

## DIFFUSION POLARISATION OF THE HYDROGEN ELECTRODE\*

## I. THEORY

A. H. M. COSIJN\*\*

*Laboratory for Analytical Chemistry, State University, Utrecht (The Netherlands)*

(Received November 18th, 1960)

## I. INTRODUCTION

The water-hydrogen redox system ( $\text{H}_2\text{O}$ ,  $\text{H}^+$ ,  $\text{OH}^-$ ,  $\text{H}_2$ ) takes a particular place in the electrochemistry of aqueous solutions as this system forms the boundary at the reduction side of the electrochemical stability region of water. In  $E$ -pH diagrams the position of this boundary is commonly calculated from the NERNST equation using the standard potential of the normal hydrogen electrode as the  $E_0$ -value. In actual experiments, however, it depends on the reversibility of the water-hydrogen system at the concerning electrode whether this theoretical boundary will be realised. At various electrodes and in various solutions, for instance, activation polarisation shifts the boundary to more negative values of  $E$ .

So the question arises whether the system really behaves reversibly at the platinised platinum-hydrogen electrode over the entire pH range 0-14. If this is the case, the polarisation curves measured at a stationary hydrogen electrode during direct-current electrolysis of the solutions will be controlled by the limiting rates of diffusion of the species participating directly or indirectly in the electrode process.

The first inquiries into this matter were made by NERNST<sup>1</sup>, EUCKEN<sup>2</sup>, FRESSENIUS<sup>3</sup> and later on by ATEN<sup>4</sup>. In recent years the interest revived again with the studies of KING<sup>5</sup>, SMITTENBERG<sup>6</sup>, NAGEL AND WENDLER<sup>7,8</sup>, COUPEZ<sup>9,10</sup> and BREITER<sup>11</sup>.

These studies show some gaps in both the theoretical and experimental work. The experimental data are insufficient for a thorough testing of the theory and the theory is at the same time lacking in giving a detailed current-potential relation for solutions containing partly dissociated electrolytes. Thus *e.g.* NAGEL<sup>7,8</sup> and BREITER<sup>11</sup> have overlooked the influence of the hydrogen sulphate ion on the polarisation curves of the hydrogen electrode in acidic or neutral sulphate solutions.

This paper is concerned with the presentation of general equations for the current-potential relation at the stationary hydrogen electrode on the basis of pure diffusion polarisation for solutions containing completely or partly dissociated solutes with an excess of supporting electrolyte. Furthermore equations are derived for the current

\* The work reported in this paper was taken from the Doctorate Thesis of A. H. M. COSIJN, Utrecht, The Netherlands, July, 1959.

\*\* Present address: Central Laboratory, Koninklijke Industriële Maatschappij v/h Noury & van der Lande N.V., Deventer, The Netherlands.

density and the overvoltage\* at the inflexion point of the polarisation curves. With the aid of these various equations the voltammetric behaviour of the hydrogen electrode in 0.1 M KCl and 0.1 M K<sub>2</sub>SO<sub>4</sub> solutions with pH 3–11 and in (1:1) acetate and (1:1) phosphate buffer solutions with varying concentrations is calculated. In a subsequent part experiments will be described which have been carried out at the platinised platinum–hydrogen electrode in order to verify the theory.

## 2. THEORETICAL

### (a) *Partial current density in stirred solutions containing an excess of supporting electrolyte*

On the basis of the NERNST theory of the diffusion layer one can write the following expression for the partial current density due to a reacting ion *p*, in solutions which are stirred with a constant speed and which contain an excess of supporting electrolyte

$$i_p = -\frac{|z_p|}{z_p} \frac{RT}{F} \lambda_p \cdot 10^{-3} \frac{c_p - oc_p}{\delta} \quad (1)**$$

where  $i_p$  = current density (A cm<sup>-2</sup>);

$z_p$  = valency of ion *p*\*\*\*;

$\lambda_p$  = equivalent conductance of ion *p* in the medium (A cm<sup>2</sup> eq<sup>-1</sup> V<sup>-1</sup>);

$c_p$  = concentration in the bulk of the solution (moles liter<sup>-1</sup>);

$oc_p$  = concentration at the electrode surface (moles liter<sup>-1</sup>);

$\delta$  = thickness of the diffusion layer (cm).

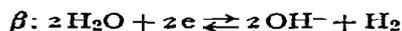
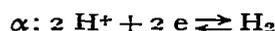
The partial current density due to an uncharged component participating in the electrode process is given by

$$i_p = -nFD_p \cdot 10^{-3} \frac{c_p - oc_p}{\delta} \quad (2)$$

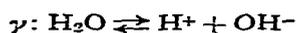
where  $D_p$  = diffusion coefficient of component *p* in the medium concerned (cm<sup>2</sup> sec<sup>-1</sup>).

### (b) *Current–potential equation of the hydrogen electrode in solutions containing completely dissociated solutes*

In aqueous solutions containing completely dissociated solutes the following reactions may occur at the hydrogen electrode<sup>12</sup>



Both reactions are correlated by the dissociation of water



If one assumes that the rates of the dissociation and recombination of water are large

\* In this paper overvoltage is understood to be the difference between the potential measured at the indicator electrode when a certain current is passing across the surface and the potential measured at the same electrode when the current intensity is equal to zero.

\*\* A positive (negative) current corresponds to an anodic (cathodic) reaction at the electrode surface.

\*\*\* The assumption is made that the number of electrons *n* participating in the electrode process equals the valency  $z_p$ .

with regard to the rates of the electrochemical reactions, the concentrations of  $H^+$  and  $OH^-$  ions near the electrode will obey the equation\*:

$$Q_w = {}_0c_H \cdot {}_0c_{OH} \quad (3)$$

in which  $Q_w$  is the ionic product of water.

