

STUDIES IN ELECTRODIFFUSION.

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by

H. M. F. Fleischmann, A.R.C.S., B.Sc.

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Imperial College of Science,
London.



ETHOS

Boston Spa, Wetherby
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I N T R O D U C T I O N.

Definition.

By the term electrodiffusion is meant the diffusion into the bulk of a metal of hydrogen deposited electrochemically at its surface.

Previous work.

The aims of previous workers fall into several unrelated groups. Very little direct study of the kinetics of diffusion has been made, the closest approach being the determination of the coefficient of diffusion through palladium (54) as a function of the activity of the ingoing interface and the measurement of the rates of steady permeation of palladium and iron membranes under a variety of conditions.

Measurements at the steady state, however, can give no information on the kinetics of diffusion, and it is difficult to assess the value of such data.

The main approach to the kinetics of the diffusion lies in the indirect measurements of the diffusion of potential through, and of potential and resistance along, cathodically charged membranes and wires respectively. Nernst and Lessing (7), Schmidt and Lucke (22) and Kohler (34) attempted to relate the change in the potential with time of the outgoing

interface of membranes (palladium and platinum, platinum and iron, and platinum respectively), to the thickness of the membrane. As will be shown below, it appears that the assumptions necessary in the theoretical treatment are untenable and that the experimental technique was inadequate to demonstrate the deduced relationship. Furthermore, these workers were only concerned with demonstrating the presence or absence of a true diffusion process and not with the diffusion system as such. Coehn and co-workers investigated the migration of potential, of resistance, and of a photographic latent image along the surface of a cathodically charged palladium wire in experiments designed to demonstrate the nature of the diffusing entity. Again, the diffusion system was not investigated as such. No complete investigation of the diffusion characteristics has in fact been carried out. The majority of the measurements have been concerned with relating the rates of diffusion or the solubility to some other property of the interface or the bulk of the metal. Hence it is difficult to correlate the previous work in a consistent manner. It would appear that the clearest classification is achieved by considering the bias of a particular group of investigations rather than the nature of the diffusion system. Previous work then falls into the following categories :-

1. Measurements of the amount dissolved as a function of the interface potential and of factors affecting the solution or the bulk of the metal.
2. Measurements of the expansion of the lattice and the change in the resistance of the metal as a function of the concentration of dissolved hydrogen.
3. Measurements of the change in the photo-electric effect of the outgoing interface of membranes on cathodic and anodic polarisation of the ingoing interface.
4. Measurements of the transfer of potential at potentials both positive and negative to the reversible hydrogen electrode potential.
5. Measurements of the rate of permeation of membranes as a function of the cathodic current density, concentration of acid on the ingoing interface, temperature, presence of poisons and various media on the interfaces, and the alteration of factors affecting the bulk of the metal.

1. Measurements of the amount of dissolution.

The dissolution of hydrogen in sheets and wires has frequently been measured as a function of the conditions on the ingoing interface. The solubility at potentials more positive than the reversible potential has been determined by direct measurement of the quantity of electricity flowing into

the electrode and at potentials more negative than the reversible value by similar measurements, a correction being made for hydrogen evolution; by measuring the relative change in resistance on charging with hydrogen; and by measuring the volume of hydrogen evolved after interrupting the cathodic current.

Many early authors investigated the dissolution in palladium and iron. For example, Thoma (6) found two regions of hydrogen dissolution in palladium. These two regions were later correlated by Nylén (50), and by Frumkin and Aladjalova (57) with the alpha- and beta-phases of the palladium-hydrogen system observed at higher temperatures in equilibrium with the gas phase. It would appear that the alpha-beta transition, occurring during the electrodiffusion of hydrogen through palladium, takes place at the same atom percent ratio as does that occurring at higher temperatures, and that the potential (ca. +0.05v) at which both phases are in equilibrium with the solution corresponds to the equilibrium pressure of hydrogen at the transition point at the higher temperatures.

Frumkin and Aladjalova (57) showed that for potentials more negative than the alpha-beta transition potential there is a linear relation between the concentration of dissolved hydrogen and the time-dependent portion of the overpotential.

This time-dependent potential was regarded as an "equilibrium potential" conditioned by an increase in the surface concentration of adsorbed hydrogen. This increase itself was caused by the slow removal of hydrogen from the interface by diffusion through the solution. It is difficult to see how such an explanation could account for a continued linear relationship on the positive side of the reversible hydrogen potential, where diffusion through the solution can hardly be effective in raising the concentration of hydrogen on the interface.

