126. Concentration Polarisation in Acid Solutions.

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The electrical technique recently developed by Hickling and Salt for overvoltage measurements permits concentration polarisation effects to be studied at high current densities. This paper describes the measurement of cathode concentration polarisation in acid solutions, and the observations include the effects of acid concentration, temperature, the presence of neutral salts and weak acid, and the time decay after switching off the polarising current. The results suggest that in the presence of excess of neutral salt, concentration polarisation in acid solutions is limited at high current densities by the buffer action of water in the alkaline pH region, the electrolyte becoming alkaline in the immediate vicinity of the electrode. In pure acid solutions it is shown that this electrode layer cannot become alkaline, and it appears that the greater part of the observed polarisation is due to a state of slight electrical unbalance which obtains at high current densities and sets up a diffuse double layer potential of the same polarity as normal concentration polarisation. The greater part of the polarisation observed in pure acids is probably due to this diffuse double layer potential.

Concentration polarisation is an effect observed at a working electrode which is passing an appreciable current, and refers to the deviation of the electrode potential from its reversible value caused by local concentration changes in the immediate vicinity of the electrode. The effect is of interest in relation to electrodeposition and to the acid corrosion of active metals, *e.g.*, magnesium (Coates, *J. Inst. Metals*, in the press).

Previous experimental studies have been confined to measurements at very low C.D.'s, commonly involving oxidation–reduction processes (Wilson and Youtz, *Ind. Eng. Chem.*, 1923, **15**, 603; Goldschmidt, *Z. Elektrochem.*, 1900, **7**, 267; Nernst and Merriam, *Z. physikal. Chem.*, 1905, **53**, 235; Glasstone and Reynolds, *Trans. Faraday Soc.*, 1933, **29**, 399). Butler has studied polarisation effects at high current densities from the aspect of passivity and the formation and reduction of oxide films (Butler and Armstrong, *Proc. Roy. Soc.*, 1932, *A*, **137**, 604; 1933, *A*, **139**, 406; Armstrong, Himsworth, and Butler, *ibid.*, 1933, *A*, **143**, 89; Pearson and Butler, *Trans. Faraday Soc.*, 1938, **34**, 806, 1163). The accurate measurement of cathode concentration polarisation in aqueous solutions of acids has hitherto been impossible because the product of the C.D. with the resistance of the electrolyte gives a potential which is not separable from the concentration polarisation. By Hickling and Salt's technique (*ibid.*, 1940, **36**, 1226; 1941, **37**, 450) this difficulty can be overcome. The principle of the method, developed for overvoltage measurements at high C.D.'s in strongly acid solutions, is as follows: by means of an electrical circuit including a gas-filled relay, the polarising current is interrupted several times a second, the duration of the period of interruption being controllable from 20 microseconds to periods of any desired length. During the period of interruption the potential is measured with an accuracy of about 0·02 volt by means of a potentiometer incorporating another gas-filled relay. During these very short periods of interruption the hydrogen overvoltage of a suitable (*e.g.*, platinised platinum) cathode falls only slightly; by measuring the potential for various periods and extrapolating to zero the overvoltage is obtained free from error due to the resistance of the electrolyte. The method is well suited to measurement of concentration polarisation.

Agar and Bowden (*Ann. Reports*, 1938, **35**, 90—113) have discussed some theoretical aspects of concentration polarisation on the basis of the Nernst diffusion layer, particularly the effect of the addition of neutral salts. The following symbols are used: C_0 = concentration of hydrogen ions in the body of the solution, C_e = concentration of hydrogen ions at the cathode surface, d = thickness of the diffusion layer, k = diffusion coefficient of the acid, I = current density, T_+ = transport number of hydrogen ions, $\boldsymbol{F}$ = the faraday, η_c = concentration polarisation (*i.e.*, the difference between the working and reversible electrode potential, minus the hydrogen overvoltage).