Premising furthermore that the electrochemical reactions occur very quickly in comparison with the mass-transfer processes, the following relations are obtained for the overvoltage  $\eta$  in solutions containing an excess of supporting electrolyte:

$$\eta = \frac{RT}{F} \ln \frac{{}_0c_H}{c_H} + \frac{RT}{2F} \ln \frac{c_{H_2}}{{}_0c_{H_2}} \quad (4)$$

$$\eta = \frac{RT}{F} \ln \frac{c_{OH}}{{}_0c_{OH}} + \frac{RT}{2F} \ln \frac{c_{H_2}}{{}_0c_{H_2}} \quad (5)$$

The current density is given by

$$i = i_H + i_{OH} \quad (6)$$

in which the terms  $i_H$  and  $i_{OH}$  are the partial current densities related to the formation or consumption of  $H^+$  and  $OH^-$ . Provided the hydrogen molecule moves only by diffusion\*\*, the current density is also equal to the partial current density related to the formation or consumption of the  $H_2$  molecule.

$$i = i_{H_2} \quad (7)$$

Eqns. 1 and 2 are applicable to the partial current densities and in abridged form give the following relations:

$$i_H = k_H({}_0c_H - c_H) \quad (8)$$

$$i_{OH} = k_{OH}(c_{OH} - {}_0c_{OH}) \quad (9)$$

$$i_{H_2} = k_{H_2}(c_{H_2} - {}_0c_{H_2}) \quad (10)$$

where  $k$  is the transport coefficient in the medium concerned\*\*\*. The corresponding limiting currents ( $i_0$ ) are given by

$$i_{0H} = -k_H c_H \quad (11)$$

$$i_{0OH} = k_{OH} c_{OH} \quad (12)$$

$$i_{0H_2} = k_{H_2} c_{H_2} \quad (13)$$

By combining (7), (10) and (13) one has

$$\frac{c_{H_2}}{{}_0c_{H_2}} = \frac{i_{0H_2}}{i_{0H_2} - i} \quad (14)$$

From (14), (4) and (5) one obtains for  $i < i_{0H_2}$ :

$${}_0c_H = c_H(1 - i/i_{0H_2})^{1/2} e^{\eta F/RT} \quad (15)$$

$${}_0c_{OH} = c_{OH}(1 - i/i_{0H_2})^{-1/2} e^{-\eta F/RT} \quad (16)$$

\* For the sake of simplicity the signs of ions in index figures are omitted.

\*\* If the current density surpasses ten times the limiting current density of  $H_2$  hydrogen molecules will escape from the electrode surface in the form of gas bubbles<sup>13</sup>, in which case the condition of transport by diffusion is not fulfilled.

\*\*\* Note that  $k = k' \cdot 10^{-3}$  in which  $k'$  has the dimension  $A \text{ cm mol}^{-1}$ .

Next substituting (15) and (16) in (8) and (9) and making use of (6), (11) and (12) the following equation is obtained:

$$i = i_{\text{OH}} [1 - (1 - i/i_{\text{H}_2})^{1/2} e^{\eta F/RT}] + i_{\text{OH}} [1 - (1 - i/i_{\text{H}_2})^{-1/2} e^{-\eta F/RT}] \quad (17)$$

This is the general current-potential relation of the hydrogen electrode in the case of pure diffusion polarisation when the solution contains completely dissociated acids or bases in addition to an excess of a supporting electrolyte.

Eqn. 17 may be converted into an expression for  $\eta$  as follows: transpose all terms of the right-hand side of eqn. 17 to the left-hand side and multiply by  $e^{\eta F/RT}$ , thus obtaining a quadratic equation, the resolution of which is given by

$$e^{\eta F/RT} = \frac{-I \pm (I^2 - 4 i_{\text{OH}} i_{\text{OH}})^{1/2}}{2 i_{\text{OH}} (1 - i/i_{\text{H}_2})^{1/2}} \quad (17a)$$

where  $I = i - i_{\text{OH}} - i_{\text{OH}}$ .

Since  $i_{\text{OH}}$  has a negative value and  $i_{\text{OH}}$  a positive value, the square root in the numerator is always greater than the absolute value of  $I$ . The denominator is always negative because of  $i_{\text{OH}}$ . Consequently, one has to extract the negative square root in the numerator since  $e^{\eta F/RT}$  can only be positive. This results in the following value for the overvoltage at 25°:

$$\eta = 0.0591 \log \frac{-I - |I| \left(1 - \frac{4 i_{\text{OH}} i_{\text{OH}}}{I^2}\right)^{1/2}}{2 i_{\text{OH}}} - 0.0295 \log(1 - i/i_{\text{H}_2}) \quad (18)$$

The expressions (17) and (18) have also been derived in less clear forms by BREITER<sup>11</sup> and NAGEL<sup>8</sup>, respectively.

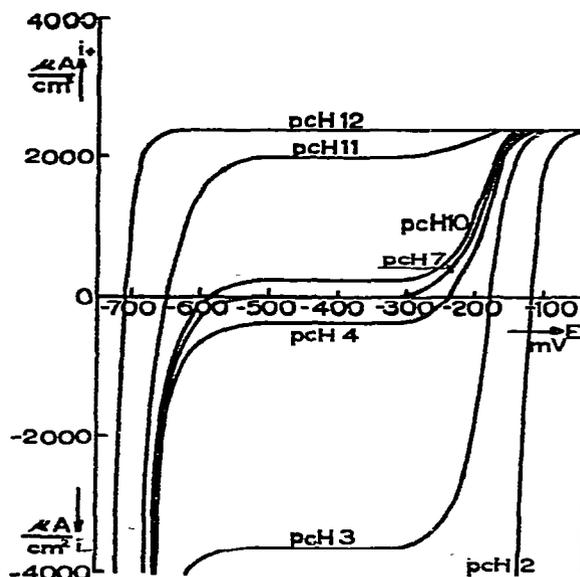


Fig. 1.  $i$ - $E$  curves of the hydrogen electrode in solutions containing completely dissociated solutes, calculated from eqn. 18.

From (18) one calculates easily  $E$  as a function of  $i$  for each value of  $p_{\text{cH}}^*$ . As an example, current-potential curves are plotted in Fig. 1 and Fig. 2 for the following data:  $k_{\text{H}} = 3.6$ ,  $k_{\text{OH}} = 2$  and  $i_{\text{gH}_2} = 2.4 \cdot 10^{-3} \text{ A cm}^{-2}$ .

