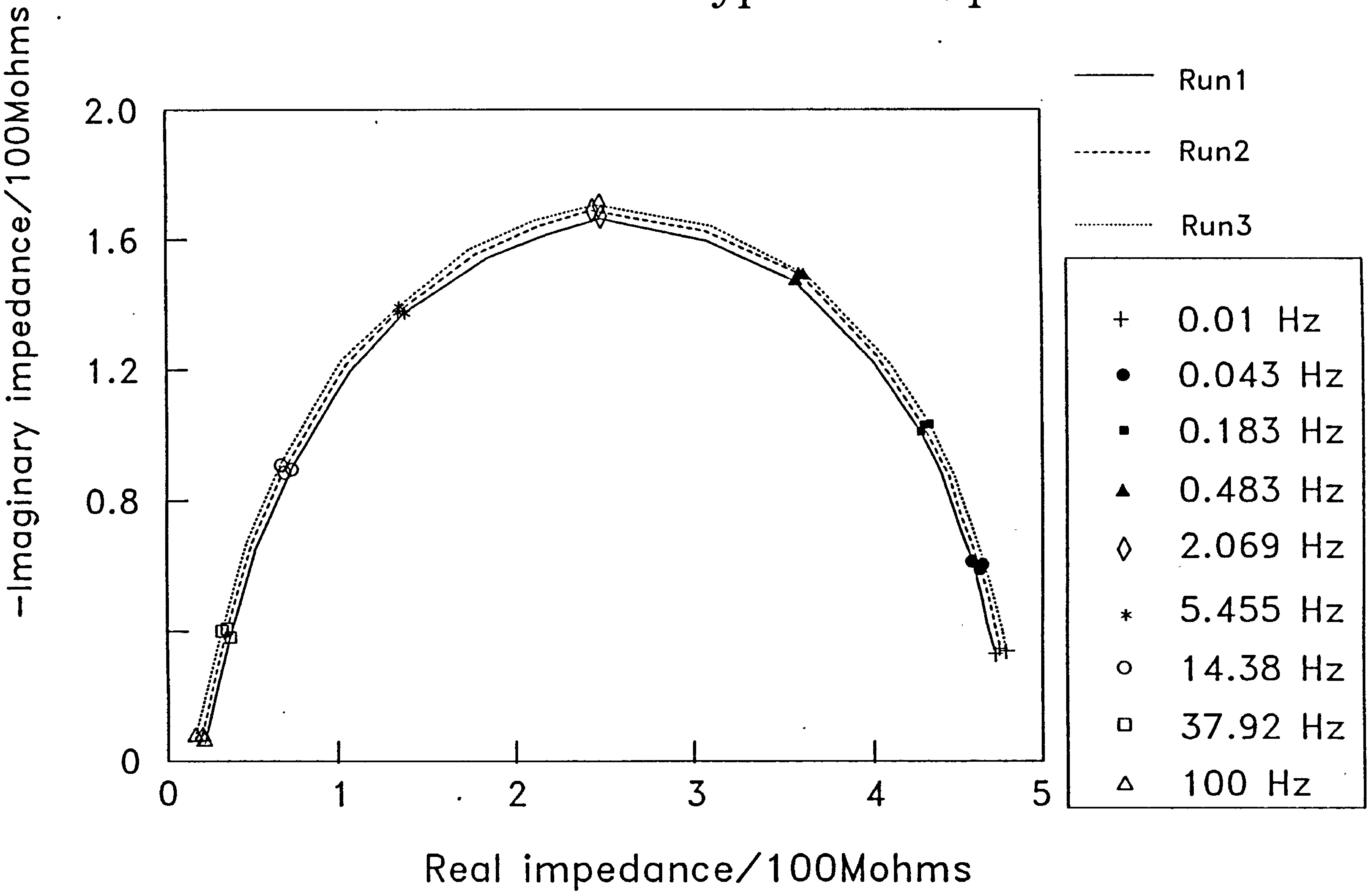


Figure 9.8

Reproducibility

Electrode type 8400B/pH7



membrane and the other to the activation resistance of slow ion exchange at the membrane surface and a double-layer capacitance. The former was associated with high frequencies and the latter with lower frequencies.

There are, however, some marked differences between the present observations and those of Sandifer and Buck. Firstly the impedances reported in their work are in the order of megohms, whereas those now reported are in the order of 100's of megohms, and are consistent, it should be pointed out, with the "D.C resistance" values of 150 to 600 megohms quoted by the manufacturer. Secondly, Sandifer and Buck found that the peaks of the semi-circles occurred at 356 Hz and 63 Hz, whereas in the present work the peak on the high frequency semi-circle occurred at about 20 Hz and that on the incomplete low frequency semi-circle at about 0.01 Hz.

These deviations can presumably be ascribed to material and physical differences between the electrodes employed, those of Sandifer and Buck being Beckman G.P type which could be quite dissimilar from the Polymetron types used in the present work. These differences may very well affect the bulk and surface impedances to different degrees; a change in membrane thickness for instance could have a marked effect on the former but not the latter. This raises the point that the semi-circles in the present work may be transposed compared to those of Sandifer and Buck, the bulk impedance now being associated with the right hand semi-circle and the left one with the surface processes. If this is so the peak of the semi-circle for the surface processes would correspond, in the present work, to 20 Hz as opposed to Sandifer's value of 63 Hz, and the ion exchange "transfer resistance" to 200 MΩ as opposed to 10 MΩ.

The impedance plots relating to type 8400B electrodes in Figs 9.7 and 9.8 revealed only one semi-circle over the frequency ranges investigated, showing no signs of a second forming even at 0.01 Hz. Experiments were therefore carried out over much higher frequencies, up to 1000 Hz, and much lower, down to 10^{-4} Hz, to explore the possibility of a second semi-circle appearing in these regions. At the highest frequencies, Fig 9.9, the impedance simply continued its progression towards the origin, and at the lower frequencies, Fig 9.10, erratic, and in consequence inconclusive, behaviour was observed. This behaviour may have been due to limitations of the circuitry or perhaps to noise which could have been eliminated by increasing the number of integration cycles from 10 to some higher figure. This would have been very time consuming (1 cycle at 10^{-4} Hz takes approximately 3 hours) and since this aspect of the work was a digression from the central task it was abandoned.

It should be said in passing, however, that the presence of one rather than two semi-circles is not necessarily in conflict with Sandifer and Buck's twin parallel RC model.

Figure 9.9 High frequency characteristics
Electrode types 8404S/8400B at pH 4

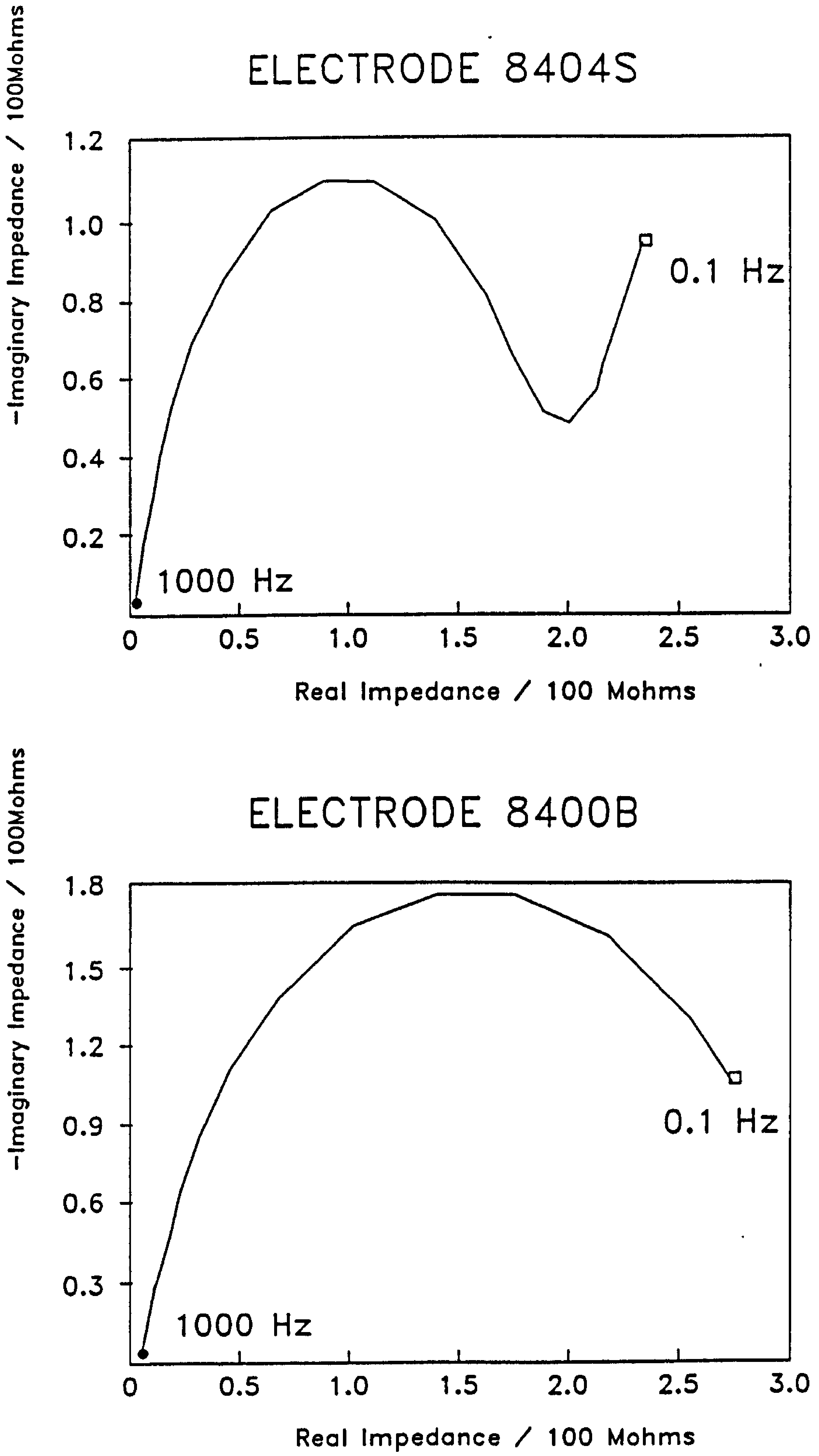
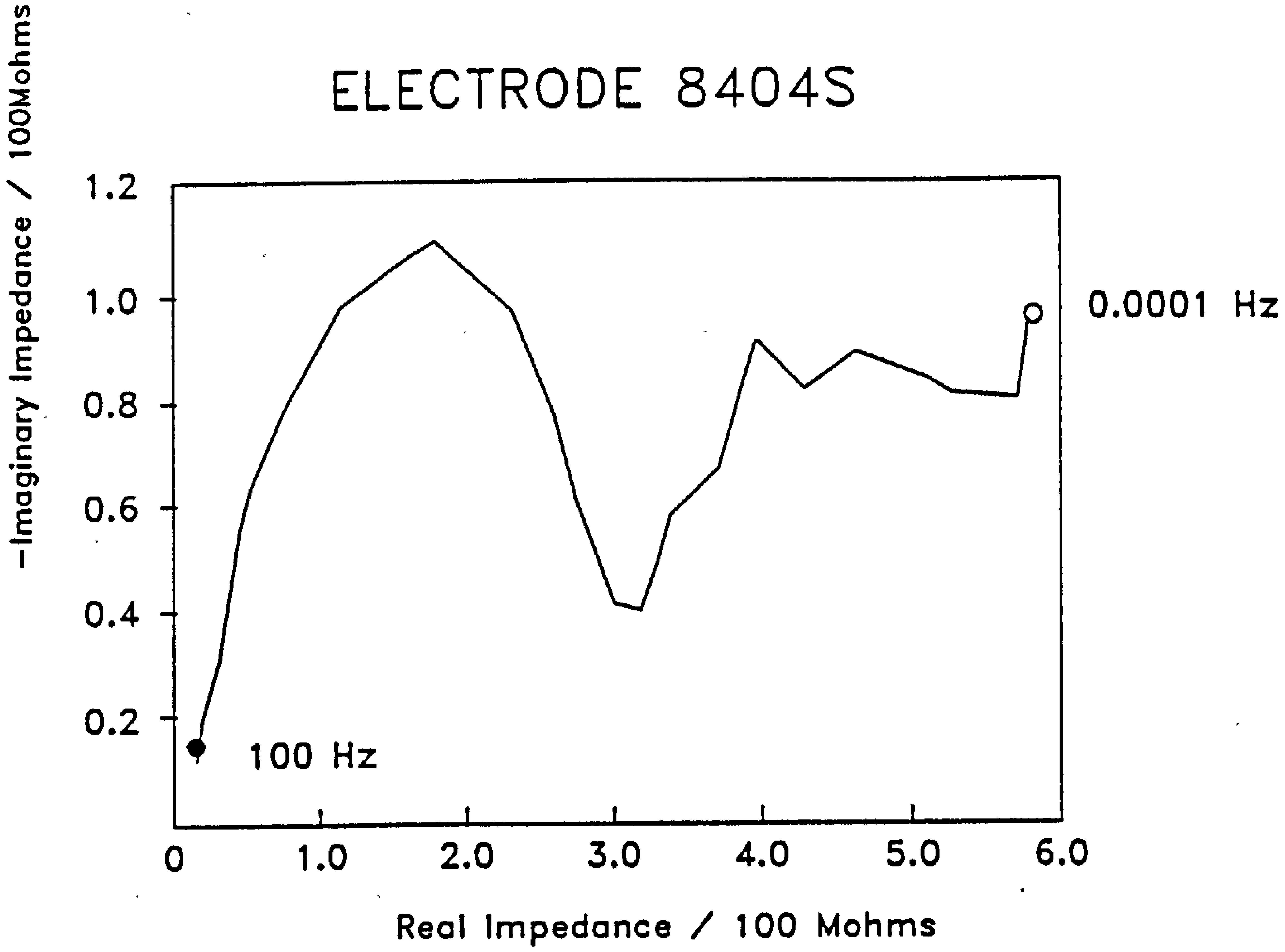
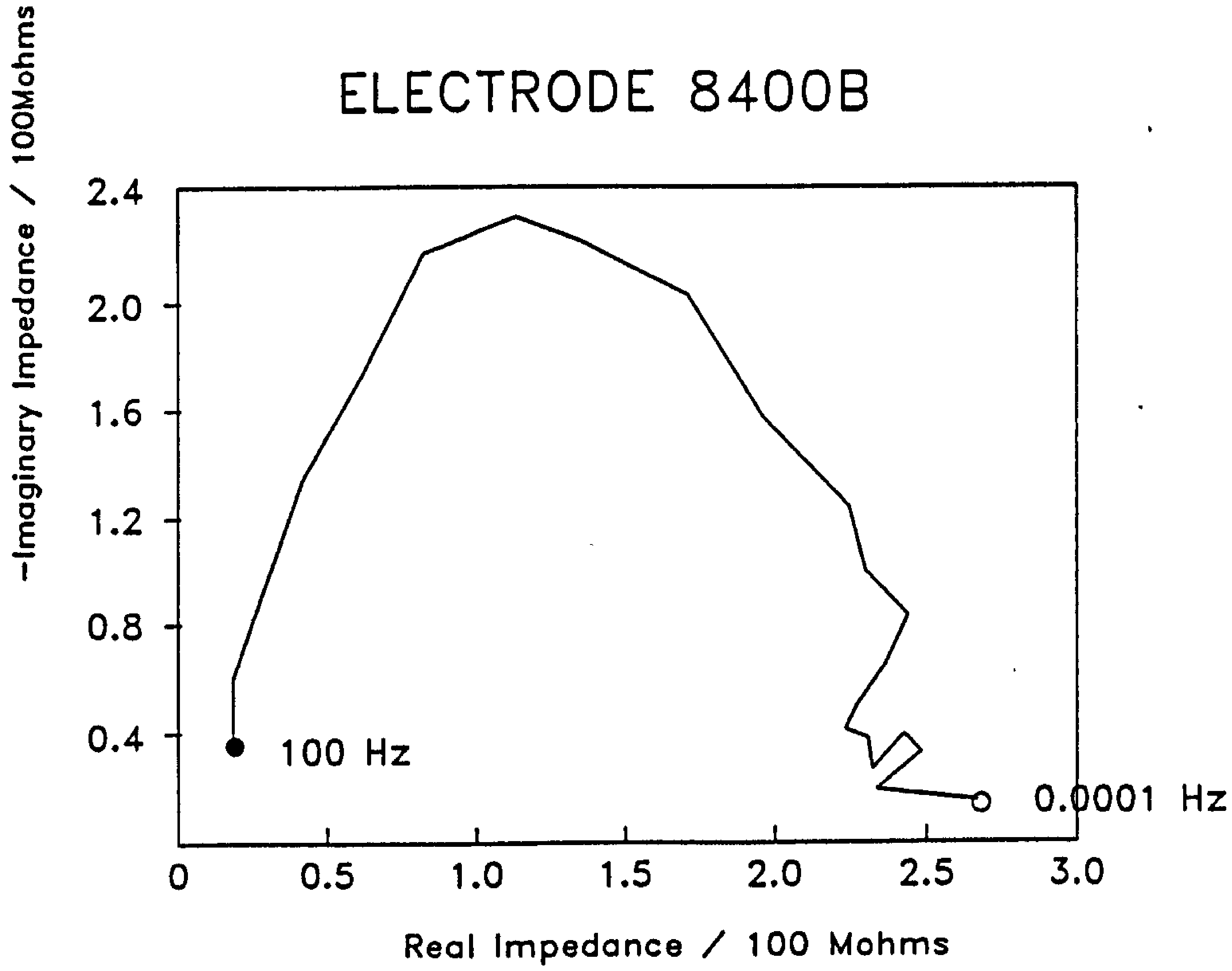


Figure 9.10 Low frequency characteristics

Electrode types 8404S/8400B at pH 4





It may simply imply that for electrode type 8400B the impedances of the surface processes and the membrane bulk give rise to time constants of similar magnitude.