Agar and Bowden show that in the absence of cations other than hydrogen ions, the rate of removal of the latter by discharge, $I/\boldsymbol{F}$ (g.-equiv. cm.$^{-2}$ sec.$^{-1}$), is balanced by migration at a rate $T_+I/\boldsymbol{F}$ and by diffusion at a rate $k(C_0 - C_e)/d$. Hence

$$T_+I/\boldsymbol{F} + k(C_0 - C_e)/d = I/\boldsymbol{F}$$

Since C_e cannot be less than zero, the limiting current which can be maintained by migration and by diffusion is $I_{max.} = \boldsymbol{F}kC_0/d(1 - T_+)$. If a large excess of neutral salt (*e.g.*, potassium chloride) is added to the solution, the acid concentration remaining unchanged, then hydrogen ions will be supplied to the electrode by diffusion only, since practically the whole of the current is carried by the ions of the neutral salt. In this case $I_{max.} = \boldsymbol{F}kC_0/d$. Neglecting activity coefficients, Agar and Bowden arrive at expressions for η_c for the two cases:

(*a*) without neutral salt, $\eta_c = 2(1 - T_+)(\boldsymbol{R}T/\boldsymbol{F}) \ln (1 - I/I_{max.})$
(*b*) with excess neutral salt, $\eta_c = (\boldsymbol{R}T/\boldsymbol{F}) \ln (1 - I/I_{max.})$

These expressions show that η_c should increase slowly with I until I approaches $I_{max.}$, whereupon η_c should change very rapidly. In Fig. 1 the broken line is the theoretical polarisation [excess neutral salt, equation (*b*)] for $I_{max.}$ = 0·3 amp. cm.$^{-2}$, and some experimental points for 0·2N-hydrochloric acid + 2N-potassium chloride ($I_{max.}$, determined experimentally, also 0·3 amp. cm.$^{-2}$) are shown by circles. The theoretical line and the experimental points both show the rapid increase of polarisation as the current approaches $I_{max.}$, but the observed polarisation does not change quite so rapidly as the calculated. The most important feature, however, is the contrast between the theoretical discontinuity at $I_{max.}$ and the observed behaviour at higher C.D.'s.

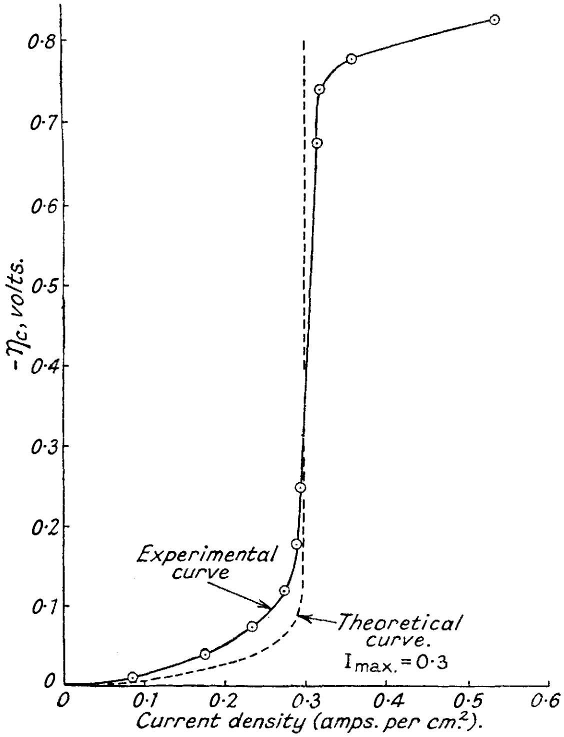
Several additional points have to be considered when the process involves the evolution of hydrogen gas.