Most curves show two current plateaus. The first plateau results from the limiting rates of diffusion of the hydrogen and (or) hydroxyl ions; it moves from the cathodic

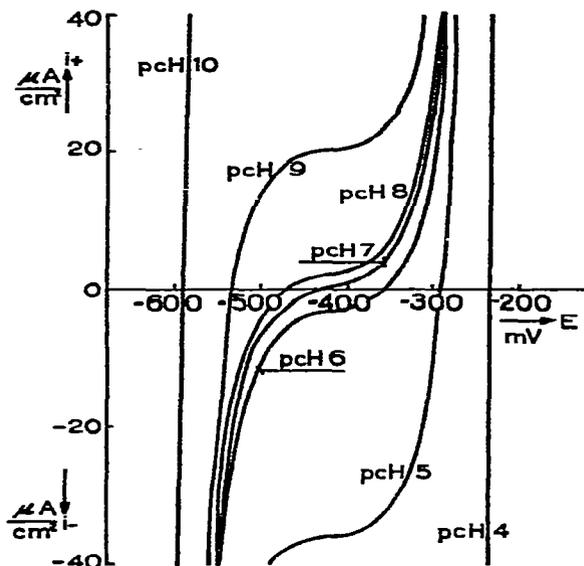


Fig. 2.  $i$ - $E$  curves of the hydrogen electrode in solutions containing completely dissociated solutes, calculated from eqn. 18.

to the anodic part of the curve when the solution is gradually changed from acidic to basic. The second plateau results from the limiting rate of diffusion of the hydrogen molecules and appears only in the anodic part of the curve.

It may be worthwhile to note here that the curve at  $p_{\text{cH}} = 7$  seems to point to an irreversible electrode process whereas it in fact results from two correlated reversible reactions.

(i) *Simplified current-potential relationship.* For  $|i| \ll i_{\text{gH}_2}$  eqn. (17) reduces to

$$i = i_{\text{gH}}(1 - e^{\eta F/RT}) + i_{\text{gOH}}(1 - e^{-\eta F/RT}) \quad (19)$$

In this case the second term in the right-hand side of (18) can be omitted. One can calculate that for  $|i| < 0.08 i_{\text{gH}_2}$  this omission causes an error in  $\eta$  of less than 1 mV.

(ii) *The inflexion point of the curves.* Differentiation of (19) leads to

$$\frac{di}{d\eta} = -i_{\text{gH}} \frac{F}{RT} e^{\eta F/RT} + i_{\text{gOH}} \frac{F}{RT} e^{-\eta F/RT} \quad (20)$$

From this equation it follows that the polarisation curves have no maxima or minima

\*  $p_{\text{cH}} = -\log c_{\text{H}}$ .

since the right-hand side of (20) is always positive. By differentiating (20) one obtains

$$\frac{d^2i}{d\eta^2} = -i_{gH} \left(\frac{F}{RT}\right)^2 e^{\eta F/RT} - i_{gOH} \left(\frac{F}{RT}\right)^2 e^{-\eta F/RT} \quad (21)$$

Thus, at the inflexion point of the curves one has

$$i_{gH} e^{\eta_b F/RT} + i_{gOH} e^{-\eta_b F/RT} = 0 \quad (22)$$

The combination of (19) and (22) yields the current density at the inflexion point ( $i_b$ ):

$$i_b = i_{gH} + i_{gOH} \quad (23)$$

The expression for the overvoltage at this point ( $\eta_b$ ) may be obtained by substituting (11) and (12) in (22) and rearranging the terms. This gives at 25°

$$\eta_b = 0.0591 (p_{cH} - 7 - \frac{1}{2} \log q/p) \quad (24)$$

in which  $q = k_H/k_{OH}$  and  $p = Q_w \cdot 10^{14}$ .

From (24) it can easily be derived that the electrode potential at this inflexion point is given by

$$E_b = 0.0591 (\log f_H - 7 - \frac{1}{2} \log q/p) \quad (25)$$

where  $f_H$  is the activity coefficient of  $H^+$  in the medium concerned. The combination of (20), (22) and (24) results in the expression for the slope at the inflexion point of the curve

$$\left(\frac{di}{d\eta}\right)_b = \frac{2F}{RT} \cdot k_H \left(\frac{p}{q}\right)^{1/2} \cdot 10^{-7} \quad (26)^*$$

From eqns. 23, 24, 25 and 26 one sees that for solutions containing equal concentrations of the same supporting electrolyte in which  $f_H$ ,  $p$  and  $q$  may be considered as constants, *the current density and the overvoltage at the inflexion point of the curve depend on pH whereas the electrode potential and the slope at this point are independent of pH.* Figs. 1 and 2 illustrate these facts.

It is clear that for  $i_{gOH} < |i_{gH}| \cdot 10^{-3}$  (which means  $pH < 5.5 + \frac{1}{2} \log q/p$ ) eqn. 23 takes the simplified form

$$i_b = i_{gH} \quad (27)$$

Likewise (23) reduces to

$$i_b = i_{gOH} \quad (28)$$

when  $pH > 8.5 + \frac{1}{2} \log q/p$ .

Since  $\frac{1}{2} \log q/p$  has a low value, it may be said that in the range  $5.5 < pH < 8.5$  the height of the ionic plateaus is controlled by both hydrogen and hydroxyl ions whereas in acidic media virtually only hydrogen ions and in alkaline solutions only hydroxyl ions govern the plateau.

The calculation of  $i_b$  from (23) would be incorrect if the current-potential relation near the plateau were to be given by (17) instead of (19).

The correction  $\Delta i_b$ , however, which in such a case has to be added to the value of

\* Thanks are due to Mr. P. REIJNEN who derived eqn. 23 and in different forms eqns. 24 and 26.

$i_b$  calculated from (23) in order to obtain the correct value, proves to be low (see Table I). This is a consequence of the fact that an increase of the ratio  $|i_b|/i_{0H_2}$  is accompanied by a rise of  $|\eta_b|$ ; consequently the second terms within the brackets of the right-hand side of eqn. 17 remain low until this ratio has come close to unity.