(ii) Behavioural Consistency

The frequency response of three different samples of electrode type 8404S in buffer pH 7 are presented in Fig 9.11 for a frequency range of 0.01 to 100 Hz. Over this small sample it is seen that two of the electrodes show almost identical behaviour, but the third, although having the same "twin hump" shape, displays impedance values which are considerably different, in fact up to 15% lower on the real axis, and 50% lower on the imaginary. It is clear therefore that the characteristics of one electrode cannot automatically be transferred to another even though they are nominally of the same type.

(iii) Effect of pH

The frequency response characteristics of an electrode type 8404S at pH values of 2, 7 and 9 are presented in Fig 9.12 for a frequency range of 0.01 to 100 Hz. All the curves have the same twin-hump shape, and are fairly close together. This superficial agreement between the curves, however, tends to mask underlying differences which become more apparent when groups of points corresponding to the same frequency are compared. When this is done the effect of pH is seen to be more complex than would appear at first sight. For example, at the lower frequency 0.01 Hz, the highest real component of

Figure 9.11 Comparison of electrodes within a group

Electrode type 8404S

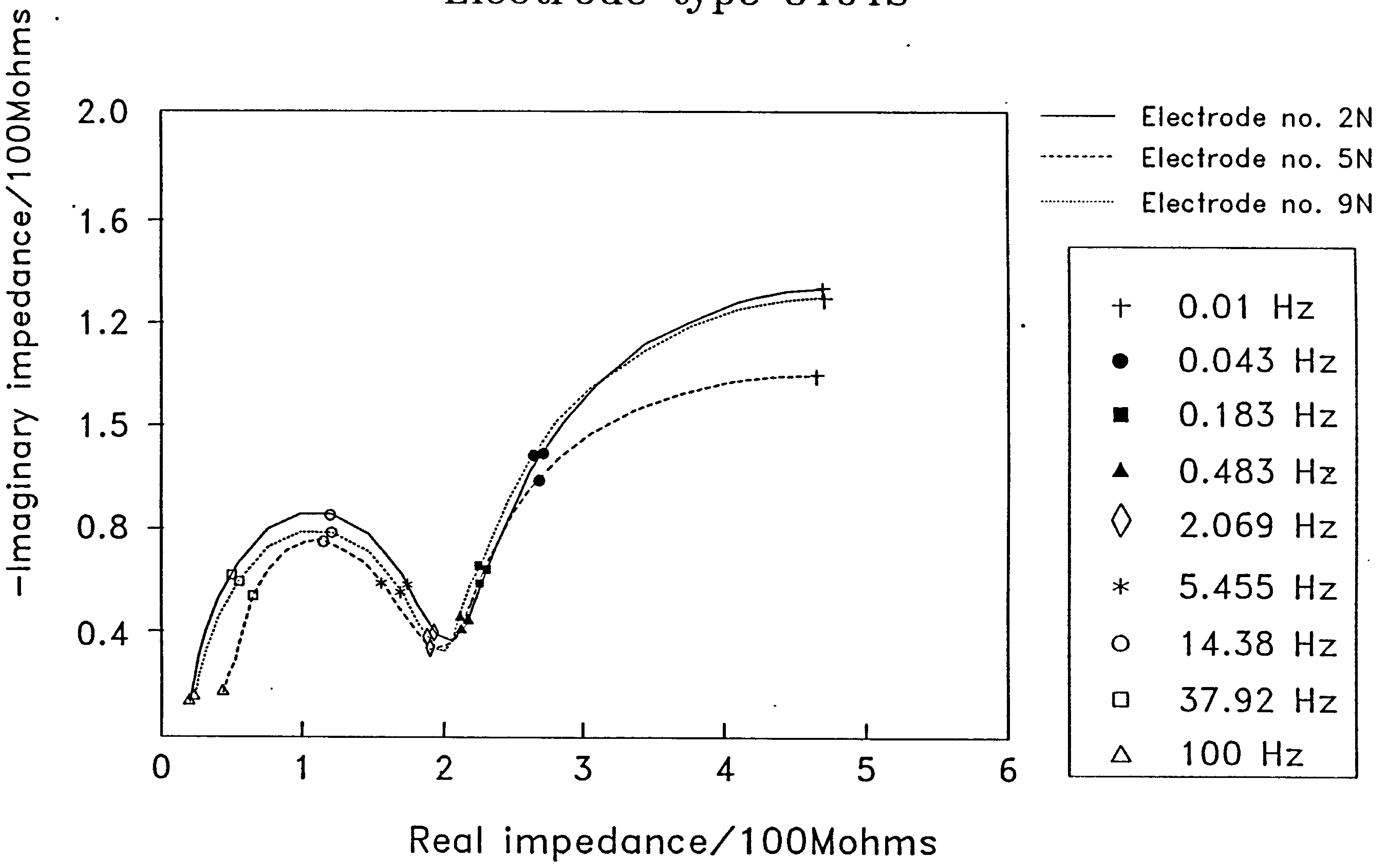
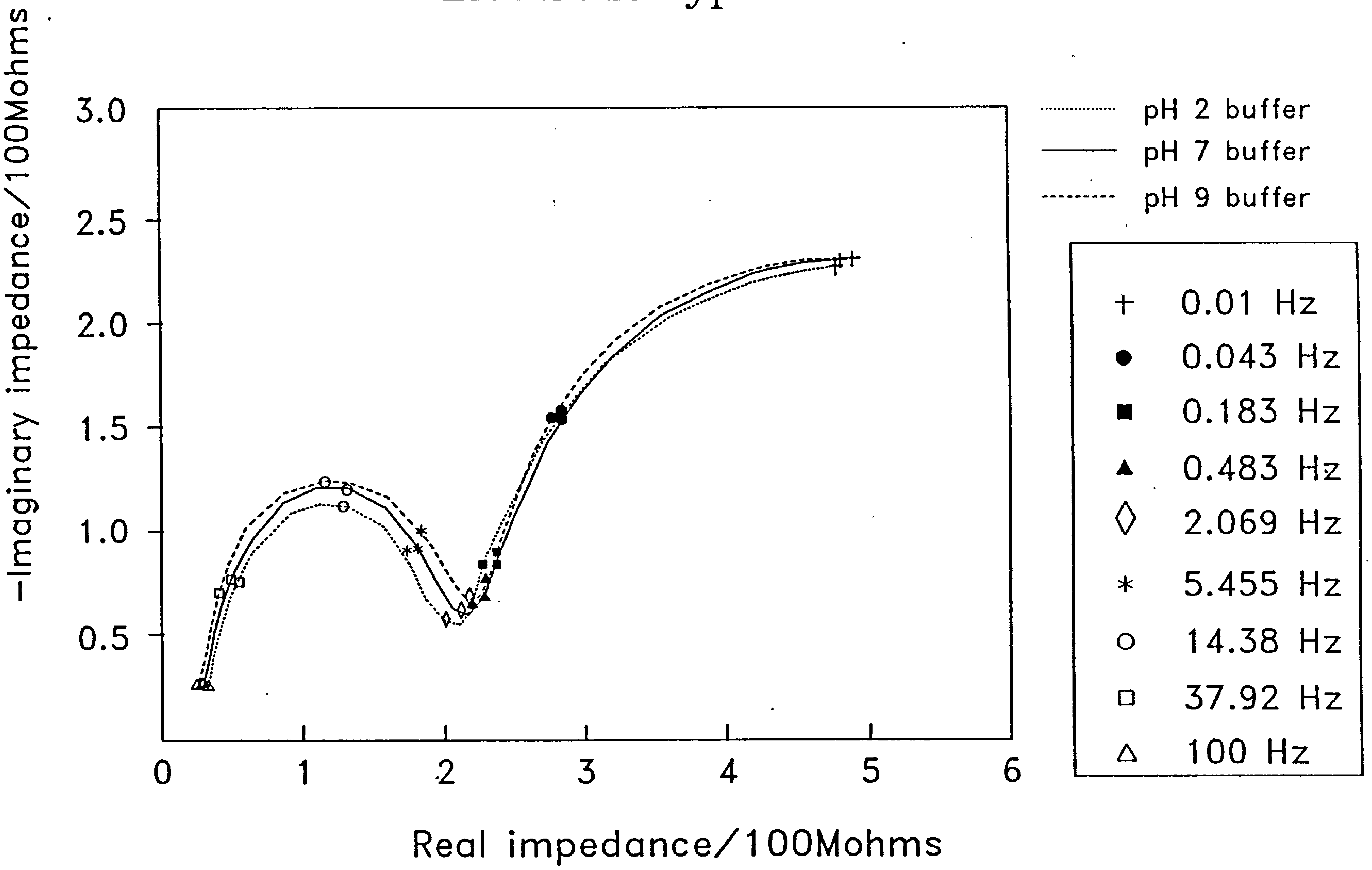


Figure 9.12



Effect of pH

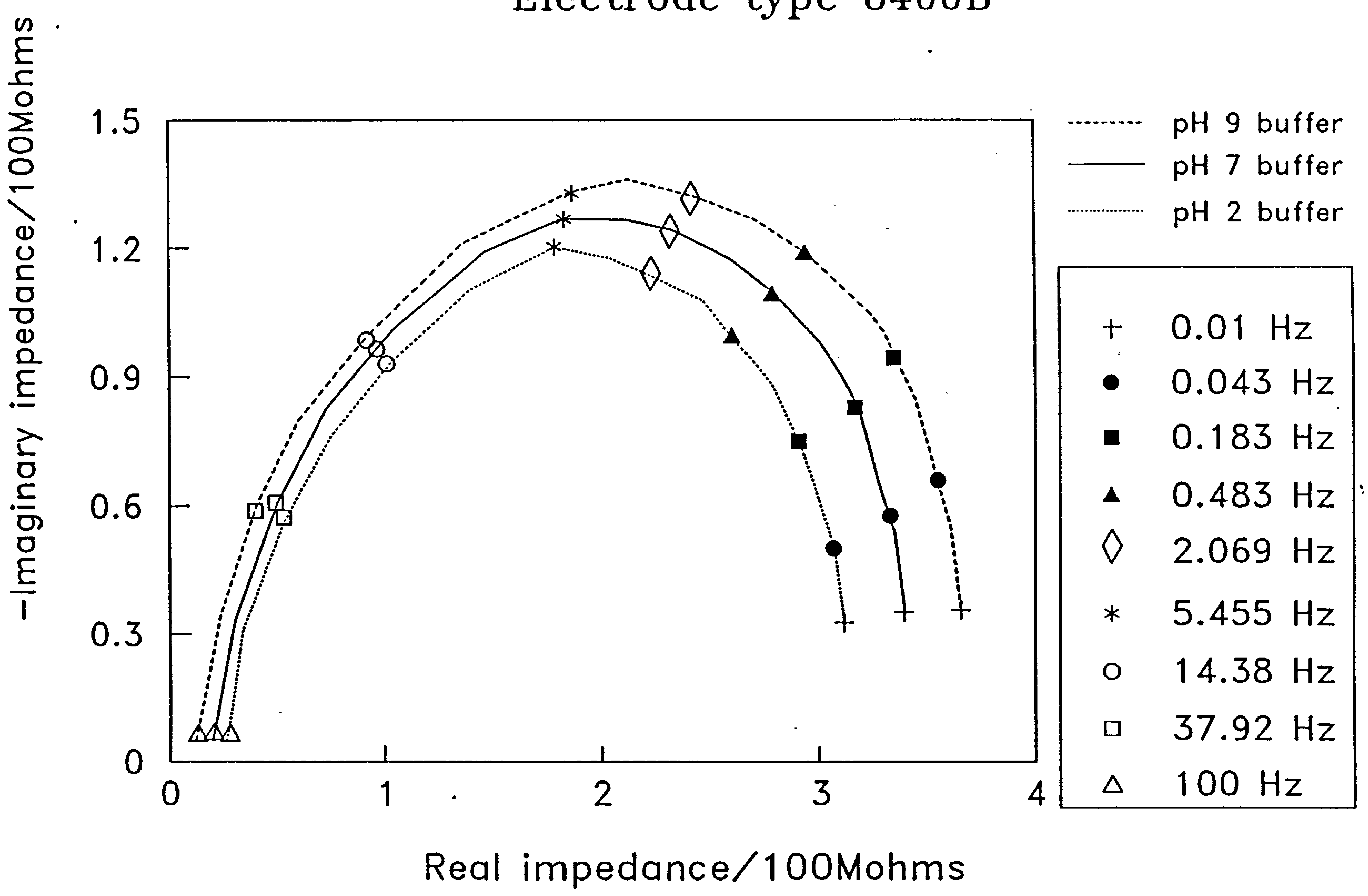
Electrode type 8404S

impedance corresponds to the highest pH, namely pH 9, but as the frequency is raised this component falls relatively more quickly at high pH so that by the time the frequency has reached 100 Hz the position is reversed, and pH 2 corresponds to the highest real impedance value. Looking at the imaginary component in the same way reveals that there is virtually no effect of pH at the highest and lowest frequencies, but in the mid range, particularly around 3 Hz a drop in pH produces a fall in this component. These effects produce differences of up to 30% in the real and 40% in the imaginary component as the pH goes from 2 to 9.

The characteristics for an electrode type 8400B for the same pH range are shown in Fig 9.13. As expected they take the form of single semi-circles and are arranged in a fashion which is broadly speaking concentric. The order which the curves take up, however, bears no simple relationship to pH, the outermost being for pH 9, the innermost pH 7 and the intermediate one pH 2.

Taking groups of points corresponding to the same frequency it can be seen that, although in the middle of the frequency range (2.069 Hz) the real component of impedance is virtually the same for pH 7 and pH 9, at the highest frequency the value for pH 9 is some 50% less than that for pH 7. At the lowest frequency the opposite is true, pH 7 now has the lower value but not proportionally by the same amount, 13% in fact. As noted

Figure 9.13



Effect of pH

Electrode type 8400B

before the values for pH 2 fall in between these two. This behaviour is reversed in the imaginary component, the values for pH 7 and pH 9 being roughly the same at the high and low ends of the frequency range, but differing in the middle of the range, that for pH 9 being greater by some 15%. Again the values for pH 2 lie between those for pH 7 and pH 9.

Nernstian slopes were also measured at this stage of the work. From the relationship between pH and E (electrode potential) given by equation 7 (Section 3.23) it follows that the Nernstian slope, the rate of change of E with pH, will theoretically be given by

$$\frac{\Delta E}{\Delta(pH)} = \frac{2.303RT}{F}$$

with F equal to 96487 Coulombs, R, 8.314 J/mol K [AVS/mol k] and T, 298 K the above gives a value of 59.1 mV per pH. Typical values observed in the present work for both types of electrode are presented in Table 9.14 below, and on average are seen to be within 2% of the calculated value i.e within the accuracy of the buffers.