First, d was assumed constant but is known to vary very much with the amount of stirring, and since the evolution of hydrogen gas has a stirring effect, d should decrease as the C.D. increases. For this reason η_c should change with I less rapidly than as indicated by Agar and Bowden's equation; this agrees with the discrepancy between the theoretical line and experimental points of Fig. 1 for C.D.'s less than $I_{\text{max.}}$. Secondly, there is the problem of what happens when the limiting current, given by the above expressions, is exceeded. Hydrogen ions must then be provided by some mechanism in addition to diffusion and migration, presumably by the dissociation of water. Hence it is to be expected that η_c should abruptly increase at the critical current density $I_{\text{max.}}$, and should reach a value corresponding to an electrode pH (*i.e.*, pH of the solution at the electrode surface) in the region in which water itself has a high buffer capacity, *i.e.*, from about pH 12 upwards. The experimental points in Fig. 1 corresponding to C.D.'s greater than $I_{\text{max.}}$ illustrate this effect; the polarisation is then limited by the dissociation of water to values of 0·7—0·8 volt, which are of the same order as reversible hydrogen electrode potentials for alkaline solutions. If some other reaction capable of supplying hydrogen ions can take place at a lower pH, then, above the critical current density, η_c may be expected to reach a lower value corresponding to this lower pH. For example, if the solution contains a weak acid of dissociation constant K in addition to a strong acid, then for low C.D.'s the contribution of the weak acid to the total hydrogen-ion concentration is negligible, but when, as a result of concentration polarisation, the pH at the electrode approaches pK, hydrogen ions may be supplied by the dissociation of the weak acid. When this occurs η_c may be expected to remain at a value corresponding to a pH in the neighbourhood of pK until at still greater C.D.'s hydrogen ions are discharged at a rate faster than they can be replaced by the combined migration and diffusion of strong acid from the body of the solution and the diffusion of weak acid and its subsequent dissociation, whereupon η_c should again increase.

A somewhat similar effect may occur in the presence of a salt which forms an insoluble hydroxide at a pH <12. For example, magnesium hydroxide is precipitated at about pH 10·5; hence, in the presence of magnesium salts η_c should, above the critical C.D., remain for a range of C.D. at a value corresponding to an electrode pH of about 10·5.

The experiments described below were designed to examine these effects, and the influence of acid concentration and temperature. Since the apparatus permitted the observation of the decay of concentration polarisation with time after the polarising current is switched off, this also was measured.

FIG. 1.



Concentration polarisation; acid in the presence of excess neutral salt (0·2N-HCl + 2·0N-KCl).

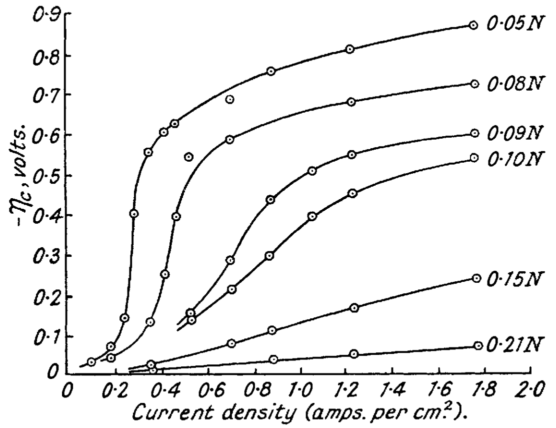
EXPERIMENTAL.

The method consisted of measuring by Hickling and Salt's technique the potential of the working cathode against that of a reversible hydrogen electrode in the same solution. Resistance error is eliminated, and the measured potential (extrapolated to zero time of interruption) is the sum of the hydrogen overvoltage and any concentration polarisation. The electrode material, provided it is inert, naturally does not affect concentration polarisation. By the use of electrodes of known and reproducible hydrogen overvoltage, this term may be subtracted from the total polarisation, leaving the concentration polarisation. Hickling and Salt (*loc. cit.*) found that tungsten and platinised platinum gave the most reproducible overvoltages, particularly the latter, which has the additional advantage of a very small overvoltage, errors in which would be practically negligible. These materials (mainly platinised platinum) were used in this work.