TABLE I  
CORRECTION  $\Delta i_b$  AS A FUNCTION OF  $p_{cH}$

$p_{cH}$	$\Delta i_b(\%)$
8	-0.007
9	-0.007
10	-0.007
11	-0.014

(iii) *The pseudo-neutral point.* The combination of (23) with (11) and (12) yields the  $p_{cH}$  of the solution for which the polarisation curve and abscissa intersect at the inflexion point ( $i_b = 0$ ):

$$p_{cH} = 7 + \frac{1}{2} \log q/p \quad (29)$$

It is obvious that this point on the  $p_{cH}$ -scale is not identical with the neutral point, from which it deviates by  $\frac{1}{2} \log q$  ( $\approx 0.1$ ) units\*.

We propose to call it the *pseudo-neutral point*.

(iv) *The point of neutral current density.* It is easy to derive that the point of the curve at which  $i_H = i_{0H}$ , is given by

$$i_s = 2 i_b \quad (30)$$

We propose to call it the *point of neutral current density*. Thus the flux of the ion which is not exhausted at the electrode surface does not become equal to the flux of the exhausted ion before the current density has attained a value twice that at the inflexion point of the curve. At the pseudo-neutral point where  $i_b = 0$ , the inflexion point and the point of neutral current density are identical (Fig. 3).

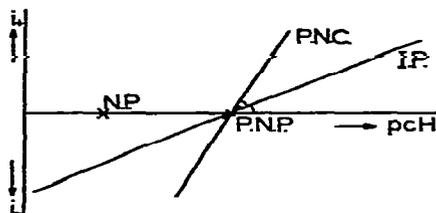


Fig. 3. Position of P.N.C. and I.P. as function of  $p_{cH}$ : N.P. is neutral point; P.N.P. is pseudo-neutral point; I.P. is inflexion point; P.N.C. is point of neutral current density.

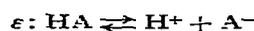
\* In neutral solutions the concentration of  $H^+$  equals that of  $OH^-$ . Since  $c_{OH^-} = p \cdot 10^{-14}$ , the  $p_{cH}$  of such solutions is given by  $p_{cH} = 7 - \frac{1}{2} \log p$ .

(c) *Current-potential equation of the hydrogen electrode in solutions containing partly dissociated solutes*

In aqueous solutions containing partly dissociated solutes the current-potential relationship of the hydrogen electrode is more complicated. Restricting the problem to the case of a weak monobasic acid, the following electrochemical reaction occurs in addition to the reactions  $\alpha$  and  $\beta$ .



and in addition to the equilibrium  $\gamma$  a second dissociation equilibrium is found



Assuming that the rates of dissociation and recombination of HA are large with regard to the rates of the electrochemical reactions the following relation holds at the electrode surface

$$Q_{\text{HA}} = \frac{c_{\text{H}} c_{\text{A}}}{c_{\text{HA}}} = \frac{o c_{\text{H}} o c_{\text{A}}}{o c_{\text{HA}}} \quad (31)$$

where  $Q_{\text{HA}}$  is the molar dissociation quotient.

Assuming furthermore that the electrochemical reactions occur quickly in comparison with the mass transfer processes the overvoltage at the electrode is given by eqn. 4.

The current density which passes across the electrode surface, is the sum of the partial current densities related to the formation or consumption of  $\text{H}^+$ ,  $\text{OH}^-$  and HA (or  $\text{A}^-$ ), respectively.

$$\text{Thus} \quad i = i_{\text{H}} + i_{\text{OH}} + i_{\text{HA}} \quad (32)$$

$$\text{or} \quad i = i_{\text{H}} + i_{\text{OH}} + i_{\text{A}} \quad (33)$$

The partial current densities due to HA and  $\text{A}^-$  are given by

$$i_{\text{HA}} = k_{\text{HA}}(o c_{\text{HA}} - c_{\text{HA}}) \quad (34)$$

$$i_{\text{A}} = k_{\text{A}}(c_{\text{A}} - o c_{\text{A}}) \quad (35)$$

which lead to the limiting current densities:

$$i_{\text{gHA}} = -k_{\text{HA}} c_{\text{HA}} \quad (36)$$

$$i_{\text{gA}} = k_{\text{A}} c_{\text{A}} \quad (37)$$

Combining (4), (14) and (31) one obtains

$$\frac{o c_{\text{A}}}{o c_{\text{HA}}} = \frac{c_{\text{A}}}{c_{\text{HA}}} (1 - i/i_{\text{gH}_2})^{-1/2} e^{-\eta F/RT} \quad (38)$$

During the electrolysis the total concentration of A is constant.

Hence, assuming  $D_{\text{HA}} \approx D_{\text{A}}$ , one has

$$c_{\Sigma\text{A}} = c_{\text{HA}} + c_{\text{A}} = o c_{\text{HA}} + o c_{\text{A}} \quad (39)$$

From (38) and (39) it follows

$$o c_{\text{HA}} = c_{\Sigma\text{A}} \left[ 1 + \frac{c_{\text{A}}}{c_{\text{HA}}} (1 - i/i_{\text{gH}_2})^{-1/2} e^{-\eta F/RT} \right]^{-1} \quad (40)$$

Next substituting (40) and (36) in (34) one obtains the expression for  $i_{\text{HA}}$  which in

combination with the expression for the sum of  $i_H + i_{OH}$  given by (17), yields the equation

$$i = i_{gH} [1 - (1 - i/i_{gH_2})^{1/2} e^{\eta F/RT}] + i_{gOH} [1 - (1 - i/i_{gH_2})^{-1/2} e^{-\eta F/RT}] + i_{gHA} + k_{HAC\Sigma A} \left[ 1 + \frac{c_A}{c_{HA}} (1 - i/i_{gH_2})^{-1/2} e^{-\eta F/RT} \right]^{-1} \quad (41)$$

When using (33) instead of (32) one derives in the same way

$$i = i_{gH} [1 - (1 - i/i_{gH_2})^{1/2} e^{\eta F/RT}] + i_{gOH} [1 - (1 - i/i_{gH_2})^{-1/2} e^{-\eta F/RT}] + i_{gA} - k_{AC\Sigma A} \left[ 1 + \frac{c_{HA}}{c_A} (1 - i/i_{gH_2})^{1/2} e^{\eta F/RT} \right]^{-1} \quad (42)$$

Both eqns. 41 and 42 represent the general current-potential relationship of the hydrogen electrode in the case of pure diffusion polarisation when the solution contains a weak monobasic acid in addition to an excess of supporting electrolyte.