The above linear relationship may well hold at small cathodic current densities; but it has been shown by Coehn and Jurgens (39) that at high current densities (of the order of 1 amp./sq. cm.) the amount dissolved approaches a limit with increasing current density. It is evident that a similar limit would be found if the results were plotted against the potential. It would be of interest to investigate the over potential - time relationships in this current density region.

Different results were obtained by Stout (58). It was again found that the amount dissolved increased linearly with the negative potential. Stout, however, apparently regarded these potentials as being governed by the amount of beta-phase

in equilibrium with the alpha-phase and the amount dissolved as being limited by the complete conversion of the alpha-phase into the beta-phase. Such a view is difficult to accept as observations of the expansion of the lattice (42) and of the change of resistance (39) (42), with increasing hydrogen concentration indicate that the beta-phase is fully formed on the positive side of the reversible hydrogen potential. Furthermore in the potential region in which Stout obtained an increase of the resistance with concentration, a decrease in resistance has been found to take place (42). It seems probable that the data of Stout do not in fact refer to equilibrium conditions, the charging of the wire having been carried out at too high a current density. Hence his plot of potential against the atom percent ratio of hydrogen is presumably in error. It appears possible that Stout's results also indicate that the alpha-beta transition takes place on the positive side of the reversible potential.

The dissolution of hydrogen in palladium-silver alloys has been investigated by various authors. It was found by Nowack and Tamman (20), Coehn and Jurgens (39), and Kruger and Gehm (42) that the hydrogen content corresponding to the complete formation of the beta-phase increased with increasing silver content to about 20-30% silver and then decreased until

at 70% silver no significant dissolution could be found. The linear decrease in solubility with increasing silver content found by Kruger and Sacklowski (28) (and other authors) over the whole range of silver concentrations was attributed (42) to a decrease of the diffusion coefficient of hydrogen through the alloy with increasing silver concentration resulting in non-attainment of equilibrium. A similar linear decrease of hydrogen concentration with increasing gold content of palladium has been observed by Berry (10). It would appear that here also the amount dissolved was not measured under equilibrium conditions. In palladium-silver alloys the amount dissolved on the negative side of the reversible potential was found to decrease with increasing silver content. (39).

Very little is known about the kinetics of the dissolution. The results of Stout (58) show that the hydrogen concentration affects the kinetics of the electrode reaction on palladium. Frumkin and Aladjalova (57) considered the diffusion of hydrogen through the bulk of palladium to be rapid compared with the rate of its removal from the interface on the cathodic side of the reversible potential.

The addition and removal of hydrogen in the region of the alpha-beta phase transition has been investigated by Nylén (50) and by Frumkin and Aladjalova (57). Considerable

hysteresis in the potential-concentration plot was found by both workers for the electrolytic charging and discharging process. It was found that the presence of oxidising systems such as the ferrous-ferric did not alter the potential of palladium charged with hydrogen to the alpha-beta phase transition potential. Clearly the rate of removal of hydrogen by oxidation is lower than the rate of diffusion through the bulk of the metal.

Small potential shifts were found in acid solutions on polarisation. With alkaline solutions much larger potential shifts were found (50) (57). The potential shifts for addition and removal of hydrogen were found to be symmetrical and the slopes of the potential-current density curves were found to be the same as those for the cathodic evolution of hydrogen. (57). The diffusion through the bulk was again regarded as being rapid, the electrode potential due to dissolved hydrogen remaining constant. The potential shifts were attributed to the slowness of the electrochemical reaction. A breakdown of the observed relationships would be expected on the basis of this explanation at high current densities.

If Stout's (58) electrodes are regarded also as being at the alpha-beta phase transition in the neighbourhood of the

reversible hydrogen potential, then it would appear that the addition and removal of hydrogen does not take place symmetrically in acid solutions, the removal being relatively hindered. It would appear possible that the binding energy of the hydrogen to the palladium surface is dependent on the nature of the anion as is indicated for platinum by the data of Frumkin and Slygin (47) and that the simple explanation of Frumkin and Aladjalova is not adequate.

The constant potential at the alpha-beta phase transition has frequently (13) (31) (50) been used to develop an electrode suitable for measuring the pH of solutions where it is desirable to use reversible electrodes in equilibrium with a low partial pressure of hydrogen.

The solubility of hydrogen in iron is of a much smaller order. It appears from the data of many workers that both the concentration of dissolved hydrogen and the kinetics of dissolution are influenced by the presence of poisons (41). The system has never been thoroughly investigated, the bulk of the measurements having been concerned with the permeation of membranes. It appears that the dissolution is irreversible and that poisons affect the retention of hydrogen by iron.