TABLE 9.14 ELECTRODE POTENTIALS AND NERNSTIAN SLOPES: Clean Environment

Electrode Type	Buffer pH	Electrode Potential E, mV	Nernstian Slope mV/pH (average)
8404S	2	-240	
	7	51	58.4
	9	168	
8400B	2	-256	
	7	38	58.7
	9	155	

(iv) Effect of Ageing

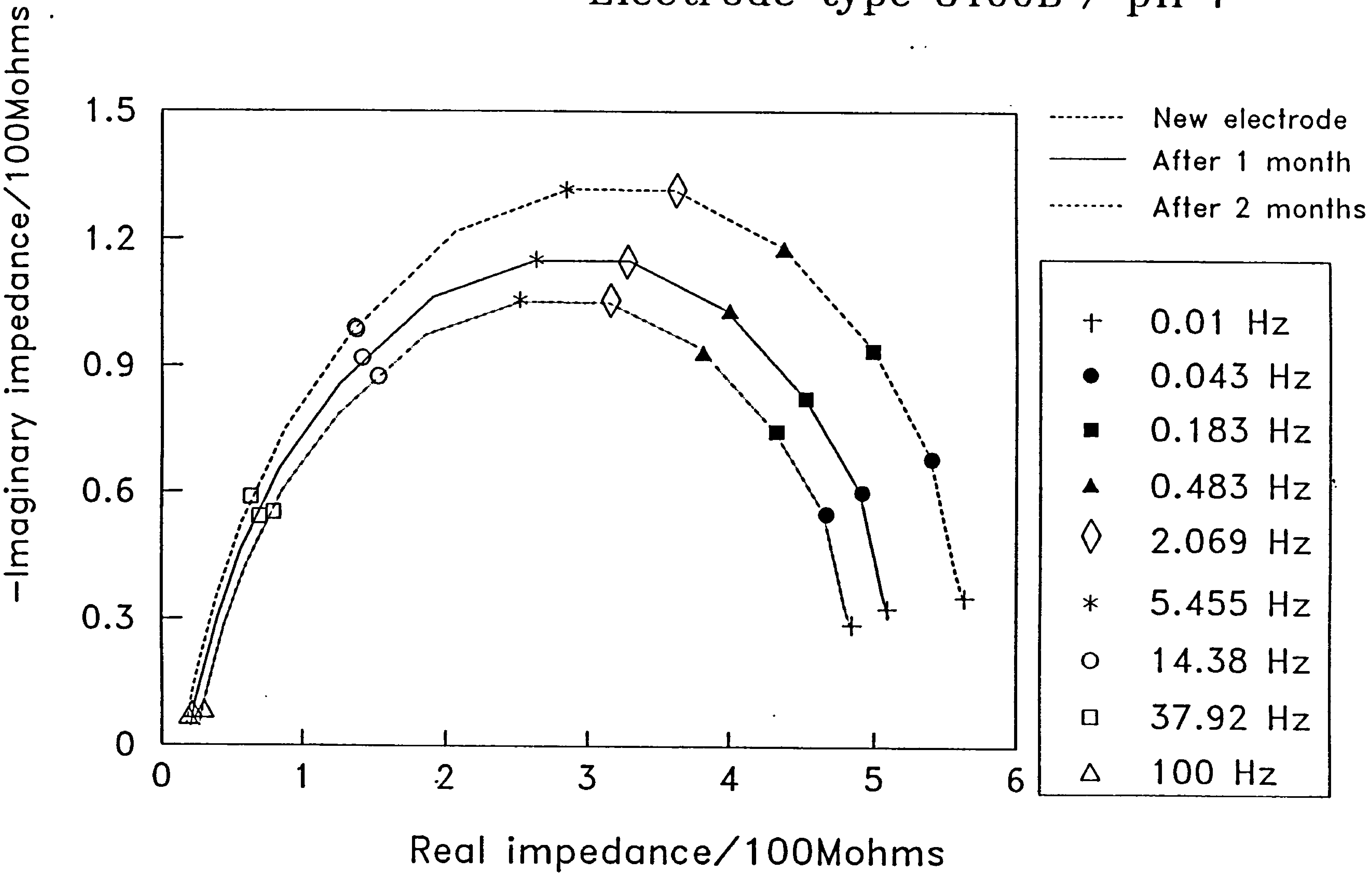
A type 8400B electrode was left in a pH 7 buffer for a period of two months and at intervals of time its frequency response was determined. The initial impedance plot and plots after periods of time of one month and two months are shown in Fig 9.15.

Over the two month period it can be seen that at the higher frequencies (>= 14.38Hz) the real component of impedance tended to drift upwards whereas at the lower frequencies the opposite was true. The changes which occurred were of the order of 20%, with the rate of change falling at the lower frequencies but holding up at the higher. Over the same period the imaginary component remained virtually unchanged at the high and low end of the frequency band (100 and 0.01Hz) but tended to drift downwards, albeit at a decreasing rate, at the

Figure 9.15

Effect of ageing

Electrode type 8400B / pH 7



intermediate frequencies. At 2.069 Hz the fall over 2 months was of the order of 25%.

It is presumed that the ageing effect is due to increased hydration of the membrane interphase, which would affect the ion exchange properties of the electrode and hence the 'transfer resistance' and double layer capacity. If this is so it would tend to indicate that the 'single hump' response over the 0.01 - 100 Hz range has some association with these surface processes.

9.4 Adverse Environments

Environments were used which were intended to simulate the effects of precipitation, the presence of an immiscible oil phase and physical damage, and the results obtained will now be discussed.

(i) Precipitation

The addition of NaOH solution to a stirred solution of $HCl/AlCl_3$ results in the formation of a white precipitate, alumina, at pH's in excess of pH 2.

This precipitate remains in evidence until the pH of the solution is increased by the addition of excess NaOH to a value above pH 10, at which point the precipitate dissolves to give a solution of a slightly hazy appearance.

The reaction follows the equilibrium

$$3NaOH + HCl \longleftrightarrow Al(OH)_3 + NaHCl_4$$

Dissolution in the presence of excess NaOH is due to the formation of the complex aluminate, $NaAlO_2$.

In order to investigate the system, which was known (see Section 8.3.1) to impair the performance of the glass electrodes, 100 ml of an aqueous solution, 0.7M wrt HCl and 1.5M wrt $AlCl_3$, was gradually neutralised by the addition of 4M NaOH. At pH 2.9 a precipitate appeared which, with further addition of NaOH, initially became thicker and then began to redissolve, eventually disappearing again at pH 5.5. By observing the behaviour of both types of glass electrode at a number of intermediate pH levels it was possible to gain some idea on how their behaviour was dependent on the amount of precipitate present. In practice this was achieved by adding the NaOH stepwise and after each addition carrying out a frequency response run. Nernstian slopes were measured as described in Section 8.4

After exposure to the precipitate the electrodes were cleaned by dipping into 0.1M HF and their frequency response determined again.

Typical impedance behaviour for both types of electrodes is shown in Figs 9.16 and 9.17, in which behaviour in a

Figure 9.16 Effect of precipitate

Electrode type 8404S

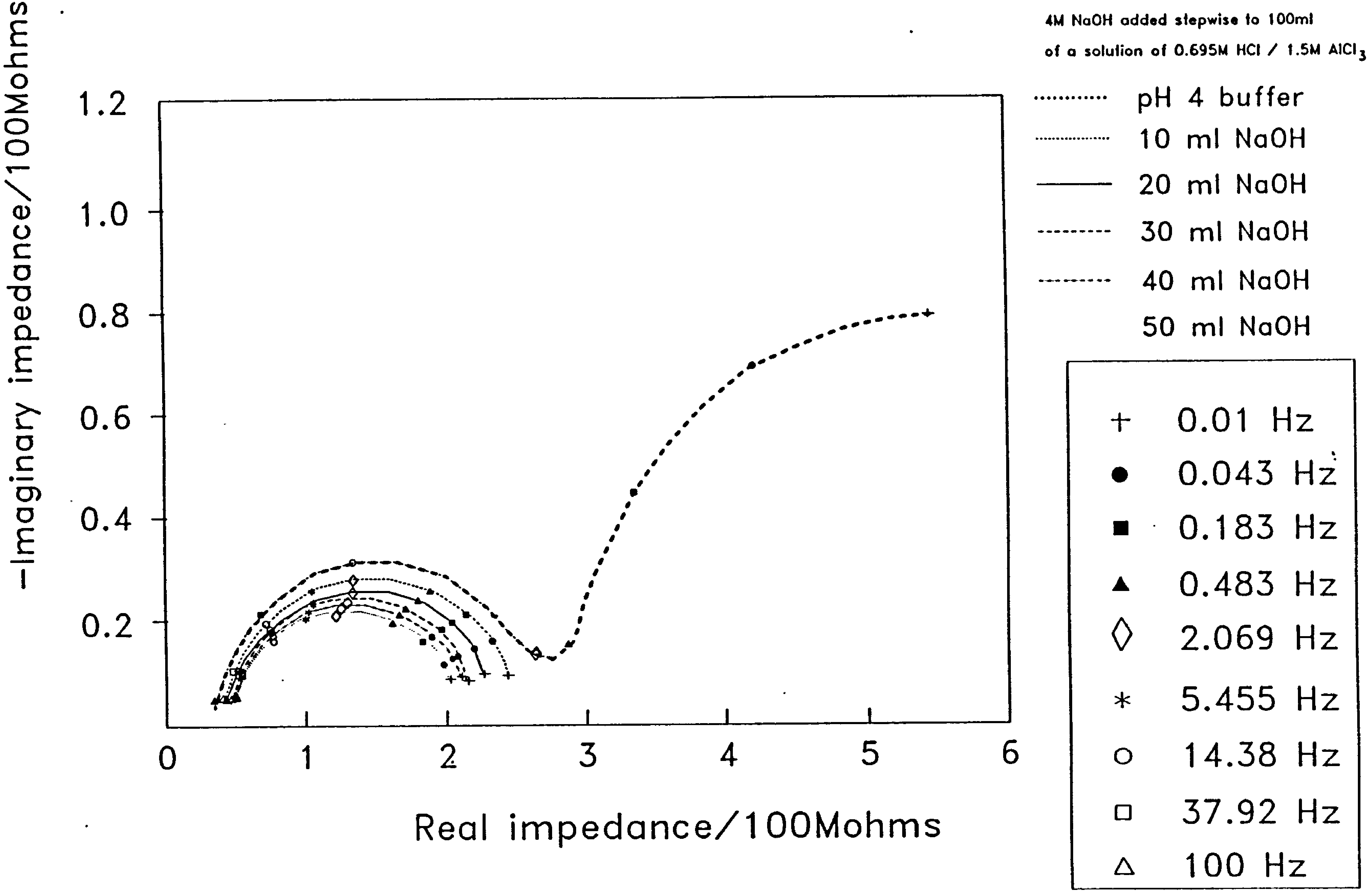
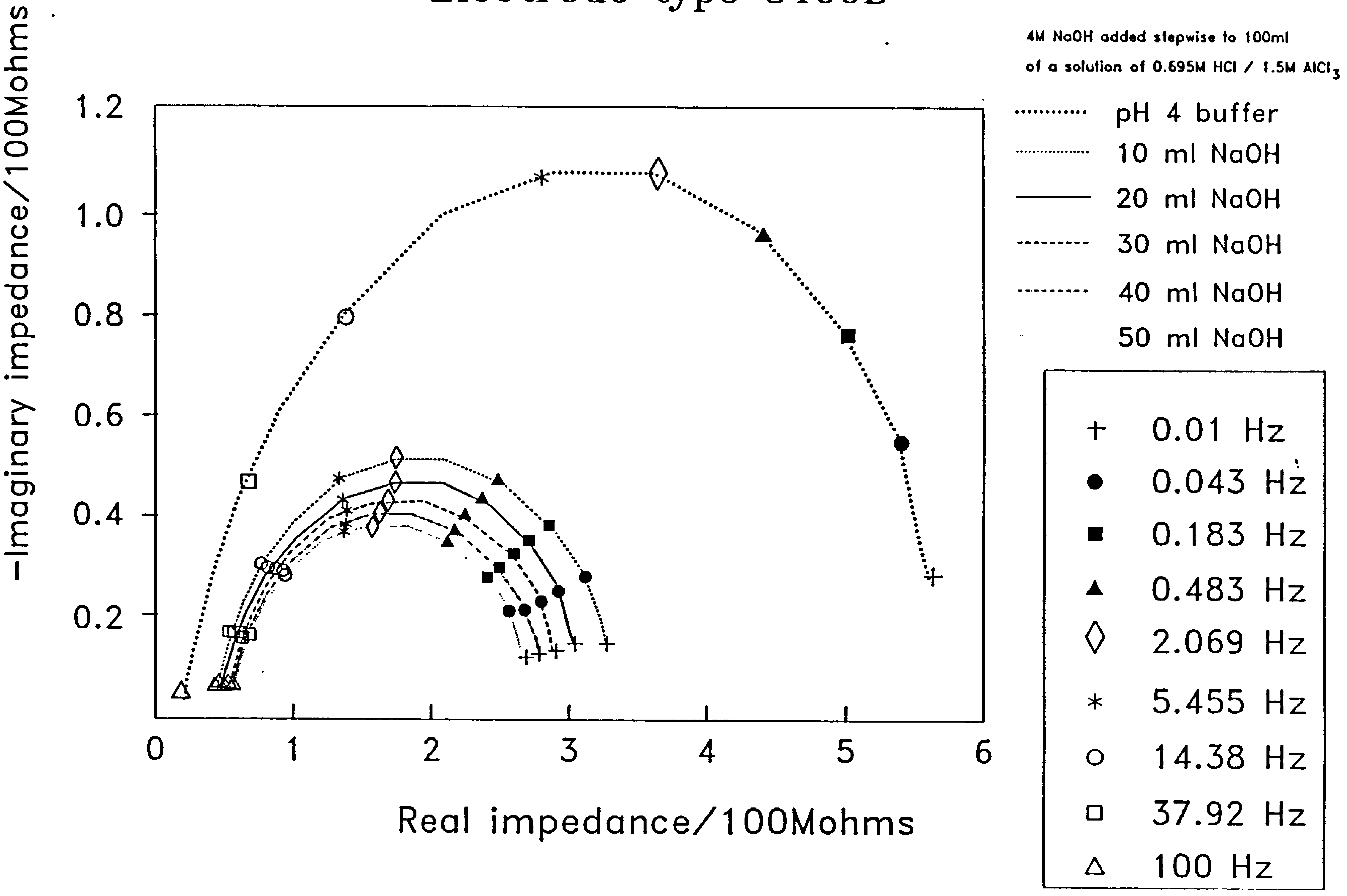


Figure 9.17 Effect of precipitate

Electrode type 8400B



clean environment pH 4 is included for comparison. Nernstian slopes for the electrodes are presented in Table 9.18.

The impedance curves show a dramatic change from the norm, becoming ever smaller as the precipitate thickens, and in the case of electrode type 8404S the character of the curve has also changed in that the second (low frequency) semi-circle has been removed altogether. These changes represent a reduction in both total impedance and phase angle ϕ, the reductions occurring over the entire frequency range but more pronounced at the low frequency end. When the electrodes were cleaned at the end of the experiment their frequency response in a clean environment was found to be restored to normality.

The distortion of the frequency response characteristics observed in the presence of precipitate did not necessarily mean that the electrodes were not capable of responding correctly to pH value. It was to make a judgement of this nature that their Nernstian slopes were measured and it can be seen from Table 9.18 that in the presence of precipitate they were well wide of the norm for both types of electrode, attesting to the fact their pH response had indeed been impaired.

Table 9.18

Effect of Precipitation of Alumina on the Nernstian slopes of types 8404S and 8400B Glass electrodes

4M NaOH added to 100 ml of 0.7M HCl / 1.5M $AlCl_3$

i) Type 8404S

NaOH /ml	pH	E/mV	Nernstian slope mV/pH
10	1.43	0.307	42.6
20	2.56	0.246	64.0
30	3.11	0.230	91.0
40	3.46	0.198	125.8
50	4.28	0.091	

ii) Type 8400B

NaOH /ml	pH	E/mV	Nernstian slope mV/pH
10	1.65	0.324	56.1
20	2.95	0.251	50.9
30	3.52	0.222	73.1
40	4.15	0.176	111.6
50	5.27	0.051	

(iii) Presence of Immiscible Oil

If a glass electrode is used in circumstances where there is a dispersed oil phase there is a clear possibility that some droplets of oil may adhere to the membrane surface and therby affect its performance, a situation which was simulated in the present studies by smearing Vaseline petroleum jelly over roughly half the membrane surface of samples of both 8404S and 8400B type electrodes. These electrodes were then submitted to both frequency response and Nernstian slope measurements.

The frequency response measurements were made in buffers pH 4 and pH 7 and the results, together with those obtained for the electrodes when clean for ease of comparison, are presented in Figs 9.19 and 9.20. From these Figures it is seen that, while the shape of the characteristic remains the same, the general effect of the Vaseline is to double its size. At the lower frequencies the measured impedances showed increases compared to the clean electrode of between 60 and 100%, but at the higher frequencies, 14.38Hz and greater, the increase fell to between 10 and 30%, and in fact at 100Hz in the case of electrode 8400B no increase at all was observed.

After cleaning, by wiping with tissue paper, the original clean behaviour was restored.