As is clear, both equations still hold when the solution is buffered with a salt of the acid concerned and a strong base. The value of  $i_{HA}$  or  $i_A$  depends on the total amount and on the ratio of both buffer components as well as on the dissociation quotient of the acid. One notes that if HA represents a strong acid so that  $c_{HA} = 0$  and  $c\Sigma A = c_A$ , eqns. 41 and 42 reduce to (17).

As was pointed out in section 2(b), the current-potential curve in unbuffered solutions shows one ionic plateau which is controlled by the concentrations of  $H^+$  and  $OH^-$  in the bulk of the solution. In buffer solutions of a weak acid the situation is more complicated. In the first place the cathodic plateau is also controlled by the concentration of the undissociated acid\*. In the second place there will appear a second ionic plateau in the anodic part of the curve when the current density due to the anion  $A^-$  attains its limiting value, provided the dissociation quotient  $Q_{HA}$  is small. If  $Q_{HA}$  is too large, the partial current density  $i_H$  will be large enough to suppress the appearance of this anodic plateau, unless the buffer concentration is extremely high. Hence only a sufficiently small dissociation quotient  $Q_{HA}$  and a sufficiently high buffering capacity of the solution may cause two ionic plateaus, *viz.* one in the cathodic part and the other in the anodic part of the curve.

In the same way as eqns. 23 and 24 were derived in section 2(b)(ii) the equations of the current density and the overvoltage at the inflexion points of these plateaus can be obtained *via* the second derivatives of eqns. 41 and 42. Neglecting the term  $(1 - i/i_{gH_2})$  differentiation of (41) leads to the expression for the current density at the cathodic inflexion point

$$i_b = i_{gH} + i_{gOH} + i_{gHA} + k_{HAC\Sigma A} \left[ \left( 1 + \frac{c_A}{c_{HA}} e^{-\eta F/RT} \right)^{-1} + \frac{c_A}{c_{HA}} e^{-\eta F/RT} \left( 1 + \frac{c_A}{c_{HA}} e^{-\eta F/RT} \right)^{-2} - 2 \left( \frac{c_A}{c_{HA}} \right)^2 e^{-2\eta F/RT} \left( 1 + \frac{c_A}{c_{HA}} e^{-\eta F/RT} \right)^{-3} \right] \quad (43)$$

\* The molecule HA may be reduced directly at the electrode or may supply a deficiency of hydrogen ions. This makes no difference for the current-potential relation provided the direct reduction does not involve transition overvoltage.

If the concentrations of the reacting species in the bulk of the solution are not too small, the overvoltage  $\eta_b$  will be high enough to increase, in combination with a suitable ratio  $c_A/c_{HA}$ , the value of the term

$$\frac{c_A}{c_{HA}} e^{-\eta F/RT}$$

well above unity, for which (43) reduces to

$$i_b = i_{gH} + i_{gOH} + i_{gHA} \quad (44)$$

Likewise one derives from (42) for the current density at the anodic inflexion point

$$i_b = i_{gH} + i_{gOH} + i_{gA} \quad (45)$$

when

$$\frac{c_{HA}}{c_A} e^{\eta F/RT} \gg 1$$

On the same conditions for which eqns. 44 and 45 hold, one obtains by way of the second derivatives of eqns. 41 and 42 the following expressions for the overvoltage at the inflexion points of the curve<sup>14</sup>,  
cathodic:

$$\eta_b = 0.0591 \left[ p c_H - 7 - \frac{1}{2} \log \left( q/p + \frac{c_{\Sigma A} k_{HA}}{p Q_{HA} k_{OH}} \right) \right] \quad (46)$$

anodic:

$$\eta_b = 0.0591 \left[ p c_H - 7 + \frac{1}{2} \log \left( p/q + \frac{p c_{\Sigma A} k_A}{Q_{hydr.} k_H} \right) \right] \quad (47)$$

where

$$Q_{hydr.} = \frac{Q_w}{Q_{HA}}$$

On comparing (44) with (23) and (46) with (24) the difference between the buffer solution of a weak acid and the solution of a strong acid emerges quite clearly. This difference increases as  $Q_{HA}$  decreases.

The above equations have been evaluated with reference to buffer solutions of a weak acid. It will be clear, however, that similar equations may be derived which hold in buffer solutions of a weak base.

A survey of the various polarisation curves in unbuffered and buffered solutions, both containing an excess of supporting electrolyte, is given qualitatively in Fig. 4. It is assumed in this figure that the dissociation quotient of the weak electrolyte is sufficiently small and the buffering capacity is sufficiently high to give two ionic plateaus in the buffer solutions.

### 3. APPLICATION OF THE THEORY TO VARIOUS SOLUTIONS

#### (a) Current-potential curves in chloride solutions

Since hydrogen chloride, alkali hydroxides and alkali chloride salts are completely dissociated in aqueous solution, the polarisation curves measured in a chloride medium will be governed by the equations derived in section 2(b).