The dissolution of hydrogen in cathodically polarised platinum has been investigated by Laue and Masing (49) in

alkaline solutions. The amount dissolved is very small and linearly dependent on the cathodic potential. It may be noted at this stage that their data are not in agreement with the results of the present experiments. The values of the potential as a function of the current density indicate that their electrodes were heavily poisoned.

2. Measurements of the expansion of the lattice and change in resistance.

The first measurements of expansion on electrolytic charging appear to have been carried out by Thoma (6) on palladium by direct measurement. Two regions of expansion were found at low and high hydrogen content corresponding presumably on modern views to the alpha- and beta-phase. At low hydrogen contents the expansion was found to be proportional to the hydrogen concentration, and at high hydrogen contents dependent on the current density. Further, the expansion was more rapid at high hydrogen content which would appear to be consistent with modern views. The expansion of palladium and palladium-silver alloys has been investigated more recently by X-ray crystallography. (28), (59), (42). It was found that for palladium a slight expansion takes place during the formation of the alpha-phase.

At a certain stage, lines characteristic of the beta-phase appear and the intensity of the lines due to the alpha-phase decreases. The beta-phase shows a considerably increased lattice parameter. The intensity relationship of the lines is however unaffected and it was concluded that there was no change in lattice type but merely an expansion. An expansion of the beta-phase itself was found at higher hydrogen concentration.

The expansion of the alpha-lattice due to saturation with hydrogen increases with the silver content of palladium-silver alloys, while the increase in lattice parameter due to the alpha-beta phase transition and the extent of the transition decreases. At a certain stage the alpha-beta phase transition disappears (42). The dissolution in this interesting region does not appear to have been investigated.

The expansion of cathodically charged iron has been measured by Waver and Pfarr (44). A slight increase of the lattice parameter of 0.0005A was found and this decayed with time. If this small expansion is significant, it would seem to imply that the change in parameter per atom (1.2%) of hydrogen percent is similar to that of palladium and that the hydrogen is in solid solution in the iron lattice.

The measurements of the change in resistance of palladium

and palladium-silver on saturation with hydrogen are related to the measurements of expansion (9) (39) (42), see also (40). A small region, during which the resistance increases with the hydrogen content, has been found followed by a region in which there is a less rapid, linear increase in resistance with hydrogen content. This region presumably corresponds to the alpha-beta phase transition and is complete at low current densities, probably even at positive potentials, corresponding to the views of Nylén and of Frumkin and Aladjalova. Finally at negative potentials there is a decrease in the resistance, which at high values of the current (lamp.) becomes constant. This region corresponds to dissolution in the beta-phase and saturation at high current densities.

The measurements on palladium-silver further substantiate the results obtained by measurements of the expansion of the lattice. The extent of the linear increase in resistance (alpha-beta transition) and the fall off at high current densities decrease with increasing silver content. The fall off also flattens out with respect to increasing current density at high silver concentrations. The behaviour in the region in which the alpha-beta transition disappears does not appear to have been investigated.

3. Measurements of the change in photo-electric effect.

The change in photo-electric effect of the outgoing interface of iron membranes on cathodic polarisation of the ingoing interface was investigated by Ernst (16) and Eichler (15) and with the addition of the dissolving metal system by Dumpelmann and Hein (26). An increase in the photo-electric effect for both oxygen and hydrogen evolution was found by all these authors but it would appear from the data of Eichler that after an initial increase caused by hydrogen evolution, anodic polarisation produces an increase and cathodic polarisation a decrease in the photo-electric effect on the outgoing interface. The effect as studied by these authors would appear to be somewhat obscure, and was attributed by Ernst to the removal of electrons from dissolved hydrogen. It is difficult to see why oxygen should have the same effect as hydrogen. Further in addition to platinum, palladium and iron which are known to be permeable to hydrogen a positive effect was found with gold. It appears possible, however, that if the effect is real it would be much more sensitive to traces of diffusing gas than other methods of measurement and that diffusion could be detected on metals otherwise thought to be impermeable.

4. Measurement of the transfer of potential.

Measurements of the potential of the outgoing interface of membrane electrodes were used by many early workers to detect the diffusion; amongst these may be mentioned Crova (1), Helmholtz and Root (2), and Beetz (3).