Figure 9.19 Effect of Vaseline

Electrode type 8404S at pH4

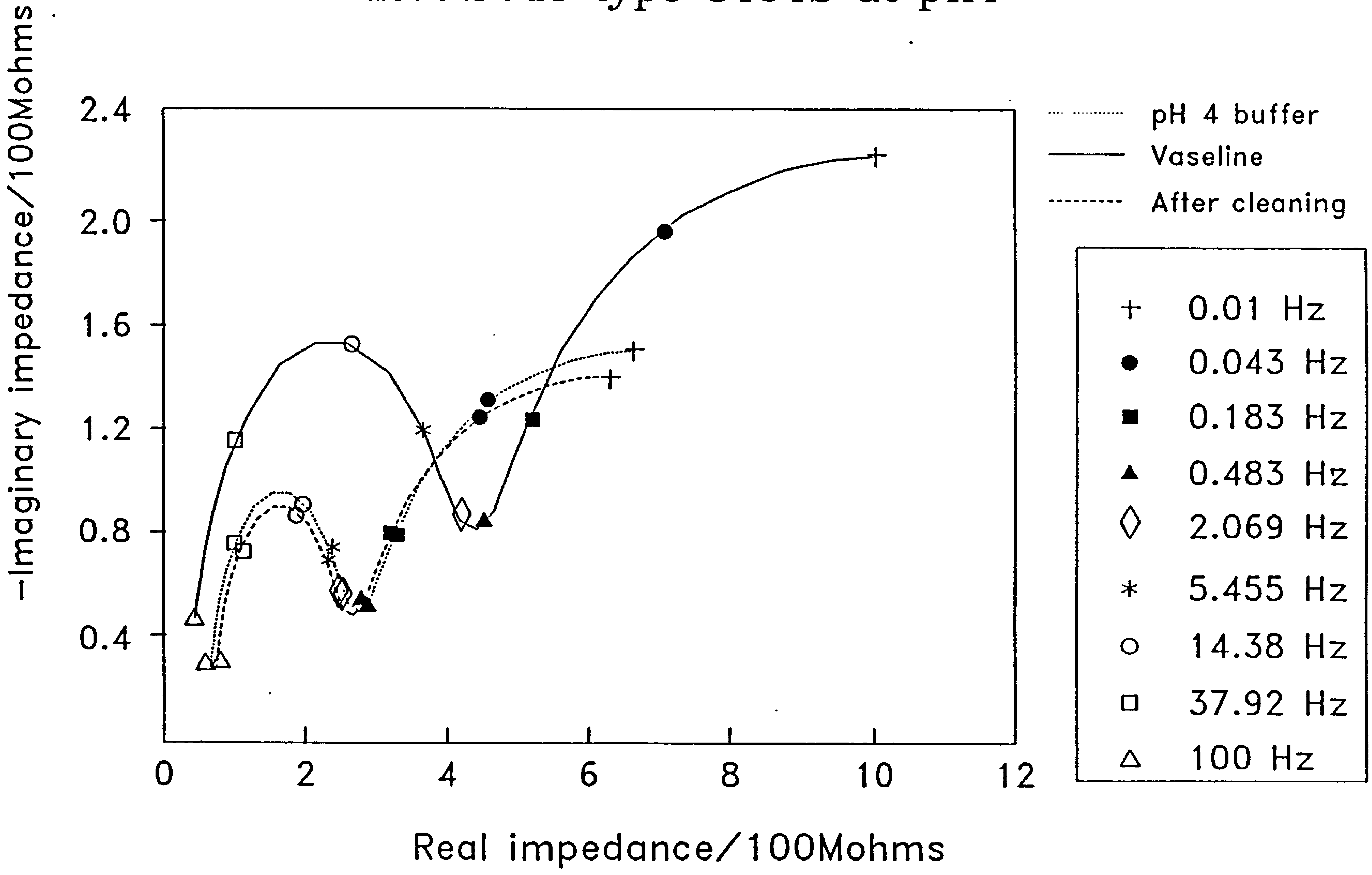
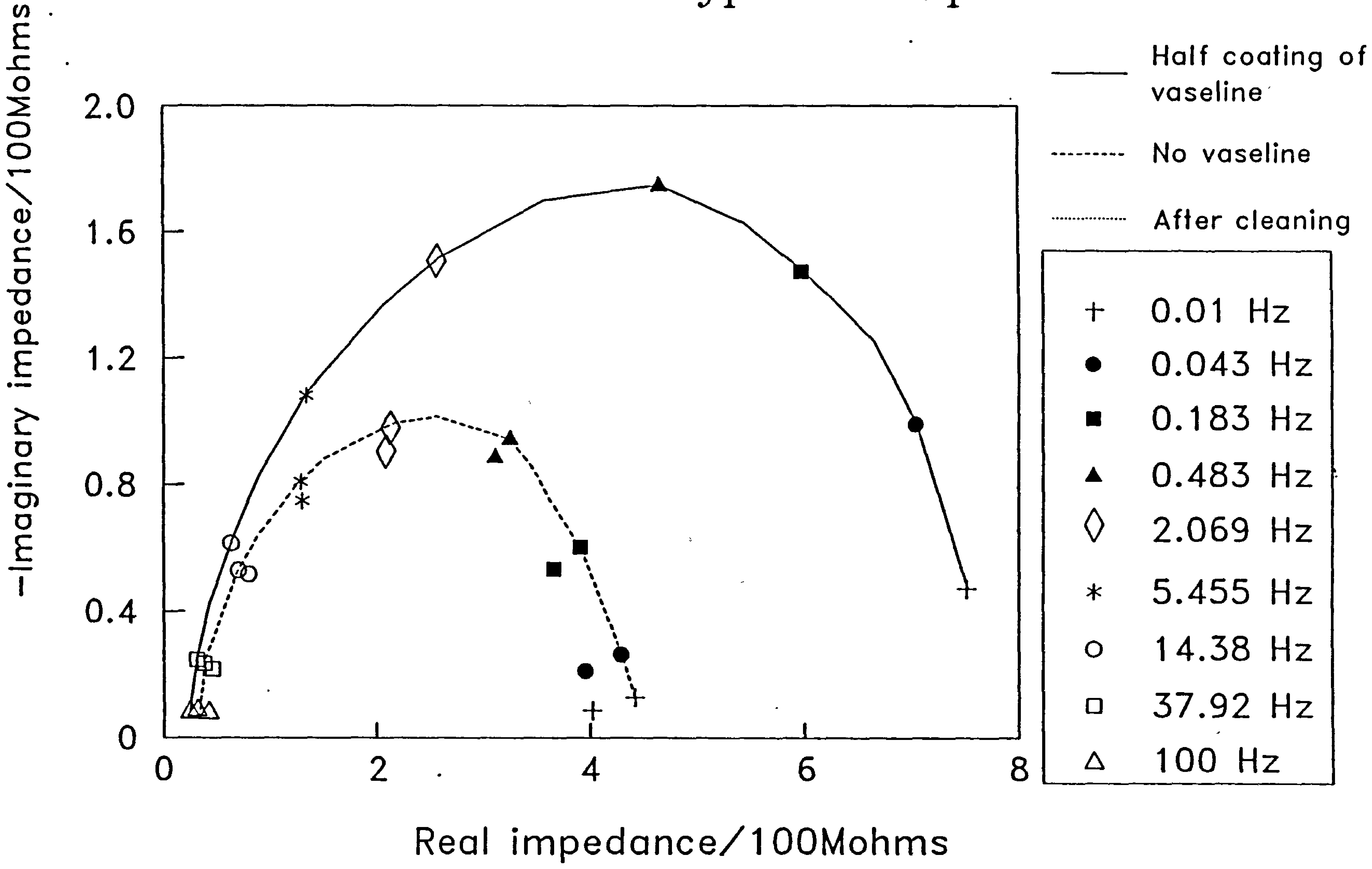


Figure 9.20 Effect of Vaseline

Electrode type 8400B/pH7



The Nernstian slopes measured between buffers pH 4 and pH 9 were unaffected by the presence of the Vaseline.

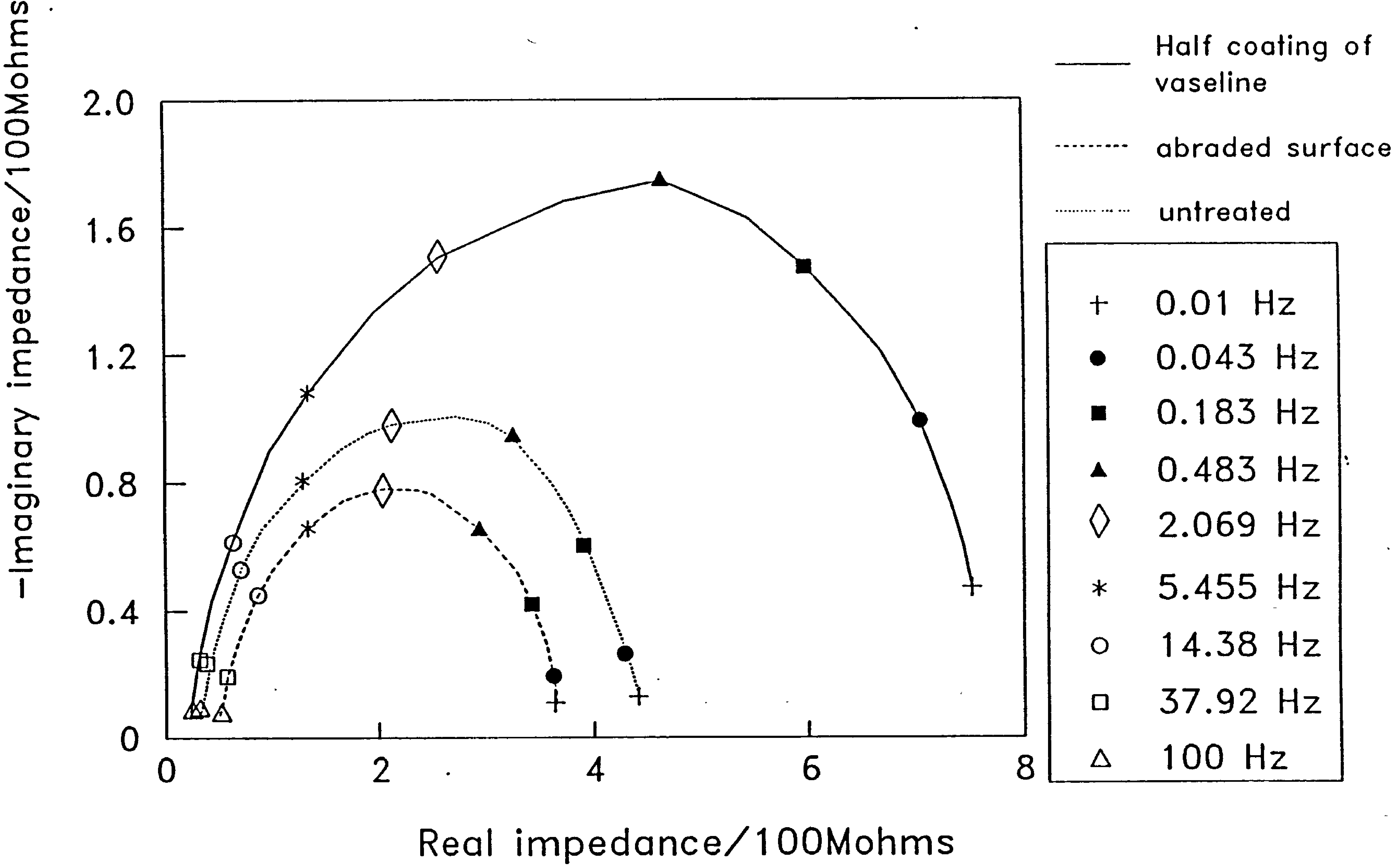
The observations at the lower freqencies tend to indicate that the Vaseline was acting merely as a stopping-off agent, and consequently would only affect the extensive properties of the electrode (i.e those dependant upon electrode area), the category into which impedance falls. On the other hand, intensive properties, such as electrode potential and Nernstian slope, would remain uchanged. Since the impedance of the electrode is influenced by the inside as well as the outside surface area, however, a simple proportional relationship between fractional coating and increase in impedance would not be expected, but on the other hand it should not be far removed from it, and the fact that covering half the surface has in general roughly doubled the low frequency impedances would therefore support a stopping-off mechanism. It would not, however, explain the high frequency behaviour.

(iii) Physical Damage

Physical damage was simulated by severely scratching the glass with emery paper. The frequency response characteristics before and after damaging a type 8400B electrode in this way are shown in Fig 9.21 for buffer pH7.

Figure 9.21 Effect of Vaseline and Abrasion

Electrode type 8400B/pH7



The behaviour was somewhat surprising, for if, as anticipated, the damage had done no more than deactivate a portion of the membrane area it would have had the same effect as a stopping-off agent and would have replicated the behaviour of partial Vaseline coating. Looking at Fig 9.21, however, quite the reverse was observed. Impedances are reduced at all frequencies and particularly at the low frequencies. One possible explanation is that the scratches have done no more than increase the surface area of the membrane, which has been accompanied by a commensurate reduction in the impedance associated with the surface processes.

The Nernstian slope was found to be unaffected by abrasion.

CHAPTER 10 APPLICATION OF THE RESULTS TO THE MONITORING OF ELECTRODE INTEGRITY

10.1 Introduction

A strategy for monitoring the integrity of the glass electrode must obviously be based upon a property having a value, or pattern of values, which is dependent upon the electrode's reliability, being consistently steady when the electrode is performing to specification, and deviating from the steady value by an unmistakable margin when performance is impaired.

From the results described in Chapter 9 it was clear that a particular value of impedance, real or imaginary, at some specific frequency did not fulfil these criteria, because a change in impedance did not necessarily imply that the response of the electrode to pH had been affected. For instance the partial coating of the membrane by Vaseline petroleum jelly virtually doubled the impedance over much of the frequency range but the electrode performance remained perfectly satisfactory, and the reduction in impedance brought about by surface damage due to scratching and by precipitation left the electrode performance unaffected in one case but severely impaired in the other. It is recalled, too, that the simple act of changing pH also affects the impedance values.

For this reason it was decided to look for an indicator based not on absolute values but on relative values, or in other words on a dimensionless property. The most obvious of these was phase angle, ϕ, the properties of which and its possible use in on-line measuring are the subject matter of the present chapter.

10.2 Behaviour of Phase Angle ϕ

The phase angle ϕ is the angle between the resultant impedance, $|Z|$, and the real axis as illustrated in the Argand diagram in Fig 10.1, where for convenience Z_I is considered positive.