(b) *Current-potential curves in sulphate solutions*

As is known, the second dissociation of sulphuric acid does not occur completely. Hence in sulphate solutions the proton is also present as a component of the hydrogen sulphate ion. For instance, in slightly acidic 0.1 *M* sulphate solutions of monovalent

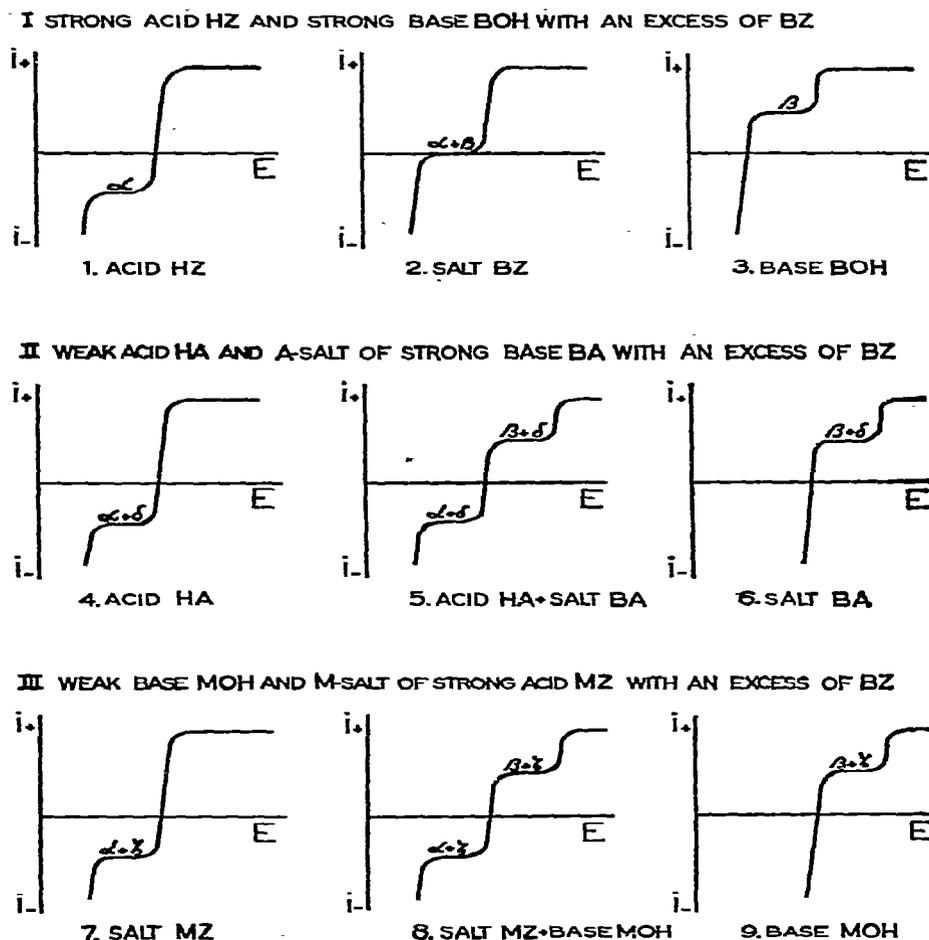


Fig. 4.  $i$ - $E$  curves in unbuffered and buffered solutions (schematically):  $\alpha$ ,  $2\text{H}^+ + 2e \rightleftharpoons \text{H}_2$ ;  $\beta$ ,  $2\text{H}_2\text{O} + 2e \rightleftharpoons \text{H}_2 + 2\text{OH}^-$ ;  $\delta$ ,  $2\text{HA} + 2e \rightleftharpoons \text{H}_2 + 2\text{A}^-$ ;  $\epsilon$ ,  $2\text{M}^+ + 2\text{H}_2\text{O} + 2e \rightleftharpoons \text{H}_2 + 2\text{MOH}$ .

cations, the dissociation quotient  $Q_{\text{HSO}_4}$  is nearly equal to  $6 \cdot 10^{-2}$  at  $25^\circ$ <sup>15</sup>. Considering such solutions it is easy to calculate that the concentrations of the bisulphate and hydrogen ions are of the same order of magnitude. Hence the hydrogen sulphate ion which behaves as a weak monobasic acid influences the polarisation curves in these solutions so long as the hydrogen ion does. As can be shown from the equations in section 2(b), the partial current density due to  $\text{H}^+$  is negligible up to the ionic plateau of the curve when  $p_{\text{CH}} > 10$ . This means that in 0.1 *M* alkali sulphate solutions with  $p_{\text{CH}} > 10$  the current-potential curve may be described up to the inflexion point by eqn. 17 which holds for completely dissociated electrolytes, but that in solutions with  $p_{\text{CH}} < 10$  eqn. 41 which holds for weak acids should be applied.

Hitherto attention has never been paid to the remarkable influence of the hydrogen sulphate ion on the voltammetric behaviour of the hydrogen electrode. Recently, both NAGEL<sup>7,8</sup> and BREITER<sup>11</sup> overlooked this influence and neglected the bisulphate ion in their calculations of the current-potential relationship in 0.1 *M* Na<sub>2</sub>SO<sub>4</sub> solutions. So they incorrectly tested their experimental curves over the entire pH range using equations which hold only for completely dissociated solutes.

The effect of the bisulphate ion on the polarisation curves may be well demonstrated by the calculation of the current density and overvoltage at the inflexion point. As a consequence of the large excess of alkali sulphate in a 0.1 *M* solution the conditions under which eqns. 44 and 46 hold will be fulfilled so that  $i_b$  and  $\eta_b$  are given by

$$i_b = i_{gH} + i_{gOH} + i_{gHSO_4} \quad (48)$$

and

$$\eta_b = 0.0591 \left[ pC_H - 7 - \frac{1}{2} \log \left( q/p + \frac{c_{\Sigma SO_4}}{pQ_{HSO_4}} \frac{k_{HSO_4}}{k_{OH}} \right) \right] \quad (49)$$

The effect of the bisulphate ion on  $i_b$  is caused by the term  $i_{gHSO_4}$ . Combining (1), (11) and (36) one obtains

$$i_{gHSO_4} = \frac{\lambda_{HSO_4}}{\delta_{HSO_4}} \frac{\delta_H}{\lambda_H} \frac{c_{HSO_4}}{c_H} i_{gH} \quad (50)$$

If a laminar flow of the solution along the electrode is realised,  $\delta$  is proportional to  $\lambda^{1/3}$ <sup>16</sup>. This yields

$$i_{gHSO_4} = \left( \frac{\lambda_{HSO_4}}{\lambda_H} \right)^{2/3} \frac{c_{HSO_4}}{c_H} i_{gH} \quad (51)$$

TABLE II  
NUMERICAL DATA  
For calculations and literature see ref.<sup>14</sup>