The electrical circuit was closely similar to that of Hickling and Salt, the main difference being the use of an a.c. mains power supply (a choke input rectifier giving up to 0·3 amp. at 200 volts, shunted by a 72 μF. condenser) in place of a 200-volt accumulator, since a suitable accumulator was not available. This arrangement was satisfactory only when an interference-suppressing filter was included in the mains input. The periods of interruption of the polarising current were measured by the method given by Hickling and Salt; the following periods were used and could be selected by a rotary switch: $4·5 \times 10^{-5}$, $8·0 \times 10^{-5}$, $1·3 \times 10^{-4}$, $2·5 \times 10^{-4}$, $3·8 \times 10^{-4}$, $1·05 \times 10^{-3}$, $3·0 \times 10^{-3}$, $5·5 \times 10^{-3}$, $1·5 \times 10^{-2}$, and $3·4 \times 10^{-2}$ sec. The polarising current was measured with a Cambridge Unipivot meter and D.C. range box, both of which had been calibrated by the makers. The electrode areas were measured with a travelling microscope. The platinised platinum electrodes consisted of a short length of platinum wire sealed into soda-glass and platinised by the usual method. The tungsten electrode consisted of tungsten wire sealed into Pyrex glass. The reference electrode was of platinised pure gold sheet, and was supplied with electrolytic hydrogen which had been passed over reduced copper at 600°. The electrolytic cell was in principle identical with that of Hickling and Salt (for overvoltage measurements) but ground joints were used in place of bungs or corks, and an extra precaution was taken against diffusion of anolyte into catholyte by means of a slow flow of electrolyte through the cell in the opposite direction. In view of the high C.D.'s no special exclusion of oxygen was necessary. The whole cell was immersed in a thermostat.

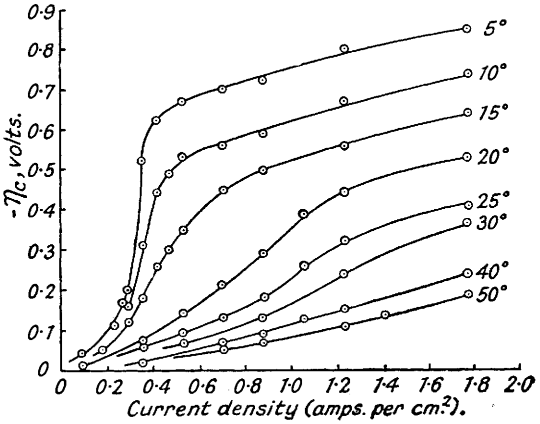
The apparatus was tested by measuring the hydrogen overvoltage of tungsten and platinised platinum in N-hydro-

FIG. 2.



Concentration polarisation in hydrochloric acid, 20°, *various concentrations.*

FIG. 3.



Concentration polarisation in 0·1N-*hydrochloric acid, various temperatures.*

FIG. 4.

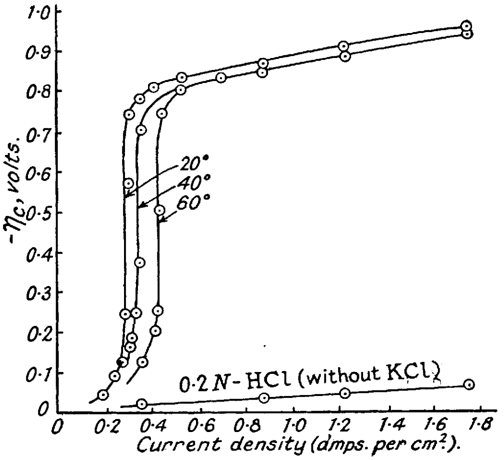
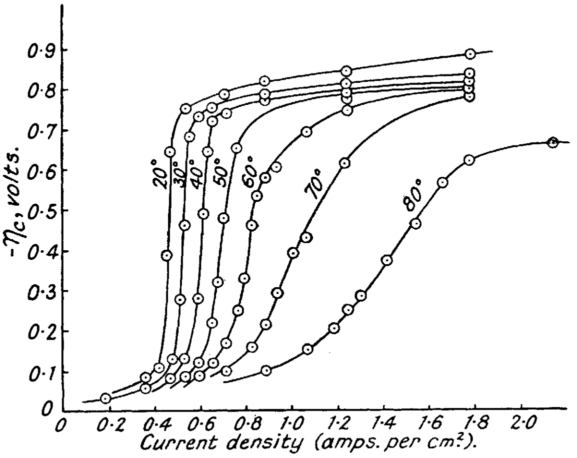


FIG. 5.