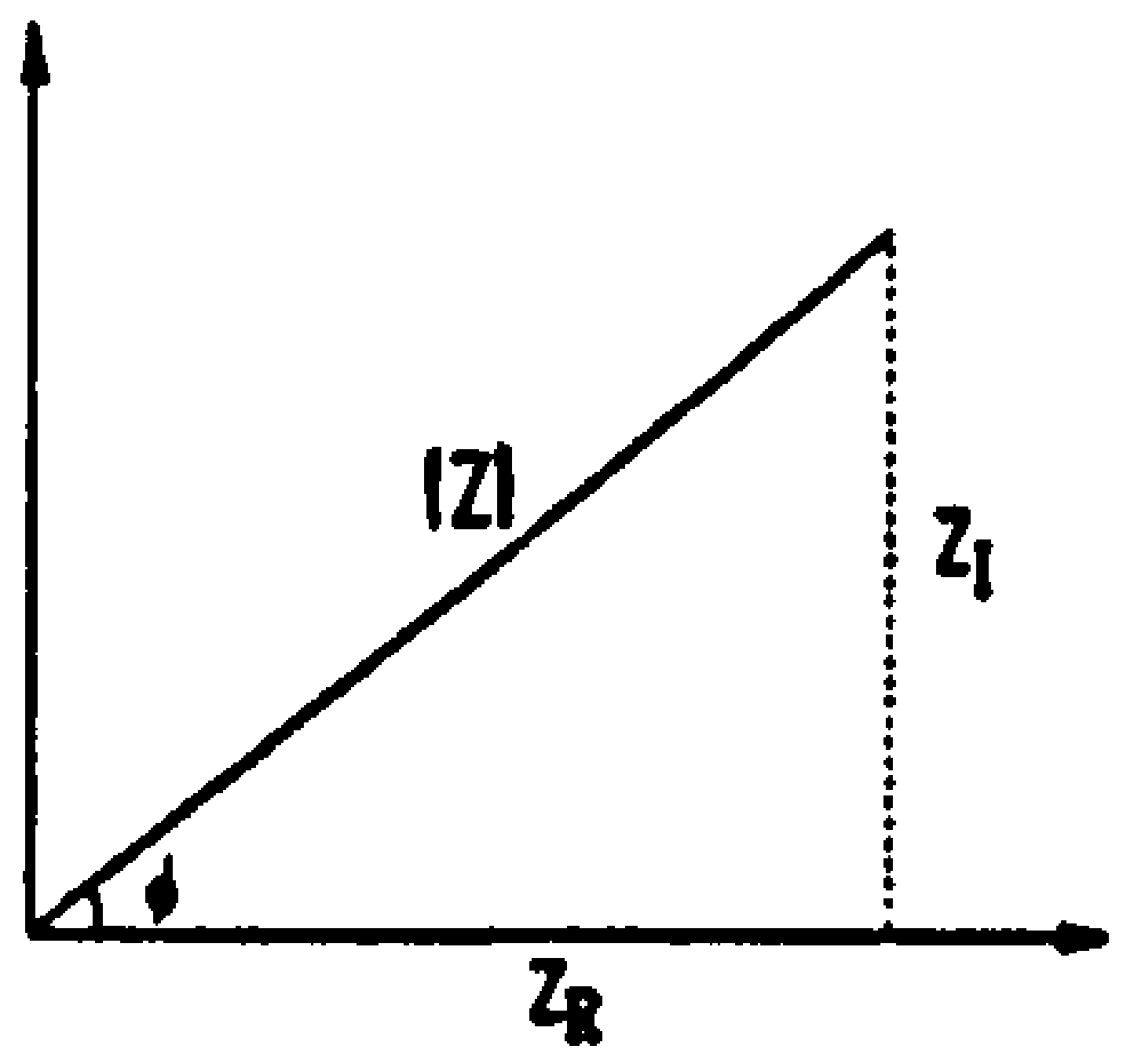


Figure 10.1 Argand Diagram

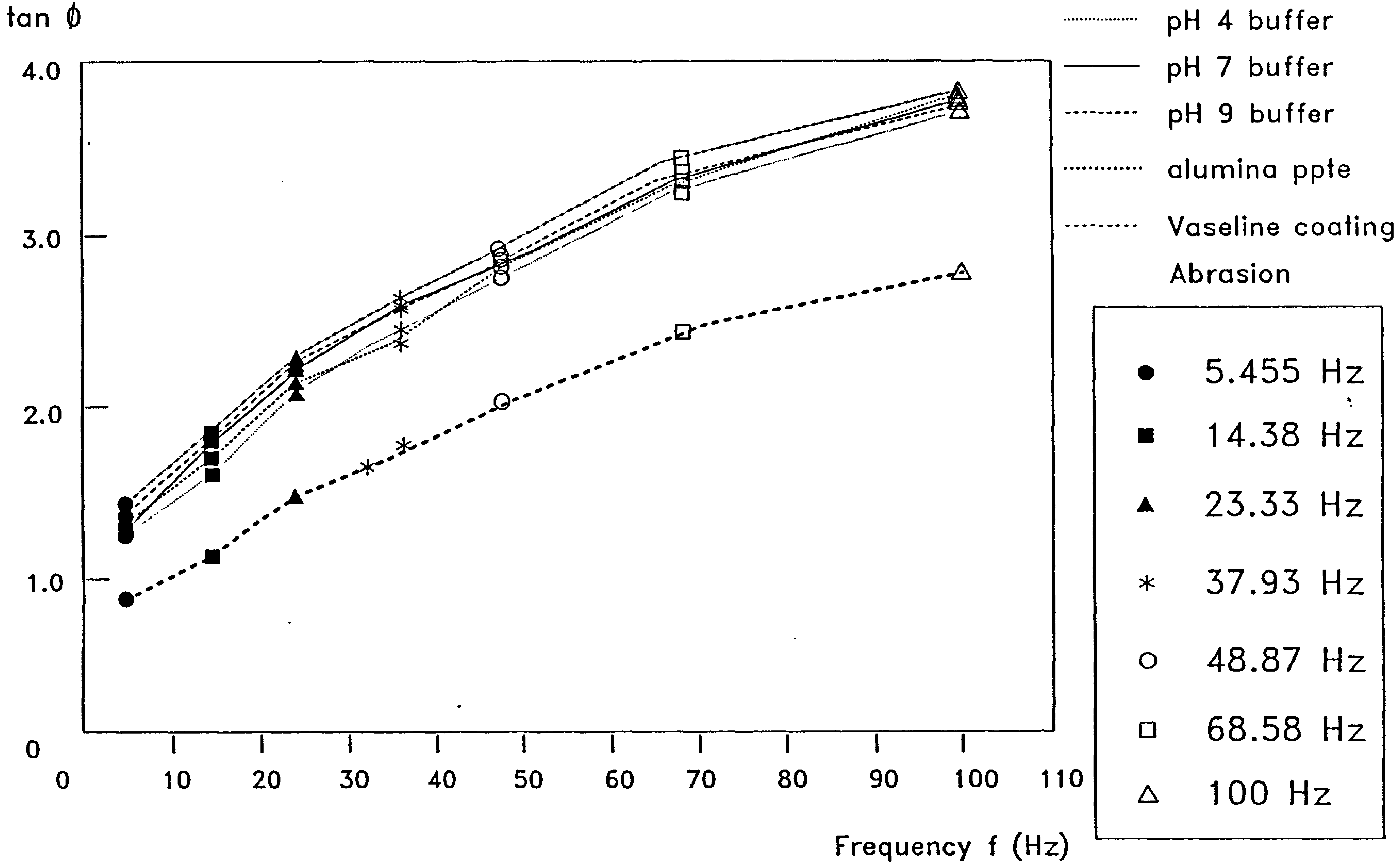
Values of ϕ are calculated from the relationship

$$\phi = \tan^{-1}(Z_I/Z_R)$$

and its behaviour in both the clean and adverse environments studied in the present work is shown in Fig 10.2 for a type 8400B electrode over the frequency range 5 to 100 Hz.

Figure 10.2 Variation of tan Ø with frequency

Electrode type 8400B



What is immediately striking about these results is that the curves corresponding to those environments in which the pH response of the electrode was normal are bunched together while that for precipitation where the electrode was notoriously unreliable lies well apart from them. In other words ϕ apparently discriminates between adverse environments where performance is normal, although impedance changes, and those where it is abnormal.

The deviation between normality and abnormality is most pronounced at the higher frequencies which is of considerable practical value from the point of view of on-line monitoring because ϕ values at 100 Hz can be determined in a fraction of a second whereas at 0.01 Hz they would take tens of minutes

The variation of ϕ at 100 Hz between four electrodes of each type is shown in Figs 10.3 and 10.4 where values of ϕ at three different pH's, 4, 7 and 9 are compared with each other and with the value observed in alumina precipitation at pH 4.

Fig 10.3 shows that in the case of type 8404S the change in ϕ has exactly the same profile for all the electrodes tested, but the profiles themselves have a spread of roughly six degrees. Each electrode taken separately shows a variation in ϕ between the pH values 4, 7 and 9 of about four degrees maximum, but the change in ϕ between pH 4 buffered and pH 4 in the presence of precipitate is in all cases in excess of 12 degrees.

Figure 10.3

Phase angle variation at 100 Hz for 4 type 8404S electrodes

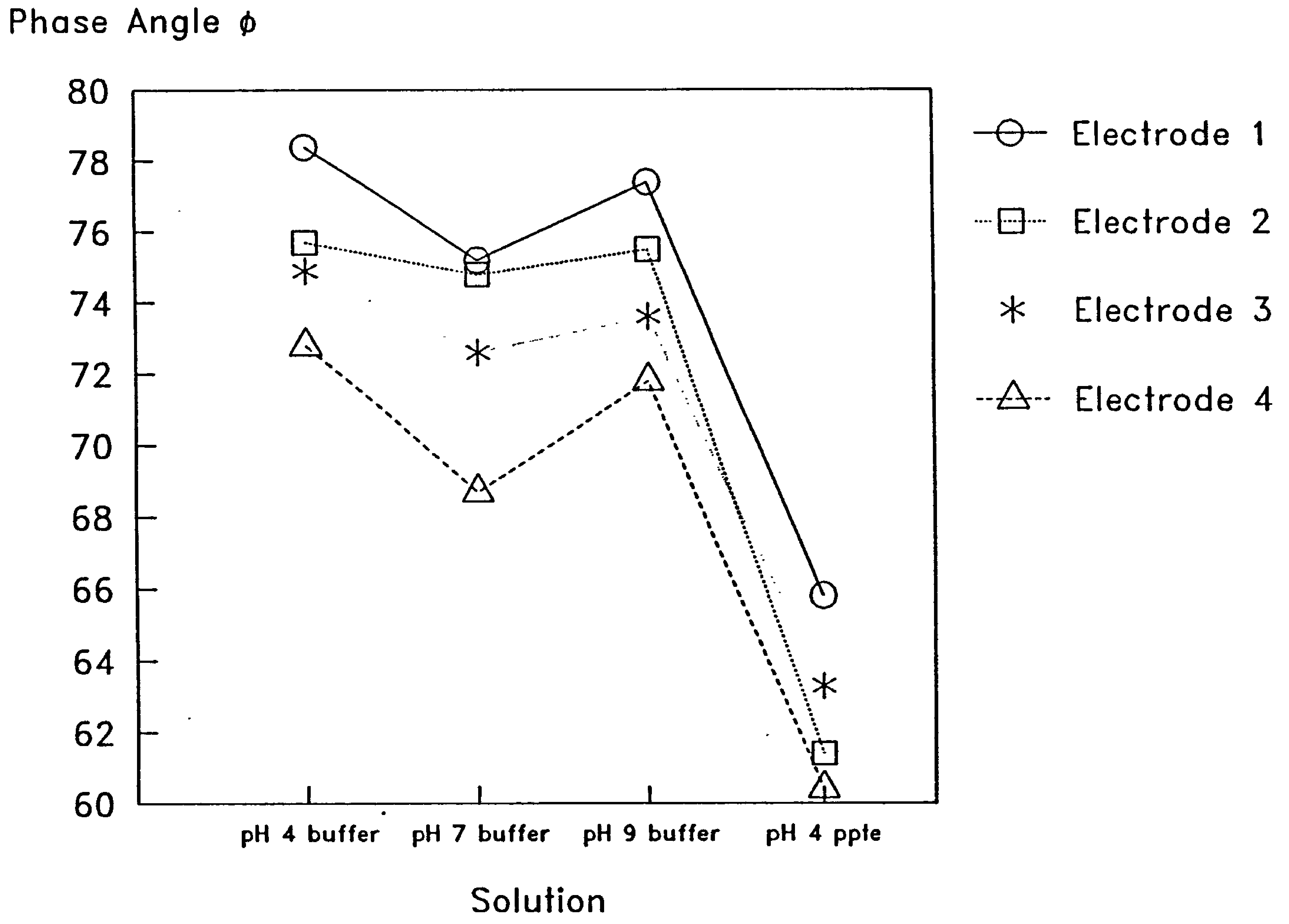


Figure 10.4

Phase angle variation at 100 Hz for 4 type 8400B electrodes

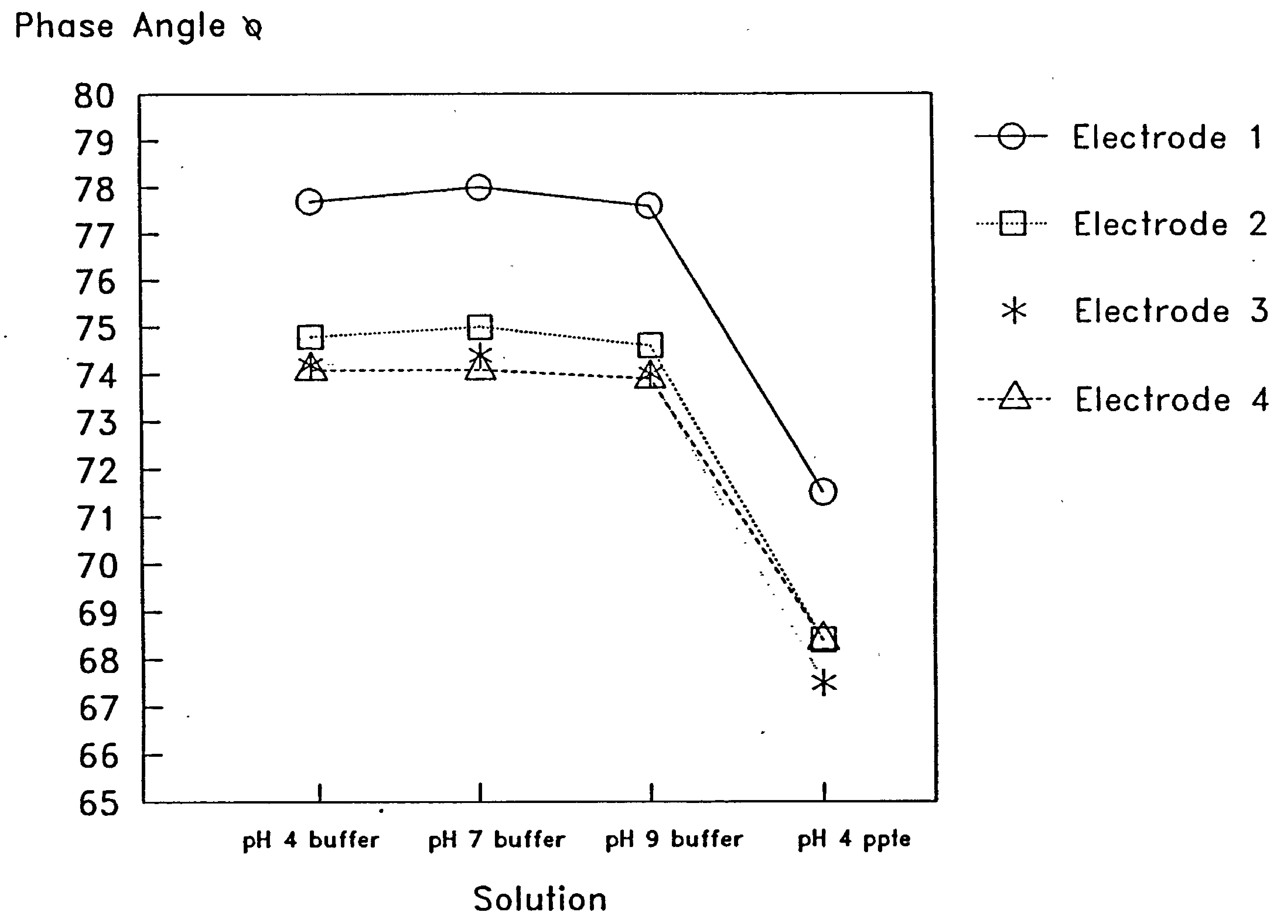


Fig 10.4 shows that the spread in the ϕ profiles for the four electrodes of type 8400B which were tested is slightly less than that for those of type 8404S, being roughly 4° as opposed to 6°. In addition, when each electrode is considered separately ϕ is seen to be much less sensitive to pH and shows a variation of not quite 0.5° between the pH values tested in contrast to the 4° for the 8404S type. The difference between ϕ for pH 4 buffered and pH 4 with alumina precipitate is, however, reduced, now lying between about 5.5° and 7°.

In the light of the observations described it was concluded that ϕ was sufficiently promising as a means of testing integrity that it warranted further exploration, and to begin with its reproducibility was investigated by making repeated measurements over an extended period of time in both benign and adverse environments.

The results obtained are discussed in the next Section, but, before proceeding to it, it may be noted in passing that the variation in ϕ between electrodes of the same type when in an identical environment poses no real difficulty because each electrode could be compared with its own historical record.

10.3 Reproducibility of ϕ at a Fixed Frequency

The reproducibility of ϕ was investigated by repeated measurements with an electrode type 8404S at a frequency of 100 Hz in buffer pH 4 and in a solution containing alumina precipitate at pH 4. The results are presented in Tables 10.4 and 10.5.

RUN NO.	IMPEDANCE		TAN φ	φ
	REAL/100MΩ	-IMAG/100MΩ	-IMAG/REAL	DEGREES
1	0.04549	0.17352	3.814	75.3
2	0.04715	0.17271	3.66	74.7
3	0.04572	0.17370	3.779	75.2
4	0.04691	0.17446	3.719	74.9
5	0.04613	0.17408	3.773	75.2
6	0.04683	0.17341	3.703	74.9
7	0.04704	0.17409	3.701	74.9
8	0.04584	0.17358	3.787	75.2
9	0.04630	0.17416	3.762	75.1
10	0.04631	0.17251	3.725	74.9
11	0.04683	0.17261	3.685	74.8
12	0.04597	0.17220	3.746	75.1
13	0.04647	0.17434	3.752	75.1
14	0.04694	0.17263	3.677	74.8
15	0.04601	0.17435	3.789	75.2
16	0.04665	0.17391	3.728	75.0
17	0.04571	0.17342	3.794	75.2
18	0.04733	0.17312	3.657	74.7
19	0.04617	0.17420	3.773	75.2
20	0.04705	0.17357	3.654	74.7
			TOTAL	1500.1

AVERAGE VALUE OF $\phi = \frac{1500.1}{20} = 75.0\,^\circ$ SPREAD = ± 0.3°

Table 10.4 Reproducibility of φ for a type 8400B electrode in a pH 4 buffer soln at a frequency of 100 Hz

RUN NO.	IMPEDANCE		TAN ϕ	ϕ
	REAL/100MΩ	-IMAG/100MΩ	-IMAG/REAL	DEGREES
1	0.04952	0.11723	2.36	67.1
2	0.04817	0.11534	2.39	67.3
3	0.04852	0.12126	2.49	68.1
4	0.04917	0.12037	2.44	67.8
5	0.05035	0.12521	2.48	68.0
6	0.04879	0.12081	2.48	68.0
7	0.05169	0.12513	2.42	67.5
8	0.05317	0.12766	2.40	67.4
9	0.05102	0.11941	2.34	66.8
10	0.04971	0.11830	2.38	67.2
11	0.04598	0.10991	2.39	67.2
12	0.04991	0.12137	2.43	67.6
13	0.05399	0.12855	2.38	67.2
14	0.05342	0.12669	2.37	67.1
15	0.05037	0.11942	2.37	67.1
16	0.04848	0.11782	2.43	67.6
17	0.05436	0.13109	2.41	67.4
18	0.05402	0.12912	2.39	67.3
19	0.05376	0.13018	2.42	67.5
20	0.05308	0.12748	2.40	67.3

TOTAL 1348.5

AVERAGE VALUE OF $\phi = \frac{1348.5}{20} = 67.4°$ SPREAD = ± 0.7°

Table 10.5 Reproducibility of ϕ for a type 8400B electrode in a pH 4 precipitate a frequency of 100 Hz

In the buffer the maximum deviation from the mean value of ϕ is 0.3° and in the presence of precipitate 0.7°. Compared to the difference between the means in the two cases, namely 7.6°, these deviations are an order of magnitude less, giving further conformation that ϕ may be an attractive candidate for integrity monitoring. As a result an on-line simulation was devised to investigate the possibility further.