Parameters	0.1 <i>M</i> KCl	0.1 <i>M</i> K <sub>2</sub> SO <sub>4</sub>
$\omega$	0.1	0.3
$\lambda_H$	314	287
$\lambda_{OH}$	176	157
$\lambda_{HSO_4}$		35
$\lambda_{H_2PO_4}$	29	25
$\lambda_{HPO_4}$	37	29
$D_H$	$8.35 \cdot 10^{-5}$	$7.63 \cdot 10^{-5}$
$D_{OH}$	$4.68 \cdot 10^{-5}$	$4.18 \cdot 10^{-5}$
$D_{HAc}$	$1.15 \cdot 10^{-5}$	
$D_{H_2}$	$4.6 \cdot 10^{-5}$	$4.6 \cdot 10^{-5}$
$q$	1.47	1.50
$k_{HSO_4}/k_H$		0.246
$f_H$	0.8	0.5
$f_{OH}$	0.8	0.75
$p$	1.6	2.7
$Q_{HSO_4}$		$6 \cdot 10^{-2}$
$Q_{H_2PO_4}$	$6.6 \cdot 10^{-8}$	$7.2 \cdot 10^{-8}$
$Q_{HAc}$	$2.8 \cdot 10^{-5}$	

By means of this equation it is possible to express  $i_{g\text{H}_2\text{SO}_4}$  with  $i_{g\text{H}}$  as unity. For instance, in a 0.1 *M*  $\text{K}_2\text{SO}_4$  solution with  $\text{p}c_{\text{H}} = 4$  one finds  $i_{g\text{H}_2\text{SO}_4} = 0.41 i_{g\text{H}}$  when using the data of Table II which have been derived or calculated from literature<sup>14</sup>. Evidently the presence of the bisulphate ion increases  $i_b$  by 40%. With decreasing  $\text{p}c_{\text{H}}$  this percentage decreases gradually since the ratio  $c_{\text{HSO}_4}/c_{\text{H}}$  also decreases; with rising  $\text{p}c_{\text{H}}$  the percentage also begins to decrease from  $\text{p}c_{\text{H}} = 5.5$  since  $i_{g\text{OH}}$  increases.

By subtracting (24) from (49) one can calculate easily from the data given in Table II that the presence of the hydrogen sulphate ion alters the overvoltage at the inflexion point by 4 mV. So the remarkable fact is found that the presence of the hydrogen sulphate ion in acidic and neutral 0.1 *M* sulphate solutions increases the current density considerably, whereas the overvoltage hardly deviates from the value calculated neglecting the bisulphate ion.

### (c) Difference between chloride and sulphate solutions

As an illustration of the difference between chloride and sulphate solutions Fig. 5 shows a graph of  $\Delta \log |i_b|$ , the difference in  $\log |i_b|$  for 0.1 *M*  $\text{K}_2\text{SO}_4$  and 0.1 *M*  $\text{KCl}$

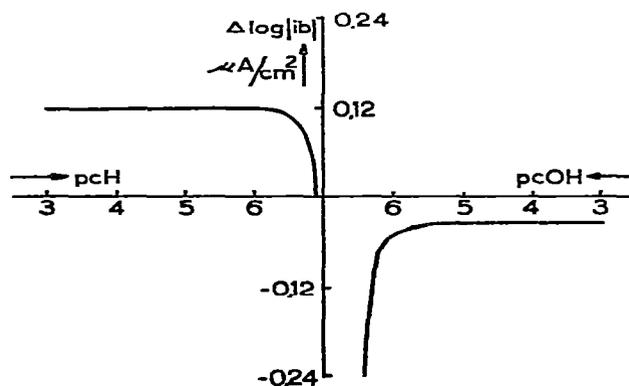


Fig. 5.  $\Delta \log |i_b|$  as a function of  $\text{p}c_{\text{H}}$  and  $\text{p}c_{\text{OH}}$ .

solutions, against  $\text{p}c_{\text{H}}$  and  $\text{p}c_{\text{OH}}$ . The various values of  $i_b$  in both solutions were expressed, taking the transport coefficient of the hydrogen ion in 0.1 *M*  $\text{KCl}$  as unity, by means of the general equation

$$k_{\text{ion}1}/k_{\text{ion}2} = (\lambda_{\text{ion}1}/\lambda_{\text{ion}2})^{2/3} \quad (52)$$

They were calculated from (23) and (48) in combination with (11), (12), (51) and (52) using the numerical data of Table II. It can be seen from this table that the equivalent conductances of both hydrogen and hydroxyl ions in both kinds of solution are different because of the difference in ionic strength of the solutions. This results in negative values of  $\Delta \log |i_b|$  in alkaline media. In acidic media, however, the presence of the bisulphate ion increases the value of  $|i_b|$  to such an extent that  $\Delta \log |i_b|$  shifts to positive values.

### (d) Current-potential curves in acetate buffers

To test the eqns. 44 and 46 a buffer of a fairly weak acid such as acetic acid is already suitable, since the conditions under which these equations hold, will be fulfilled by a

convenient ratio acid/salt. It is not sure, however, whether in such a buffer the limiting current of the anion always causes an ionic plateau in the anodic part of the polarisation curve so that eqns. 45 and 47 can be tested. That depends on the dissociation quotient of the acid and the concentration of the buffer. In order to illustrate this fact Fig. 6 shows the anodic part of the polarisation curve of a solution containing

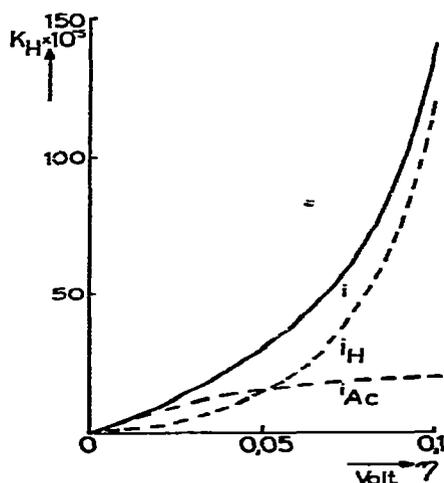


Fig. 6. Theoretical anodic curve for  $10^{-3} M$  HAc +  $10^{-3} M$  NaAc in  $0.1 M$  KCl.