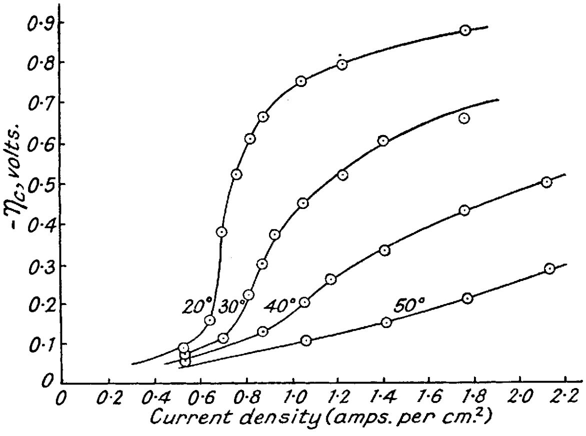


FIG. 6.

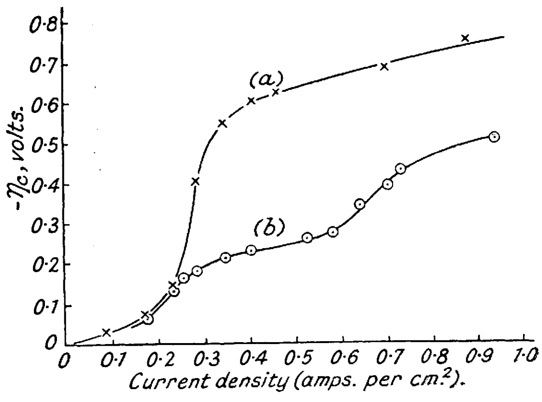
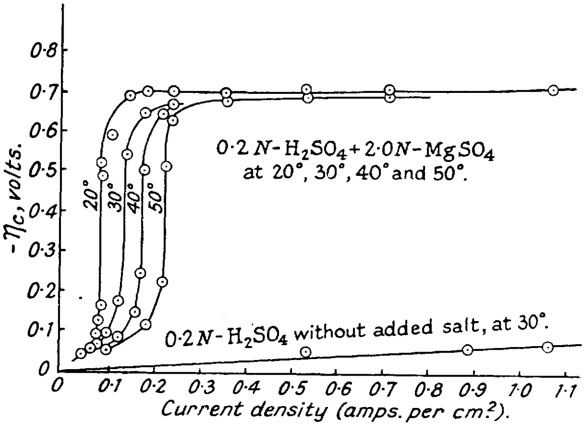


FIG. 7.

FIG. 4.—*Concentration polarisation ;* 0·2N-HCl + 2·0N-KCl *at* 20°, 40°, *and* 60°. Effect of neutral salt and temperature.
FIG. 5.—*Concentration polarisation ;* 0·2N-HCl + 0·2N-KCl. Effect of neutral salt and temperature.
FIG. 6.—*Concentration polarisation ;* 0·2N-HCl + 0·05N-KCl. Effect of neutral salt and temperature.
FIG. 7.—*Concentration polarisation ;* (*a*) 0·05N-HCl *at* 20°. (*b*) 0·05N-HCl + 0·2N-HOAc 20°.

chloric acid over a current density range 10^{-3} to 1 amp./cm.^{2}; the results agreed with those of Hickling and Salt to within 0·01—0·02 v. Then, to confirm the independence of concentration polarisation on electrode material, concentration polarisations were measured with a tungsten electrode of area 0·11 cm.^{2} and with two platinised platinum electrodes each of area 0·30 cm.^{2}, in 0·1N-hydrochloric acid at 20°, over a C.D. range of 0—1 amp./cm.^{2}. Within the accuracy of the measurements, about 0·02—0·03 v., identical values were obtained over the whole range. Practically all the remaining measurements were made with platinised platinum electrodes of area about 0·1 cm.^{2}.