10.4 Simulation of the On-line Testing of Electrode Integrity

The equipment was the same as previously employed for gathering the frequency response data, and the circuitry was that shown in Fig 6.4. The software which ran the simulation was that described in Section 7.6 and given the title "ETEST", and in essence it switched the cell, via the relay switch, to and fro between the TFA and multimeter. When attached to the TFA the response was measured to a frequency of 100 Hz and when attached to the multimeter the cell voltage was measured and converted to pH.

The time interval for integrating over 10 cycles is 0.1s, and therefore the off-line time of the electrode if tested, say, every 10s was only 1% of the total.

For each electrode tested in this way the appropriate historic values of ϕ determined at 100 Hz in buffers pH 2, 4, 7 and 9 were supplied to the program and were used as a standard against which the on-line values were compared. If deviation between the two was more than a selected percentage the program would automatically activate an alarm. The percentage deviation chosen was guided by the reproducibility of the frequency response data discussed in the previous section. From there it is evident that the reproducibility in ϕ in a buffer is of the order of 1%, whereas deviation when performance is impaired is in the order of 10%. A threshold of 5% was therefore selected for the simulations, although provision was made to vary the value.

Input to the program was enabled by the screen shown below, allowing the user to inform the system of the particular electrode under test and the amount of time between performance monitoring (i.e frequency response measurement).

```
DATE - date of run (12/11/92)

ELECTRODE TYPE - no of electrode in use

TIME BETWEEN PH AND IMPEDANCE MEASUREMENTS  - time t
```

The output from the program appeared on the screen in the format shown below and it informed the operator of the state of integrity of the electrode after the last test and an indication of the current process being executed by the software.

```
                        MEASURING PH
 Date        Elec no   Ideal φ   Measured φ      pH   State
12/11/92        1       75.0       74.9          4.1  good
```

followed by after a period of time t :

```
                      MEASURING IMPEDANCE
  Date         Elec no    Ideal φ    Measured φ      pH    State
 12/11/92         1        75.0      MEASURING       4.1   good
```

If the measured phase angle φ fell within the selected threshold the measurement of pH was allowed to continue, otherwise the alarm bell was activated and the "state" of the electrode was changed to "bad".

The system was used to monitor the pH of an $HCl/AlCl_3$ solution which was slowly neutralised by the addition of NaOH and performed satisfactorily, sounding the alarm at the first signs of precipitation.

CHAPTER 11 CONCLUSIONS

The following conclusions emerge from the present studies.

(i) The impedance plots of glass electrodes over a frequency range 0.01 to 100 Hz may comprise either one or two semi-circles. The latter form has been reported and discussed by Sandifer and Buck who proposed that the higher frequency semi-circle was due to bulk resistance and geometric capacitance of the membrane and the lower frequency one to surface processing concerning ion exchange and double layer formation. The presence of just one semi-circle rather than two does not necessarily conflict with their model; it may simply imply that the time constants of the two corresponding parallel RC circuits are more nearly equal.

(ii) Impedance values, both real and imaginary, vary from one electrode to another, even though they may be of the same type, and also vary with the surrounding environment. This behaviour is not surprising for two reasons. Firstly, the geometry of the electrodes is not entirely reproducible with the effect that even if they are of the same type they might have a different membrane thickness and surface area. If they are of different types they will also, most likely, have a glass of different composition. Secondly, a significant proportion of the impedance arises from surface processes and is therefore inextricably linked to the environment adjacent to the surface, determining as it does the concentration of hydrogen ions, anions and other cations.

(iii) The phase lag ϕ between input and output signal, equal to $\tan^{-1}(Z_I/Z_R)$, also varies from one electrode to another, but for any specific electrode at any given frequency it is relatively independent of conditions in the surrounding environment, even if they lead to stopping-off or surface damage, provided they do not affect its integrity. When conditions arise which do affect its integrity ϕ shows a significant shift in value, particular at the higher frequencies (50 - 100 Hz), so much so that it holds out the possibility of being used as a monitor. This was put to the test in the present work, and it was concluded that under the adverse conditions employed, namely the precipitation of alumina from $AlCl_3/HCl$ solutions, it performed an integrity monitoring function perfectly satisfactorily.

Clearly there is a great deal more work still to be done to prove the system. The proposed methodology would need, for instance, to be tested in more systems, over much longer periods and with more realistic electrical shielding, since the amount of shielding used in the present work may prove to be impractical in many process plants. The work will also need to be extended to other temperatures.

In addition, and not least, would be the further development of the associated circuitry. If it were envisiged that ultimately a small self-contained unit would be attached to each electrode the circuitry employed in the present work would need to be reduced in size several fold and would require the benefits of micro electronics.

NOMENCLATURE

Symbol	Unit	
A	-	channel on Transfer Function Analyser
A	-	Debye-Huckel parameter
a	-	vector
a_{H^+}	usually, M	activity of hydrogen ion
B	-	channel on Transfer Function Analyser
B_O	-	partial differential coefficient
B_R	-	partial differential coefficient
C	F	capacitance
C_d	F	double layer capacity
C_s	F	capacitive component of Faradaic impedance
c^S_O	M, mol/cm^3	concentration of O at the electrode surface
c^S_R	M, mol/cm^3	concentration of R at the electrode surface
C_R	M, mol/cm^3	concentration of R
C_O	M, mol/cm^3	concentration of O
c^b_R	M, mol/cm^3	bulk concentration of R
c^b_O	M, mol/cm^3	bulk concentration of O
D_R	cm^2/s	diffusion coefficient of R
D_O	cm^2/s	diffusion coefficient of O
E,e	V	voltage
E_H	V	hydrogen potential
E_H°	V	Standard hydrogen potential
E_C	V	potential of counter electrode
E_S	V	potential of reference solution
E°	V	standard potential
E_{cell}	V	potential of the cell

Symbol	Unit	
E_j	V	junction potential
E_{asy}	V	asymmetry potential
E_b	V	boundary potential
E_{SCE}	V	potential of calomel electrode
E_{AgAgCl}	V	electrode potential of internal cell
ΔE		change in potential
F	C	the Faraday, charge on one mole of electrons
f_{Cl^-}	-	activity coefficient for chloride ion
f_{H^+}	-	activity coefficient for hydrogen ion
G_1	-	silicic acid gel
G_2	-	dry glass phase
G_3	-	silicic acid gel
Gl^-	-	glass cation
H^+	-	Hydrogen ion
i	A	current
i_c	A	current flowing through a capacitor
i_f	A	Faradaic current
j	-	$\sqrt{-1}$
J	-	time constant
K	-	equilibrium constant
n	-	number of integration cycles
ΔpH	-	change in pH
pH_s	-	pH of the reference solution
Q,q	C,μC	charge
R	Ω	resistance
R_1	Ω	resistance of resistor 1
R_2	Ω	resistance of resistor 2

Symbol	Unit	
R_{ct}	Ω	resistance due to charge transfer
R_s	Ω	resistive component of Faradaic impedance
T,t	s	time
T	K	temperature
x_1	cm	distance of the IHP from the electrode surface
x_2	cm	distance of the OHP from the electrode surface
w	rad/s	angular velocity
W_1	-	test solution
W_2	-	internal aqueous reference electrode
X_a	V	real component of voltage
X_c	Ω	capacitive reactance
Y_a	V	imaginary component of voltage
Z	Ω	impedance
Z(Re), Z_{Re}	Ω	real component ofimpedance
Z(Im), Z_{Im}	Ω	imaginary component ofimpedance
Z_T	Ω	total impedance
Z_W	Ω	diffusional impedance (Warburg impedance)

Greek Symbols

Symbol	Unit	
ϕ	rad	phase angle
▲w1-g1	V	potential difference between phase boundaries W_1 and G_1
σ	C/cm^2	charge density
α^L	-	transfer coefficient(low frequencies)
α^H	-	transfer coefficient(high)

Abbreviations

Symbol	
A.C, a.c	alternating current
Ag	silver
Cl	chlorine
Ca	calcium
D.C, d.c	direct current
DCE	data communications equipment
DTE	data terminal equipment
emf	electromotive force
EOC	end of conversion
IHP	inner Helmholtz plane
LED	light emitting diode
MS	most significant
OHP	outer Helmholtz plane
RMS	route mean squared
RM	Research Machines
SIM	serial interface module
TFA	transfer functional analyser (frequency response analyser)

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APPENDIX

A1 INTERFACE MODULES

A1.1 Serial Interface Module

The serial interface module is in the form of an external board in its own box which can be simply plugged into the piconet socket of the Nimbus. The serial interface has two connectors. One of these is a 6-way Bell connector , the other is a 25-way D-type connector as used on earlier Research Machine computers.

The 25-way D-type connector has the following RS232c interchange circuit to pin assignments

Signal Direction SIM=DCE SIM=DTE	Interchange Circuit	D-type	Pin no
-	Signal ground	7	7
FROM DCE	Received data	2	3
FROM DCE	Clear to send	4	5
FROM DCE	Data set ready	20	6
FROM DCE	Data carrier detected	8	8
FROM DCE	Ring indicator	-	22
FROM DCE	Receiver data clock	24	17
FROM DCE	Transmitted data clock 1	-	17
FROM DTE	Transmitted data	3	2
FROM DTE	Request to send	5	4
FROM DTE	Data terminal ready	6	20
FROM DTE	Transmitted data clock 2	17	24

DCE - DATA COMMUNICATIONS EQUIPMENT eg modem

DTE - DATA TERMINAL EQUIPMENT eg printer, plotter

The remaining pins in the D-type connector carry no interchange circuit allocation.

Interface characteristics

The RS232C characteristics, the handshake protocol and the time/date data are stored in virtual registers inside the serial module. Access to the registers can be made via an application program.

A1.2 Parallel Interface Module

The parallel module is also housed in a small plastic case which can be plugged into the Nimbus piconet socket. Each parallel device to be used by Nimbus at any one time requires its own parallel module.

There are three connectors on the parallel module giving two common parallel interfaces and one analogue interface. These are

- Standard Parallel Interface
- Parallel (BBC) Interface
- Analogue (BBC) Interface

i) SERIAL PARALLEL INTERFACE

The standard parallel interface uses a 25-way D-type connector. The pin outs are as follows:

PIN	FUNCTION	INPUT/OUPUT
1	Data in 0, Busy in	I
2	Data in 2	I
3	Data in 4	I
4	Data in 6	I
5	Data out 0	O
6	Data out 2	O
7	Data out 4	O
8	Data out 6	O
9	+5V	-
10	Input strobe	I
11	Handshake out 1	O
12	Handshake out 2	O
13	Handshake out 3	O
14	Data in 1	I
15	Data in 3	I
16	Data in 5	I
17	Data in 7	I
18	Data out 1	O
19	Data out 3	O
20	Data out 5	O
21	Data out 7,Output Strobe	O
22	Ground	-
23	Ground	-
24	Input ready	O
25	Handshake input 1	I

ii) PARALLEL (BBC) INTERFACE

This interface was not needed during testing and is therefore not listed.

iii) ANALOGUE (BBC) INTERFACE

This interface uses a 15-way D-type connector and provides all the facilities of the BBC analogue port.

Pin out's for this interface are as follows

PIN	FUNCTION	INPUT/OUPUT
1	+5V	-
2	Digital ground	-
3	Digital ground	-
4	Channel 3	I
5	I/O ground	-
6	Digital ground	-
7	Channel 1	I
8	I/O ground 6	-
9	not used	-
10	Button 1	I
11	VREF	O
12	Channel 2	I
13	Button 0	I
14	VREF	O
15	Channel 0	I

The analogue driver will start a new conversion when one of the following occurs:

1) Dummy data is written to the analogue start register

2) The analogue channel is changed

3) The conversion resolution is changed

Reading the analogue data MS Byte Virtual Register (28H) returns the most significant byte of the last data conversion. Before reading this register the input status register (24H) should be read to check the state of the EOC flag. The data registers may be updated only when the EOC flag indicates that the conversion is complete.

A1.3 Module operation

Output

When there is data in the transmit buffer an output may take place. When the Output Strobe is disabled then data sent down is simply latched into the parallel output port. In the strobed output modes, the data is latched into the port and then the output strobe is taken active and returned inactive to give a short pulse (about 1 microsec). If no BUSY input is expected from the peripheral , then the next output may take place on the next pass through the background task. However, if a BUSY input is expected the BUSY IN signal is polled on each pass through the background until BUSY IN is false. When the peripheral is no longer busy, the next byte of data can then be sent.

Input

When there is space in the receive buffer, data may be read in. Transparent input modes simply read the data that is currently available on the pins of the input port.