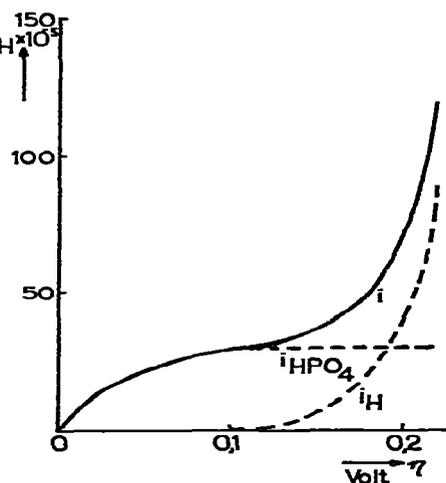


Fig. 7. Theoretical anodic curve for  $1.25 \cdot 10^{-3} M$   $\text{KH}_2\text{PO}_4$  +  $1.25 \cdot 10^{-3} M$   $\text{Na}_2\text{HPO}_4$  in  $0.1 M$  KCl.

$10^{-3} M$  acetic acid (HAc),  $10^{-3} M$  NaAc and  $0.1 M$  KCl. The current density has been expressed, taking the transport coefficient of the hydrogen ion ( $k_{\text{H}}$ ) as unity, by means of eqn. 52\* and by using the numerical data of Table II.

For calculating the concentration of the hydrogen ions the experimentally determined pH of the solution was used together with the activity coefficient  $f_{\text{H}}$  in  $0.1 M$  KCl from Table II.

The figure shows that, for the given buffer concentration,  $i_{\text{H}}$  surpasses  $i_{\text{Ac}}$  before the latter has reached its limiting value. Consequently, the anodic part of the curve does not show an ionic plateau. Even when the buffer concentration increases considerably, the ionic plateau will fail to appear for then  $i_{\text{H}_2}$  reaches its limiting value before  $i_{\text{Ac}}$  does.

#### (e) Current-potential curves in phosphate buffers

To test eqns. 45 and 47 a buffer of an acid much weaker than acetic acid is needed. A buffer such as  $\text{KH}_2\text{PO}_4$ – $\text{Na}_2\text{HPO}_4$  is suitable, since the second dissociation constant of phosphoric acid has a low value whereas  $K_1$  and  $K_3$  differ sufficiently from  $K_2$  to prevent interference with the possible oxidation of  $\text{H}_2\text{PO}_4^-$  to  $\text{H}_3\text{PO}_4$  in the anodic part of the curve and the reduction of  $\text{HPO}_4^{2-}$  to  $\text{PO}_4^{3-}$  in the cathodic part of the curve. This may be demonstrated easily by calculation<sup>14</sup>.

Consequently, in electrolysis a  $\text{KH}_2\text{PO}_4$ – $\text{Na}_2\text{HPO}_4$  buffer behaves as a buffer of a monobasic weak acid which gives rise to an ionic plateau in both the cathodic and

\* In the case of HAc:  $k_{\text{H}}/k_{\text{HAc}} = (D_{\text{H}}/D_{\text{HAc}})^{2/3}$ .

anodic part of the polarisation curve. Fig. 7 which has been calculated in the same way as Fig. 6 illustrates the latter.

#### ACKNOWLEDGEMENT

The author wishes to express his gratitude to Prof. J. SMITTENBERG for his stimulating interest in this study.

#### SUMMARY

This paper is concerned with the presentation of general equations for the current-potential relationship at the stationary hydrogen electrode, on the basis of pure diffusion polarisation, for solutions containing completely dissociated acids or bases and for solutions containing weak monobasic acids, both types of solutions being supplied with an excess of supporting electrolyte. With the aid of these various equations the occurrence of several plateaus in the polarisation curves of unbuffered and buffered solutions has been discussed. Furthermore equations have been derived for the current density and the overvoltage at the inflexion points of the curves.

Applying the theory to some actual solutions, it has been calculated that the presence of the hydrogen sulphate ion in acidic and neutral sulphate solutions causes a considerable increase in the current density at the inflexion point of the curve. Furthermore it has been shown that (1:1) mono-dihydrogen phosphate buffers give rise to two ionic plateaus whereas in (1:1) acetic acid-sodium acetate buffers only one ionic plateau can be expected.

#### REFERENCES

- <sup>1</sup> W. NERNST AND E. MERRIAM, *Z. physik. Chem.*, 53 (1905) 235.
- <sup>2</sup> A. EUCKEN, *Z. physik. Chem.*, 59 (1907) 72.
- <sup>3</sup> L. R. FRESENIUS, *Z. physik. Chem.*, 80 (1912) 481.
- <sup>4</sup> A. H. W. ATEN, *Rec. trav. chim.*, 42 (1923) 337.
- <sup>5</sup> C. V. KING, *J. Electrochem. Soc.*, 102 (1955) 195.
- <sup>6</sup> J. SMITTENBERG, *Electrodereacties II*, mimeographed ed. of lectures given in the Laboratory for Analytical Chemistry, Utrecht, The Netherlands 1956.
- <sup>7</sup> K. NAGEL AND F. WENDLER, *Z. Elektrochem.*, 60 (1956) 1064.
- <sup>8</sup> K. NAGEL AND F. WENDLER, *Z. Elektrochem.*, 63 (1959) 213.
- <sup>9</sup> J. COUPEZ, *Anal. Chim. Acta*, 16 (1957) 582.
- <sup>10</sup> J. COUPEZ, *Anal. Chim. Acta*, 17 (1957) 300.
- <sup>11</sup> M. BREITER, *Z. Elektrochem.*, 62 (1958) 161.
- <sup>12</sup> P. DELAHAY, *J. Am. Chem. Soc.*, 74 (1952) 3497.
- <sup>13</sup> M. BREITER, H. KAMMERMAIER AND C. A. KNORR, *Z. Elektrochem.*, 60 (1956) 119.
- <sup>14</sup> A. H. M. COSIJN, *Dissertation*, Utrecht, 1959.
- <sup>15</sup> C. F. BAES, *J. Am. Chem. Soc.*, 79 (1957) 5611.
- <sup>16</sup> W. VIELSTICH, *Z. Elektrochem.*, 57 (1953) 646.