FIG. 8.



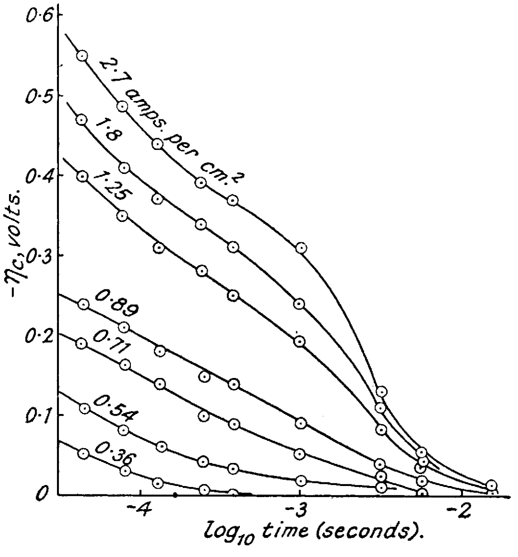
Concentration polarisation.

Results.—(1) *Acid concentration.* Fig. 2 shows the variation of concentration polarisation with C.D. for hydrochloric acid from 0·05 to 0·21N. at 20°. With 0·15 and 0·21N-acid, η_c is small and increases practically linearly with C.D.; with 0·05 and 0·08N-acid the critical C.D. effect is well marked and the flattening of the curves at high C.D.'s is clearly evident.

(2) *Temperature.* Fig. 3 shows the effect of temperature variation for a constant acid concentration of 0·1N. Viscosity decreases as temperature increases; hence diffusion and migration rates increase with temperature, and the curves show the expected decrease of η_c with increasing temperature. It is difficult to relate the effect of temperature quantitatively to the known effect on viscosity on account of the variation of *d*, the thickness of the diffusion layer, with C.D. owing to the stirring effect mentioned above.

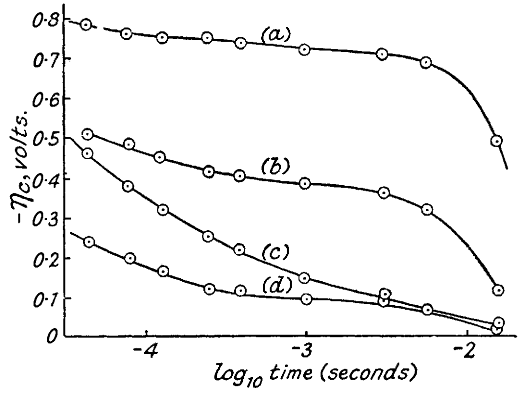
(3) *Neutral salts.* The effect of the addition of potassium chloride to 0·2N-hydrochloric acid is shown in Figs. 4, 5, and 6. Whereas Fig. 2 shows no sign of an abrupt rise of polarisation with 0·21N-hydrochloric acid alone up to 2 amps./cm.^{2}, high polarisations were observed in nearly all cases when potassium chloride was added. With 0·2N-hydrochloric acid + 2·0N-potassium chloride at 20° the critical C.D. was 0·29 amp./cm.^{2}, corresponding to a diffusion layer thickness about 0·002 cm., which is a normal value for stirred solutions (stirring in this case is by gas evolution). Hence the ratio of critical C.D. with and without excess neutral salt is evidently considerably greater than 6.* The theoretical ratio should be 6, *i.e.*, $(1 - T_+)^{-1}$, on the assumption that *d* remains constant. Since the critical C.D. decreases with the addition of neutral salt, the stirring due to gas evolution also decreases; hence *d* is likely to be greater at the critical C.D. in the presence of neutral salt than in the pure acid. This means that the diffusion rate is smaller in the presence of neutral salt and the ratio should be greater than $(1 - T_+)^{-1}$, which agrees with these observations.