Data is read into the input latch when INPUT READY is high and STROBE is high. This causes the INPUT READY output to go low indicating that no more data can be latched in. When data is read from the latch, normally by the firmware, INPUT READY returns high. The STROBE should only be a short pulse of about 20microsec to ensure that the same input byte is not latched twice.

```
Function findmin(x:arr2;numb:GSXInt):real;

{ Finds minimum value in an array }

   var tempmin:real;
       i:integer;
      begin
        tempmin:=x[1];
        For i:=2 to numb do
           If x[i] < tempmin then tempmin:=x[i];
        findmin:=tempmin
      end;

procedure limits;

{ Sets limits for graph axes }

   begin
     fend:=findmax(logf,int);
     If fend < 0 then fend:=fend+1.2
       else fend:=fend+0.2;
     fstart:=findmin(logf,int);
     If fstart > 0 then fstart:=fstart-1.2
       else fstart:=fstart-0.2;
     If Aend > jBend then ylength:=Aend
       else ylength:=jBend;
     If Astart < jBstart then ystart:=Astart
       else ystart:=jBstart
   end;

procedure maxmin;

{ Produces scale for x and y axes }

   var i:integer;
      begin
        Aend:=findmax(realtotal,int);
        If Aend < 0 then
          begin
            If Aend > -5 then Aend:=TRUNC(Aend)+0.2
              else Aend:=Aend*0.8
          end
        else
          begin
            If Aend > 5 then Aend:=Aend*1.2
              else if Aend < 0.5 then Aend:=1.10
                   else Aend:=TRUNC(Aend)+1.2
          end;

        Amin:=findmin(realtotal,int);
        If Amin > 0 then
          begin
            If Amin < 5 then if Amin < 0.5 then Astart:=-Aend/10
                                else Astart:=TRUNC(Amin)-0.2
              else Astart:=Amin*0.8
          end
        else
          begin
            If Amin > -5 then Astart:=TRUNC(Amin)-0.2
              else Astart:=Amin*1.2
          end;
        jBend:=findmax(imagtotal,int);
```

```
        If jBend < 0 then
          begin
            If jBend > -5 then jBend:=TRUNC(jBend)+0.2
              else jBend:=jBend*1.2
          end
        else
          begin
            If jBend > 5 then jBend:=jBend*1.2
              else if jBend < 0.5 then jBend:=1.10
                     else jBend:=TRUNC(jBend)+1.2
          end;

        jBmin:=findmin(imagtotal,int);
        If jBmin > 0 then
          begin
            If jBmin < 5 then jBstart:=TRUNC(jBmin)-0.2
              else jBstart:=jBmin*0.8
          end
        else
          begin
            If jbmin > -5 then if jBmin > -0.5 then jBstart:=-1.10
                                 else jBstart:=TRUNC(jBmin)-0.2
              else jBstart:=jBmin*1.2
          end;

        If ABS(Astart) > 100 then Aend:=Aend+ABS(Astart)/10;
        If ABS(Aend) > 100 then Astart:=Astart-ABS(Aend)/10;
        If ABS(jBstart) > 100 then jBend:=jBend+ABS(jBstart)/10;
        If ABS(jBend) > 100 then jBstart:=jBstart-ABS(jBend)/10;

        nofits:=(int DIV 500) +1
      end;

procedure wait(time:integer);

{ Produces a time delay }

   var t:integer;
     begin
       t:=0;
       repeat
        t:=t+1
       until t>time
     end;

procedure transfer(nint:integer);

{ Transfer data from a file into arrays }

   var i:integer;
     begin
       reset(num);
       For i:=1 to nint do
         begin
           read(num,intro);
           read(num,freq);
           logf[i]:=ln(freq)/2.302585093;
           read(num,realtotal[i]);
           read(num,imag);
           imagtotal[i]:=-imag;
           maxmin;
           limits
         end
     end;
```

```
procedure Printdata;

{ Prints data headings }

 var fil:text;
  begin
    assign(fil,'PRN');
    rewrite(fil);

teln(fil,'********************************************************');
    write(fil,' DATE OF RUN......... ');
    writeln(fil,numfname);
    write(fil,' PH OF RUN.........');
    writeln(fil,pH);
    write(fil,'TYPE OF ELECTRODE.........');
    writeln(fil,electrode);
    write(fil,' APPROX VOLTAGE.........');
    writeln(fil,voltage);
    write(fil,' TYPE OF RUN.........');
    writeln(fil,runtype);

teln(fil,'*******************************************************')
 end;

procedure Init;

{ Initiallises graphics variables }

  begin
    OpenWorkstation(1);
    ClearWorkstation;
    DefColour(0,0,0,0);
    DefColour(1,0,0,1000);
    DefColour(2,1000,100,100);
    DefColour(3,100,1000,100);
    SetWriteMode(1);
    SetLineColour(3);
    StringColour(2);
    SetMarkerType(4);
    SetMarkerColour(1);
    SetMarkerSize(1);
    SetFillColour(1)
  end;

procedure Axes(xend,xback,yend,yback:real);

{ Produces a vertical and horizontal axis
               and plots out the graph }

  var i:integer;
      st:string;
      val,xsize,ysize:real;
    begin
      SetWindow(xback,xend,yback,yend);
      SetViewPort(0,1,0,1);
      SetLineType(1);
      If xback < 0 then
        begin
          NewPoly;
          PolyPoint(0,yend);
          PolyPoint(0,yback);
          DrawPoly
        end
      else
        begin
          NewPoly;
          PolyPoint(xback+xback/5,yend);
```

```
    PolyPoint(xback+xback/5,yback);
    DrawPoly
  end;

If yback < 0 then
  begin
    NewPoly;
    PolyPoint(xend,0);
    PolyPoint(xback,0);
    DrawPoly
  end
else
  begin
    NewPoly;
    PolyPoint(xend,yback+yback/5);
    PolyPoint(xback,yback+yback/5);
    DrawPoly
  end;

StringHeight(5);
StringAngle(0);

xsize:=xend-xback;
val:=xsize/10;
xint:=TRUNC(val)+1;

i:=TRUNC(xback);
WHILE i <= xend do
  begin
    If (i MOD xint =0) then
      begin
        If yback < 0 then
          begin
            NewPoly;
            PolyPoint(i,-0.02);
            PolyPoint(i,0);
            DrawPoly;
            str(i,st);
            PlotString(i+0.02,-0.15,st)
          end
        else
          begin
            NewPoly;
            PolyPoint(i,yback+9*yback/40);
            PolyPoint(i,yback+yback/5);
            DrawPoly;
            str(i,st);
            PlotString(i+0.01,yback+7*yback/40,st)
          end
      end;
      i:=i+1
  end;

ysize:=yend-yback;
val:=ysize/10;
yint:=TRUNC(val)+1;

i:=TRUNC(yback);
WHILE i <= yend do
  begin
    If (i MOD yint =0) then
      begin
        If xback < 0 then
          begin
            NewPoly;
            PolyPoint(xback/25,i);
            PolyPoint(0,i);
```

```
                  DrawPoly;
                  str(i,st);
                  PlotString(xback/6,i,st)
                end
              else
                begin
                  NewPoly;
                  PolyPoint(xback+9*xback/40,i);
                  PolyPoint(xback+xback/5,i);
                  DrawPoly;
                  str(i,st);
                  PlotString(xback+7*xback/40,i,st)
                end
            end;
            i:=i+1
        end
     end;

procedure Prompt(xfin,xbeg,yfin,ybeg:real);

{ Displays a message to continue when ready }

  var anychar:char;
    begin
      SetViewPort(0,1,0,1);
      StringAngle(0);
      StringColour(1);
      PlotString(2*xfin/5,10*ybeg/11,'Press RETURN to continue');
      read(anychar)
    end;

procedure Writing1(x1,x2,y1,y2:real);

{ Produces axes headings }
  begin
    StringAngle(0);
    StringHeight(15);
    StringFont(0);
    If y2 < 0 then PlotString(x1/2,7*y2/10,'REAL')
      else PlotString(x1/2,9*y2/10,'REAL');
    StringAngle(90);
    StringHeight(12);
    StringFont(0);
    If x2 < 0 then PlotString(2*x2/10,y1/2,'-IMAG')
      else PlotString(9*x2/10,y1/2,'-IMAG')
  end;
procedure Writing2(x1,x2,y1,y2:real);

{ Produces axes headings }

  begin
    StringAngle(0);
    StringHeight(15);
    StringFont(0);
    If y2 < 0 then PlotString(x1/2,5*y2/10,'log freq. ')
      else PlotString(x2/2,9*y2/10,'log freq. ');
    StringAngle(90);
    StringHeight(10);
    StringFont(0);
    StringColour(2);
    If x2 < 0 then PlotString(2*x2/10,y1/6,'Real')
      else PlotString(9*x2/10,y1/6,'Real');
    StringAngle(90);
    StringColour(3);
    If x2 < 0 then PlotString(2*x2/10,3*y1/6,'-Imag')
      else PlotString(9*x2/10,4*y1/6,'-Imag')
  end;
```

```
rocedure Plotter1(npts:GSXInt);

 Plots graph of real against -imag }

  begin
    SetViewPort(0,1,0,1);
    SetLineColour(2);
    PLINE(A,jB,npts);
    SetMarkerColour(2);
    PMARK(A,jB,npts)
  end;

rocedure Plotter2(npts:GSXInt);

 Plots a graph of log frequency against real }

  begin
    SetLineColour(2);
       PLINE(logfreq,A,npts);
       SetMarkerColour(2);
       PMARK(logfreq,A,npts);
       SetLineColour(3);
       PLINE(logfreq,jB,npts);
       SetMarkerColour(3);
       PMARK(logfreq,jB,npts)
  end;

rocedure Coords(numb,val:integer);

 Limits the number of points plotted at any one time }

 var i,npoints:integer;
  begin
    If numb <> nofits then npoints:=500
      else npoints:=int MOD 500;

    For i:=1 to npoints do
       begin
         A[i]:=realtotal[i+(numb-1)*500];
         jB[i]:=imagtotal[i+(numb-1)*500];
         If val=2 then logfreq[i]:=logf[i+(numb-1)*500]
       end;
    If val=1 then Plotter1(npoints)
             else Plotter2(npoints)
  end;

rocedure Plot(graph:integer);

 Plots a graph }

 var i:integer;
  begin
    For i:=1 to nofits do
       Coords(i,graph)
  end;

rocedure Printdump;

 Dumps the data plotted onto a printer }

  begin
    SetPrinter(PRN,LX80);
    Printdata;
    DumpScreen(Portrait)
  end;
```

```
rocedure Draw;

 Plots a graph according to type specifications }

  begin
    Init;
    If graphtype<>2 then
      begin
        Axes(Aend,Astart,jBend,jBstart);
        Writing1(Aend,Astart,jBend,jBstart);
        Plot(1);
        If printreply=1 then Printdump
        else begin
               Prompt(Aend,Astart,jBend,jBstart);
               Prompt(Aend,Astart,jBend,jBstart)
             end
      end;
    CloseWorkstation;
    Init;
    If graphtype>1 then
      begin
        Axes(fend,fstart,ylength,ystart);
        Writing2(fend,fstart,ylength,ystart);
        Plot(2);
        If printreply=1 then Printdump
        else Prompt(fend,fstart,ylength,ystart)
      end;
    CloseWorkstation
 end;

rocedure Change(ex:integer);

 Transfers impedance data from a file into structured arrays }

   Var n,finish:integer;
       inbounds,notmargin,upperbound,lowerbound,endofln:boolean;
     begin
       rewrite(txf);
       rewrite(num);
       finish:=510*ex+453;
       for n:=5 to finish do
         begin
            write(txf,store[n]);
            lowerbound:=((n-zerocount[n]) MOD 510 > 93);
            upperbound:=((n-zerocount[n]) MOD 510 < 453);
            inbounds:=(lowerbound AND upperbound);
            notmargin:=((n-zerocount[n]-93) MOD 30 > 4);
            endofln:=((n-zerocount[n]-93) MOD 30 =0);
            if (endofln) then writeln(num);
            if (notmargin AND inbounds) then write(num,store[n]);
            if ((n-noextrazeros) MOD 510 =0) then writeln(txf)
         end;
       close(txf)
     end;

rocedure storing;

 Tranfers details of a run into data file }

    Var n:integer;
     begin
      rewrite(dat);
      writeln(dat);
      writeln(dat,'**************************************************');
      write(dat,'TYPE OF RUN......');
      writeln(dat,runtype);
      write(dat,'DATE PERFORMED......');
```

```
      writeln(dat,infname);
      write(dat,'TYPE OF ELECTODE.....');
      writeln(dat,electrode);
      write(dat,'PH OF SOLUTION......');
      writeln(dat,pH);
      write(dat,'APPROX VOLTAGE EXPERIMENT RUN AT....');
      writeln(dat,voltage);
      writeln(dat,'**************************************************');
      for n:=1 to 510 do
          write(dat,store[n])
     end;

rocedure RAP;

 Command to write and send each bit }

     begin
      ZKINIT;
    { ZLINIT(1); }
      repeat
        begin
          repeat until ZKDATA;
          c:=ZKGET;
          if c=CTRLT then goto 999;
          write(chr(c));
          sendch(c,1);
        end;
      until c = COMMA;
      ZKEND;
    { ZLEND(1) }
        end;

edure TRANS(extrapage:integer);

ores experimental data sequentially in a file }

     var n,t,start,fin:integer;
         lastblank:boolean;
         index,ind : integer;
         temps : array [1..1000] of byte;
     begin
    {  ZLINIT(1);  }
     { writeln;writeln; }
       start:=(510*extrapage)+1;
       fin:=510*(extrapage+1);
       n:=start;
       t:=0;
       lastblank:=false;

       { Read in a block of data without interruption }
       index := 1;
       repeat
          if ZLDATA(1) then
          begin
             temps[index] := ZLGET(1);
             index := index + 1;
             t := 0;
          end
          else
             t := t + 1
       until (t > 10000);

       writeln('  End of block transfer ');
```

```
       { Now process the block of data }
       for ind := 1 to index do
       begin
          c := temps[ind];
          if c > 127 then c:=c-128;
          write(chr(c));
          if(c=46)AND(lastblank=true) then
          begin
             store[n]:=chr(48);
             n:=n+1;
             noextrazeros:=noextrazeros+1
          end;
          zerocount[n]:=noextrazeros;
          store[n]:=chr(c);
          n:=n+1;
          if (c=32) OR (c=45) then lastblank:=true
          else lastblank:=false;
          zerocount[n]:=noextrazeros
       end;
     { ZLEND(1) }
     end;

edure initial;

oduces empty arrays }

  var i:integer;
     begin
       For i:=1 to arrsize do
        begin
          store[i]:=' ';
          zerocount[i]:=0
        end
     end;

edure cart;

nds command to produce data in cartesian form }

     begin
     {  ZLINIT(1);  }
        sendch(EXCLAM,1);
        sendch(DIG1,1);
        sendch(COMMA,1)
      { ZLEND(1) }
     end;

edure dump4(extra:integer);

mmand to transfer experimental results from TFA down a line }

junk : byte;
     begin
      { writeln('start dump command'); }
      { ZLINIT(1);  }
      { writeln('init drivers'); }
        while ZLdata(1) do    { Read the buffer dry }
           junk := ZLget(1);
        sendch(CAPT,1);
        sendch(RBRACK,1);
        sendch(DIG4,1);
        sendch(COMMA,1);
      { writeln('end dump command'); }
      { ZLEND(1); }
      { writeln('deact drivers'); }
        TRANS(extra);
        Change(extra);
```

```
    end;

edure dump1;

mmand to dump input data down a line }

     begin
    {  ZLINIT(1);  }
        sendch(CAPT,1);
        sendch(RBRACK,1);
        sendch(DIG2,1);
        sendch(COMMA,1);
     { ZLEND(1); }
       TRANS(0);
       storing
     end;
edure storeinput;

mmand for data entry to TFA }

     begin
    {  ZLINIT(1);  }
        sendch(SLASH,1);
        sendch(DIG2,1);
        sendch(COMMA,1);
      { ZLEND(1) }
     end;

edure SPACE;

mmand to produce a space }

     begin
     {  ZLINIT(1);  }
        repeat until ZLRDY(1);
        ZLPUT(BLANK,1);
        repeat until ZLRDY(1);
        ZLPUT(COMMA,1);
        wait(10000);
      { ZLEND(1)  }
     end;

edure FORM2;

mmands to produce auto correlator range and channel B/A on TFA }

     begin
      { ZLINIT(1);  }
        writeln(   'AUTOBIAS ON  ');
        repeat until ZLRDY(1);
        ZLPUT(CAPB,1);
        repeat until ZLRDY(1);
        ZLPUT(RBRACK,1);
        repeat until ZLRDY(1);
        ZLPUT(STAR,1);
        repeat until ZLRDY(1);
        ZLPUT(COMMA,1);
        wait(10000);
        writeln(   'RMS SINE WAVE CHOSEN ');
        repeat until ZLRDY(1);
        ZLPUT(CAPV,1);
        repeat until ZLRDY(1);
        ZLPUT(STAR,1);
        repeat until ZLRDY(1);
        ZLPUT(BLANK,1);
        repeat until ZLRDY(1);
        ZLPUT(STAR,1);
```

```
        repeat until ZLRDY(1);
        ZLPUT(COMMA,1);
        wait(10000);
        writeln(   'Finding FORM2  ');
        repeat until ZLRDY(1);
        ZLPUT(PERCENT,1);
        repeat until ZLRDY(1);
        ZLPUT(DIG2,1);
        repeat until ZLRDY(1);
        ZLPUT(COMMA,1);
        wait(10000);
      { ZLEND(1) }
   end;

ocedure RAR;

Command to produce a star on TFA input }

     begin
       {  ZLINIT(1);  }
          if c=CTRLT then goto 999;
        wait(10000);
          sendch(STAR,1);
          sendch(COMMA,1);
        wait(10000);
      { ZLEND(1) }
      end;

procedure CHANNEL;

{ Command to set channels on TFA }

     begin
     {  ZLINIT(1);  }
        if c=CTRLT then goto 999;
        wait(10000);
        sendch(DIG5,1);
        sendch(DIG0,1);
        sendch(DIG0,1);
        sendch(COMMA,1);
        wait(10000);
        sendch(DIG5,1);
        sendch(DIG0,1);
        sendch(DIG0,1);
        sendch(COMMA,1);
        wait(10000);
      { ZLEND(1) }
   end;

procedure start;

{ Command to start TFA }

     begin
     { ZLINIT(1);  }
        sendch(ATSIGN,1);
        wait(10000);
        sendch(COMMA,1);
     { ZLEND(1) }
     end;

procedure echooff;

{ Command to set echo off on TFA }

     begin
       sendch(CAPD,1);
```

```
        sendch(CAPY,1);
        sendch(DIG0,1);
        sendch(COMMA,1)
     end;

procedure show;

{ Command for data display }

     begin
     { ZLINIT(1); }
        sendch(SLASH,1);
        sendch(DIG3,1);
        sendch(COMMA,1)
     { ZLEND(1) }
     end;

procedure roll(noext:integer);

{ Command for roll onto next page of data }

   var i:integer;
     begin
        For i:=1 to noext do
          begin
           { ZLINIT(1); }
             sendch(SLASH,1);
             sendch(DIG1,1);
             sendch(COMMA,1);
           { ZLEND(1); }
             wait(120000)
          end
     end;

procedure RunAndStore;

{ Input of experimental requirements and transfer of data to/from TFA }

   var mins,hrs,total,i:integer;
     begin
         write('Approx voltage of the run..... ');
         read(voltage);
         write('No. of intervals to be taken..... ');
         read(int);
         write('pH of run.....');
         read(pH);
         writeln;
         If (int MOD 12=0) then extrapages :=(int DIV 12)-1
         else extrapages:=int DIV 12;
         writeln('RUN TIME');
         writeln;
         write('Hours........ ');
         read(hrs);
         write('Minutes...... ');
         read(mins);
         total:=(mins*1440000)+(hrs*86400000);
         writeln('Do you want graphs of...');
         writeln('1..... REAL against IMAGINARY');
         writeln('2..... LOG FREQ against REAL');
         writeln('3..... BOTH');
         writeln('4..... NO GRAPHS');
         read(graphtype);
         If graphtype <=3 then
           begin
             writeln('Do you require a printout of the graphs?');
             writeln('1..... YES');
             writeln('2..... NO');
```

```
             read(printreply)
           end;
         start;
         wait(total);
         show;
         wait(200000);
         cart;
         wait(200000);
         dump4(0);
         wait(200000);
         show;
         For i:=1 to extrapages do
            begin
              wait(12000);
              roll(i);
              wait(10000);
              noextrazeros:=0;
              dump4(i);
              wait(10000);
              show
            end;
              If graphtype<=3 then
                begin
                  transfer(int);
                  Draw
                end;
            writeln;
            writeln;
            writeln('INPUT DATA');
            writeln('----------');
            writeln;
            wait(10000);
            initial;
            storeinput;
            wait(12000);
            dump1
   end;

procedure ChangeData(itemno:integer);

{ Input data for TFA and transfer of the data to TFA }

   begin
   { ZLINIT(1); }
   { writeln; }
     Case itemno of
        1:begin
            sendch(CAPF,1);
            writeln('read in start FREQUENCY and a comma,Ctrl-T to
                                                               stop');
            RAP
          end;
        2:begin
            sendch(CAPF,1);
            sendch(RBRACK,1);
            writeln('read in end FREQUENCY and a comma,Ctrl-T to stop');
            RAP
          end;
        3:begin
            sendch(CAPH,1);
            writeln('read in HARMONIC and a comma,Ctrl-T to stop');
            RAP
          end;
        4:begin
            sendch(CAPA,1);
            writeln('read in AMPLITUDE/VOLTS ,Ctrl-T to stop');
            RAP
```

```
          end;
        5:begin
            sendch(CAPA,1);
            sendch(RBRACK,1);
            writeln('read in BIAS/VOLTS and a comma,Ctrl-T to stop');
            RAP
          end;
        6:begin
            sendch(CAPI,1);
            writeln('read in INTEGRATION CYCLES,Ctrl-T to stop');
            RAP
          end;
        7:begin
            sendch(CAPD,1);
            writeln('read in DELAY and a comma,Ctrl-T to stop');
            RAP
          end;
        8:begin
            sendch(SHARP,1);
            writeln('read in INTERVALS and a comma,Ctrl-T to stop');
            RAP
          end;
        9:RunAndStore
        end;
        writeln;
      { ZLEND(1) }
    end;

rocedure DataChange;

 Provides the possibilty of changing input data to TFA }

  begin
    FORM2;
    reply:=0;
    repeat
      writeln('Data to be changed.......');
      writeln('1: Start Frequency');
      writeln('2: End   Frequency');
      writeln('3: Harmonic');
      writeln('4: Amplitude/Volts');
      writeln('5: Bias/Volts');
      writeln('6: Integration Cycles');
      writeln('7: Delay');
      writeln('8: Intervals');
      writeln('9: RUN AND STORE DATA');
      writeln;
      writeln('Enter 1-9  ?');
      read(reply);
      ChangeData(reply)
    until reply=9
end;

rocedure SetUpData;

 Initiallisation procedure for TFA }

 var item:integer;
  begin
    item:=0;
    FORM2;
    repeat
      item:=item+1;
      ChangeData(item)
    until item=5;
    RAR;
    CHANNEL;
```

```
    repeat
      item:=item+1;
      ChangeData(item)
    until item=8;
    SPACE;
    RAR;
    SPACE;
    SPACE;
    RAR;
    ChangeData(9)
 end;


n

write('TYPE OF RUN ....... ');
readln(runtype);
write('TYPE OF ELECTRODES USED......');
readln(electrode);

writeln('Enter filename for input data,based on the date [e.g IN-JN23

readln(infname);
infname:=Concat(infname,'.DAT');
assign(dat,infname);
writeln;
writeln('Enter filename for output data [e.g OUT-JN23 ]');
readln(outfname);
outfname:=Concat(outfname,'.DAT');
assign(txf,outfname);
writeln;
writeln('Enter name for results [e.g RES-JN23 ]');
readln(numfname);
numfname:=Concat(numfname,'.DAT');
assign(num,numfname);

noextrazeros:=0;
initial;

writeln('  Program to drive TFA');
writeln;
writeln('Do you wish to ....');
writeln('1.....Set up Data');
writeln('2.....Change existing Data');
writeln;
writeln('Answer 1/2 ?');
read(ans);

ZLinit(1);
echooff;
Case ans of
   1:SetUpData;
   2:DataChange
   end;
writeln('  data finished ');
ZLend(1);
```