FIG. 9.



Time decay of concentration polarisation after switching off polarising current: 0·1N-HCl *at* 20° (*platinised platinum electrode*).

FIG. 10.



Time decay.

(*a*) 0·2N-HCl + 2·0N-KCl, 20°, 0·36 amp./cm.^{2}.
(*b*) 0·1N-HCl, 5°, 0·36 amp./cm.^{2}.
(*c*) 0·05N-HCl + 0·2N-HOAc, 20°, 0·95 amp./cm.^{2}.
(*d*) 0·05N-HCl + 0·2N-HOAc, 20°, 0·6 amp./cm.^{2}.

The critical C.D. effect in the presence of 2·0N-potassium chloride is very sharp and points on the steep parts of the curves were difficult to obtain. These curves also illustrate the temperature effect.

(4) *Dissociation of weak acid.* The effect of the addition of 0·2N-acetic acid to 0·05N-hydrochloric acid is shown in Fig. 7. The lower parts of the two curves are practically identical; in the presence of 0·05N-hydrochloric acid the dis-

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* The lack of any exact knowledge about the magnitude and variation of *d* prevents the use in this connexion of known transport-number and diffusion data on solutions containing mixed hydrochloric acid and alkali chlorides [as given by Nickels and Allmand (*J. Physical Chem.*, 1937, **41**, 873) and Burrage and Allmand (*ibid.*, p. 887)].

sociation of acetic acid is negligible and has no effect until η_c reaches nearly 0·2 volt. At higher C.D.'s the curve flattens until at a polarisation possibly corresponding to a condition in which the acetic acid supplies hydrogen ions at a maximum rate, there is another rapid increase of polarisation. Fig. 7 is reminiscent of the neutralisation curve of a mixture of hydrochloric and acetic acid with a strong base, but was obtained in the absence of all cations except hydrogen ions.

(5) *The effect of insoluble hydroxides.* The addition of 2N-magnesium sulphate to 0·2N-sulphuric acid, shown in Fig. 8, has two results. First, the neutral-salt effect is shown very well by the steepness of the curves, and secondly, the curves become remarkably flat at a polarisation of 0·68—0·70 volt. Normally, above the critical C.D., η_c reaches 0·8 volt or more, but in the present case the polarisation is probably limited by the buffering effect of the formation of magnesium hydroxide. The latter, however, should take place at a pH of about 10·5, whereas a polarisation of 0·7 volt indicates, by the neutral salt equation (*b*) above, an electrode pH of about 12. The effect of magnesium is of considerable importance in connexion with the mechanism of the acid corrosion of magnesium, and this aspect is discussed in another paper.

(6) *The time decay of concentration polarisation.* Typical curves are shown in Figs. 9 and 10, in which η_c is plotted against the logarithm of the time which elapsed after the polarising current had been switched off. Hickling and Salt (*loc. cit.*) found that at a platinised platinum electrode the *overvoltage* decays very slowly with time, the decay being negligible within the time intervals of Figs. 9 and 10. When the degree of polarisation is fairly small, *i.e.*, below about 0·3 volt, the η_c–log t curves are straight during the first part of the decay period and then approach the time axis asymptotically (η_c obviously becomes zero as the time becomes large). For large C.D.'s, low acid concentrations, or low temperatures such that the polarisations are large, the η_c–log t curves are different; until about 3 millisec. after the polarising current is switched off the polarisation decreases comparatively slowly, and after about 3 millisec. it falls abruptly, reaching zero at about 0·03 sec. Unfortunately, as the initial conditions obtaining at the instant the current is switched off are unknown, the time decay cannot be calculated by Fick's diffusion equation.

DISCUSSION.