PROGRAM 'ETEST'

```
gram TERMINAL(input,output);
el 999;
st
size=510;
value=75.01;
threshhold=5.0;
3.142;
 DRIVERS.CST}
 PROSRM.CST}

e
states=(pos,neg);
stores=ARRAY[1..arrsize] OF char;
zeros=ARRAY[1..arrsize] OF integer;
arr2=ARRAY[1..125] OF real;
arr1=ARRAY[1..3] OF real;
machine=(RML480Z,BBC);
slavetype=1..30;
channeltype=0..3;
elstate=(bad,good);
 DRIVERS.TYP}
 PROSRM.TYP}

c : byte;       { Character variable }
o,s,mr,answ,i,t,rep,nofits:integer;
freq,imag,fmax,f,fmin,jBmin,Amin,fend,Aend,jBend,noint,Astart:real;
jBstart,fstart,ylength,ystart,pH:real;
logfreq,A,jB,newfreq:CoordArray;
xint,yint,int:GSXInt;
logf,realtotal,imagtotal:arr2;
ans,reply,noextrazeros,count,intro:integer;
store:stores;
zerocount:zeros;
outfname,numfname:String[30];
dat,txf,num:text;
X,y,v:integer;
tantheta,tanth:real;
electrodestate:elstate;
elecno,time,nomin:integer;
date:String[10];
ideal:ARRAY[1..5] of real;

 DRIVERS2.EXT}
 PROSRM.EXT}
 PICOLIB.EXT}
 ZP.EXT}
rocedure sendch(ch : byte; dev :byte);
egin
 repeat until ZLrdy(dev);
 ZLPUT(ch,dev)
nd;
rocedure wait(time:integer);

 Produces a time delay }

  var t:integer;
    begin
      t:=0;
      repeat
       t:=t+1
      until t>time
    end;
```

```
rocedure Change;

 Transfers impedance data from a file into structured arrays }

   Var n,finish:integer;
       inbounds,notmargin,upperbound,lowerbound,endofln:boolean;
     begin
       rewrite(txf);
       rewrite(num);
       finish:=453;
       for n:=5 to finish do
         begin
            write(txf,store[n]);
            lowerbound:=((n-zerocount[n]) MOD 510 > 93);
            upperbound:=((n-zerocount[n]) MOD 510 < 453);
            inbounds:=(lowerbound AND upperbound);
            notmargin:=((n-zerocount[n]-93) MOD 30 > 4);
            endofln:=((n-zerocount[n]-93) MOD 30 =0);
            if (endofln) then writeln(num);
            if (notmargin AND inbounds) then write(num,store[n]);
            if ((n-noextrazeros) MOD 510 =0) then writeln(txf)
         end;
       close(txf)
     end;


edure TRANS;

ores experimental data sequentially in a file }

     var n,t,start,fin:integer;
         lastblank:boolean;
         index,ind : integer;
         temps : array [1..1000] of byte;
     begin
    {  ZLINIT(1);  }
     { writeln;writeln; }
       start:=1;
       fin:=510;
       n:=start;
       t:=0;
       lastblank:=false;

       { Read in a block of data without interruption }
       index := 1;
       repeat
          if ZLDATA(1) then
          begin
             temps[index] := ZLGET(1);
             index := index + 1;
             t := 0;
          end
          else
             t := t + 1
       until (t > 1000);


       { Now process the block of data }.
       for ind := 1 to index do
       begin
          c := temps[ind];
          if c > 127 then c:=c-128;
          if(c=46)AND(lastblank=true) then
          begin
             store[n]:=chr(48);
             n:=n+1;
```

```
              noextrazeros:=noextrazeros+1
           end;
           zerocount[n]:=noextrazeros;
           store[n]:=chr(c);
           n:=n+1;
           if (c=32) OR (c=45) then lastblank:=true
           else lastblank:=false;
           zerocount[n]:=noextrazeros
        end;
      { ZLEND(1) }
      end;

cedure initial;

roduces empty arrays }

   var i:integer;
      begin
        For i:=1 to arrsize do
         begin
           store[i]:=' ';
           zerocount[i]:=0
         end
      end;
cedure beep;
roduces a beep }

      begin
       write(chr(27),'[0~D');
       write(chr(7))
      end;
cedure cart;

ends command to produce data in cartesian form }

      begin
      {  ZLINIT(1);  }
         sendch(EXCLAM,1);
         sendch(DIG1,1);
         sendch(COMMA,1)
       { ZLEND(1) }
      end;

cedure dump4;

ommand to transfer experimental results from TFA down a line }

 junk : byte;
      begin
       { writeln('start dump command'); }
       { ZLINIT(1);  }
       { writeln('init drivers'); }
         while ZLdata(1) do    { Read the buffer dry }
            junk := ZLget(1);
         sendch(CAPT,1);
         sendch(RBRACK,1);
         sendch(DIG4,1);
         sendch(COMMA,1);
       { writeln('end dump command'); }
       { ZLEND(1); }
       { writeln('deact drivers'); }
         TRANS;
         Change;
     end;
```

```
ction findtangent:real;
  var deg,rad:real;
      begin
        reset(num);
        read(num,intro);
        read(num,freq);
        read(num,realtotal[1]);
        writeln('real',realtotal[1]);
        read(num,imag);
        writeln('imag',imag);
        imagtotal[1]:=-imag;
        deg:=(imagtotal[1]/realtotal[1]);
        rad:=arctan(deg);
        findtangent:= (360/(2*pi))*rad
    end;

cedure gotoxy(x,y: byte);
      begin
        write(chr(27),'[',y:1,';',x:1,'H')
      end;

cedure clrscr;
     begin
       write(chr(27),'[2J')
     end;

cedure SPACE;

ommand to produce a space }

      begin
      {  ZLINIT(1);  }
         sendch(BLANK,1);
         sendch(COMMA,1);
         wait(10000);
       { ZLEND(1)   }
      end;

cedure FORM2;

ommands to produce auto correlator range and channel B/A on TFA }

      begin
       { ZLINIT(1);  }
         repeat until ZLRDY(1);
         ZLPUT(CAPB,1);
         repeat until ZLRDY(1);
         ZLPUT(RBRACK,1);
         repeat until ZLRDY(1);
         ZLPUT(STAR,1);
         repeat until ZLRDY(1);
         ZLPUT(COMMA,1);
         wait(10000);
         repeat until ZLRDY(1);
         ZLPUT(CAPV,1);
         repeat until ZLRDY(1);
         ZLPUT(STAR,1);
         repeat until ZLRDY(1);
         ZLPUT(BLANK,1);
         repeat until ZLRDY(1);
         ZLPUT(STAR,1);
         repeat until ZLRDY(1);
         ZLPUT(COMMA,1);
         wait(10000);
         repeat until ZLRDY(1);
         ZLPUT(PERCENT,1);
         repeat until ZLRDY(1);
```

```
        ZLPUT(DIG2,1);
        repeat until ZLRDY(1);
        ZLPUT(COMMA,1);
        wait(10000);
      { ZLEND(1) }
   end;

rocedure RAR;

Command to produce a star on TFA input }

     begin
       {  ZLINIT(1);   }
          sendch(STAR,1);
          sendch(COMMA,1);
          wait(10000);
       { ZLEND(1) }
      end;

procedure CHANNEL;

{ Command to set channels on TFA }

     begin
     {  ZLINIT(1);   }
        sendch(DIG5,1);
        sendch(DIG0,1);
        sendch(DIG0,1);
        sendch(COMMA,1);
        wait(10000);
        sendch(DIG5,1);
        sendch(DIG0,1);
        sendch(DIG0,1);
        sendch(COMMA,1);
        wait(10000);
      { ZLEND(1) }
   end;

procedure start;

{ Command to start TFA }

     begin
     { ZLINIT(1)    }
        sendch(ATSIGN,1);
        sendch(COMMA,1);
     { ZLEND(1) }
     end;

procedure show;

{ Command for data display }

     begin
     { ZLINIT(1) }
        sendch(SLASH,1);
        sendch(DIG3,1);
        sendch(COMMA,1)
     { ZLEND(1) }
     end;

procedure echooff;

{ Command to set echo off on TFA }

     begin
       sendch(CAPD,1);
```

```
        sendch(CAPY,1);
        sendch(DIG0,1);
        sendch(COMMA,1)
      end;


 procedure tantest;

       begin
         If ABS(tanvalue-tantheta) > tanthreshhold
           then electrodestate:= bad
       end;

 procedure RunAndStore;

 { Input of experimental requirements and transfer of data to/from TFA }

    var total,i:integer;
      begin
          wait(50000);
          start;
          wait(100000);
          cart;
          wait(10000);
          show;
          wait(10000);
          dump4;
          tantheta:=findtangent;
          tantest;
    end;

procedure ChangeData(itemno:integer);

{ Input data for TFA and transfer of the data to TFA }

    begin
    { ZLINIT(1); }
    { writeln; }
      Case itemno of
         1:begin
             sendch(CAPF,1);
             sendch(DIG1,1);
             sendch(DIG0,1);
             sendch(DIG0,1);
             sendch(COMMA,1);
             wait(10000);
           end;
         2:begin
             sendch(CAPF,1);
             sendch(RBRACK,1);
             sendch(DIG2,1);
             sendch(DIG0,1);
             sendch(DIG0,1);
             sendch(COMMA,1);
             wait(10000);
           end;
         3:begin
             sendch(CAPH,1);
             sendch(DIG1,1);
             sendch(COMMA,1);
             wait(10000);
           end;
         4:begin
             sendch(CAPA,1);
             sendch(PERIOD,1);
             sendch(DIG1,1);
             sendch(DIG5,1);
```

```
              wait(10000);
           end;
        5:begin
              sendch(CAPA,1);
              sendch(RBRACK,1);
              sendch(DIG0,1);
              sendch(COMMA,1);
              wait(10000);
           end;
        6:begin
              sendch(CAPI,1);
              sendch(DIG1,1);
              sendch(DIG0,1);
              sendch(COMMA,1);
              wait(10000);
           end;
        7:begin
              sendch(CAPD,1);
              sendch(PERIOD,1);
              sendch(DIG1,1);
              sendch(COMMA,1);
              wait(10000);
           end;
        8:begin
              sendch(SHARP,1);
              sendch(DIG2,1);
              sendch(COMMA,1);
              wait(10000);
           end;
        9:RunAndStore
        end
      { ZLEND(1) }
    end;

procedure DataChange;

{ Provides the possibilty of changing input data to TFA }

   begin
     FORM2;
     reply:=0;
     repeat
       writeln('Data to be changed.......');
       writeln('1: Start Frequency');
       writeln('2: End   Frequency');
       writeln('3: Harmonic');
       writeln('4: Amplitude/Volts');
       writeln('5: Bias/Volts');
       writeln('6: Integration Cycles');
       writeln('7: Delay');
       writeln('8: Intervals');
       writeln('9: RUN AND STORE DATA');
       writeln;
       writeln('Enter 1-9  ?');
       read(reply);
       ChangeData(reply)
     until reply=9
 end;


procedure startoff;
    begin
      clrscr;

      writeln('Give date....');
      readln(date);
      writeln('Give electrode no....');
```

```
      readln(elecno);
      tanth:=ideal[elecno];
      writeln('Give time for pH measurements (in mins)....');
      readln(nomin);
      time:=nomin*3500
    end;

procedure title;
    begin
     writeln;writeln;writeln;writeln;writeln;writeln;writeln;
     write('DATE   ',' ELECTRODE     ','@ EXPECTED      ','@ MEASURED');
     writeln('         PH    ','    ELSTATE');
     write('-----------------------------------------------------------');
     write('-------------------')
    end;


procedure table1;
    begin
     writeln;writeln;writeln;
     If electrodestate=good then
       begin
        write(date,'     ',elecno:3,'       ',tanth,'  ','   MEASURING ');
        write('         ',pH:7,'       ','good')
       end
     else
       begin
        write(date,'     ',elecno:3,'       ',tanth,'  ','   MEASURING ');
        write('         ',pH:7,'       ','Poor')
       end;
     GotoXY(30,30);Writeln(' MEASURING IMPEDANCE')
    end;

procedure table2;
    begin
     writeln;writeln;writeln;
     If electrodestate=good then
       begin
        write(date,'     ',elecno:3,'       ',tanth,'  ',tantheta);
        write('                     ','  good')
       end
     else
       begin
        write(date,'     ',elecno:3,'       ',tanth,'  ',tantheta);
        write('                     ','  Poor')
       end;
     GotoXY(30,30);Writeln('MEASURING PH')

    end;
procedure switchimp;
  var i:integer;
    begin
      for i:=32 to 53 do
        ZPPUT(0,i,9);

      ZPPUT(64,32,9);
      ZPPUT(1,35,9);
      ZPPUT(7,37,9);
      ZPPUT(1,39,9)
    end;
```

```
procedure phtest;
  var ch :byte;
       i :integer;
    begin

      clrscr;
      title;
      table2;
      count:=1;
      for i:=32 to 53 do
        ZPPUT(0,i,9);
      Repeat
           for ch:= 0 to 1 do
           BEGIN
               Select_Analogue_Channel(9,ch);
               Repeat
                    until End_of_Conversion(9);
               v := Analogue_Value(9,ch);
               pH:= 9.0-((106-v)/10);
               If ch= 1 then begin
                                       GotoXY(58,12);
                                       Writeln(pH:7);
                                       count:=count+1
                              end

           end;
      until (Button_status(9)=1) OR ( count=time);
      writeln(chr(27),'c')
    end;
procedure SetUpData;

{ Initiallisation procedure for TFA }

  var item:integer;
   begin
     electrodestate:=good;
     noextrazeros:=0;
     initial;
     item:=0;
     FORM2;
     repeat
       item:=item+1;
       ChangeData(item)
     until item=5;
     wait(10000);
     RAR;
     CHANNEL;
     repeat
       item:=item+1;
       ChangeData(item)
     until item=8;
     wait(10000);
     SPACE;
     RAR;
     SPACE;
     SPACE;
     RAR
  end;

gin

 ideal[1]:=75.0;
 ideal[2]:=72.1;
 ideal[3]:=69.7;
```

```
startoff;
tantheta:=0;

ZLinit(1);
 Setupdata;
ZLend(1);

repeat
  If electrodestate=bad then
      begin
       for i:=1 to 100 do
          beep
      end;
  ZPinit(9);
  pHtest;
  switchimp;
  ZPend(9);
  ZLinit(1);
  echooff;
  clrscr;
  title;
  table1;
  setupdata;
  RunandStore;
  ZLend(1);
until tantheta > 100;
:writeln('Data finished')
.
```