The polarisations observed in the presence of excess of neutral salt (Figs. 4 and 8) may be interpreted in terms of the large buffer capacity of water at a high pH. At C.D.'s above the critical $I_{\text{max.}}$, which is the greatest rate at which hydrogen ions can reach the electrode by diffusion, the pH of the solution in the immediate vicinity of the electrode rises to the alkaline region where water has a high buffer capacity. The presence of excess of neutral salt may well prevent any appreciable liquid junction potential, and the electrode pH is probably related to the polarisation by Agar and Bowden's simple equation $\eta_c = (\boldsymbol{RT}/\boldsymbol{F}) \ln C_e/C_0$. The higher polarisations observed in the presence of potassium chloride thus correspond to electrode pH values in the region 13 upwards, but at C.D.'s considerably in excess of the critical, still higher polarisations are found and it is possible that the potential then contains some additional term. The alkalinity at the electrode above the critical C.D. is strongly indicated by the polarisations observed in the presence of magnesium sulphate (Fig. 8); in this case the sharp limitation at 0·7 volt is very striking and is almost certainly connected with the buffering effect of magnesium salts at pH 10—11.

Polarisation in pure acid solutions presents a more difficult problem. For a given acid concentration the critical C.D. is very much higher than in the presence of neutral salt; this is, of course, due to the replacement of hydrogen ions at the electrode by migration in addition to diffusion, as pointed out by Agar and Bowden (*loc. cit.*). However, polarisations of the order of 0·8 volt have been observed which by equation (*a*) (no neutral salt) correspond to an impossible electrode pH of about 40. In the absence of any positive ions other than hydrogen ions, the electrode pH cannot rise above 7, otherwise there would be more negative than positive ions in the electrolyte near the cathode. It is possible that a new type of diffuse double layer is set up in these circumstances. Up to the critical C.D. the polarisation effects in pure acids are relatively simple, the discharge rate being balanced by migration and diffusion. At or about the critical C.D. hydrogen ions are removed so rapidly that in the layers of electrolyte next to the cathode a small degree of electrical unbalance is brought about by a deficit of positive ions and therefore a slight excess of negative ions. This state of affairs would result in a considerable potential between the highly disturbed and unbalanced layer and the body of the solution, the layer being negative and hence facilitating the movement of hydrogen ions towards the electrode to the extent required by the C.D. It is suggested that the pH at the cathode never rises above the weakly acid region, otherwise resistance would become excessive, and that the greater part of the observed polarisation is due to a diffuse double layer potential set up by the slight electrical unbalance in the immediate vicinity of the electrode and not to any large pH change at the electrode. This effect resembles in principle the ion-atmosphere distortion effect in Debye's conductivity theory, but since this double layer potential is likely to extend over the normal thickness of diffusion layers (*i.e.*, about 10^{-2} cm.) instead of the normal radius of an ion atmosphere (about 10^{-7} cm.) the time of relaxation is likely to be correspondingly greater than the usual " Debye " relaxation time of about 10^{-8} sec. The time decay curves (Fig. 9) show that the potential disappears completely about 10^{-2} sec. after the polarising current is switched off. The calculation of the relaxation process is difficult since the initial (steady) state is not defined; both diffusion and migration may contribute to the relaxation of the double layer. The normal ion atmosphere relaxation is complete in a time much shorter than the shortest period of interruption of the present measurements, and the curves of Fig. 9 represent, on the present theory, the process of relaxation of the diffuse double layer, which is a special type of ion atmosphere relaxation.

The author is indebted to the Magnesium Metal Corporation Limited for permission to publish this paper, to Mr. A. Brandt, Superintendent, Metal Research Section, and to Dr. A. G. C. Gwyer for their interest and advice, and to Mr. R. P. Bell, Dr. J. A. V. Butler, Dr. F. W. Salt, and Mr. K. W. Sykes for helpful discussion.

METAL RESEARCH SECTION,
MAGNESIUM METAL CORPORATION LIMITED.

[*Received, February* 28*th*, 1945.]