Nernst and Lessing (7), Schmidt and Lucke (22), and Kohler (34) used the measurement of the transfer of potential as a means of demonstrating the presence or absence of a true diffusion process on palladium, platinum, and iron. It was shown that, if the boundary condition for the outgoing interface is assumed to be $dc/dx = 0$ (c is the concentration of dissolved hydrogen and x the co-ordinate in the direction of flow), the time for the transfer of equal potentials should vary as the square of the thickness. This law, known as the Nernst law, was found to hold on palladium by Nernst and Lessing. On platinum, however, it did not hold, thick sheets being impermeable; because of this, the diffusion through thin membranes was attributed to leakage. As pointed out by Schmidt and Lucke the above boundary condition is not likely to hold for appreciable potential changes and they claimed that the Nernst law held for small potential changes (of the order of 50 mv.) on iron and thin platinum membranes. Kohler

also claimed that the law held on platinum foils of intermediate thickness. It appears likely, however, that the erratic course of the potential-time curves observed by these workers was caused by depolarisation and that the agreement with Nernst's law was to a large extent fortuitous. It will be shown later that, even when every precaution is taken to avoid depolarisation, the rate of change of potential on 0.003 inch thick platinum electrodes is much smaller than expected on the basis of the Nernst law when compared to that on 0.001 inch thick electrodes. It would appear that this means of testing the diffusion kinetics is unsatisfactory. A further reason for the non-obeyance of Nernst's law would appear to lie in the variation of the diffusion coefficient with concentration.

The measurements of the migration of potential and resistance along palladium and palladium-silver wires are related to the above measurements. It was found by Coehn and Specht (35) (36) and by Coehn and Jurgens (39) that a shift in the negative direction of the potential of a palladium wire could be detected at distances of the order of 1cm. from the cathodically polarised region after appreciable time intervals. For palladium wires, Nernst's law was obeyed up to distances of 8mm. The phenomenon appeared to show the

usual exponential dependence on temperature. By passing an electric current through the wire it was found that the potential tended to migrate in the electric field towards the negative pole and that the direction of migration could be reversed by reversing the current. It was concluded that the hydrogen migrated in the form of protons in the electric field of the wire. The extent of the migration increased with temperature, and varied linearly with the time of application of the current indicating a proportionality with the electric field, in the wire. The migration decreased with increasing silver content of palladium-silver wires. A similar migration could be detected by measuring the change in resistance of different portions of the palladium wire or the blackening of a photographic plate (45) in contact with the wire.

The measurements appear to be somewhat ambiguous since the wire was charged to complete conversion into the beta-phase and the potential whose appearance was timed at different distances corresponded to a potential in the alpha-phase. It would appear that under these conditions, the Nernst law cannot be expected to hold. It may be noted at this stage that if the Nernst law is assumed to hold, the results indicate a very rapid diffusion through palladium foils of the order of thickness used in the experiments of Frumkin and Aladjalova

and that their assumption of a rapid diffusion compared to the interface process may be substantiated.

The diffusion of potentials through iron membranes has also been investigated by Grave (11), Rathart (14), Stapenhorst (17) and Schmidt (24) in relation to passivity. The first three authors found a reduction in passivity of the outgoing interface on cathodic polarisation of the ingoing interface and an increase on anodic polarisation. Schmidt, however, claimed that both cathodic and anodic polarisation of the ingoing interface reduced the passivity.

A more recent study of the transfer of potentials through iron-chromium alloys from the point of view of passivity is that of Uhlig, Carr, and Schneider (56). A similar activation was found even in the region where the concentration of chromium in the alloy produces passivity. This region was displaced to higher chromium concentrations on cathodic polarisation. Without discussing these data further from the point of view of passivity it may be noted that the potential of the outgoing interface (in 4% sodium chloride solution) finally attained values that were insensitive to a 100% variation in current density on the ingoing interface, contrary to the results of the diffusion measurements on

many other systems. The time of attainment of the steady potential, an inverse measure of the diffusion coefficient, appeared to increase with increasing chromium content.

The transfer of potential as a function of the silver concentration in palladium-silver alloys was investigated by Coehn and Baumgarten (32). The rate of transfer of potential was found to decrease and the final potential on the outgoing interface to become less negative with increasing silver concentration. With pure palladium, cathodic potentials were finally reached. This is the first observation of negative potentials on the outgoing interface of palladium membranes due to cathodic polarisation of the ingoing interface.

More recently, the transfer of potential has assumed a further significance from the point of view of the theory of hydrogen overpotential. It is clear that if negative potentials are attained on the outgoing interface of membranes on cathodic polarisation of the ingoing interface then this potential can only be due to some electromotive activity of the diffusing hydrogen. This fact appears to have been first pointed out by Ferguson and Dubpernell (43). They investigated the potential changes on the outgoing interface of platinum membranes as a function of the current density flowing into the

ingoing interface. They failed to observe any negative potential, however, and on the strength of the irreproducibility of the phenomenon concluded that the diffusion was caused by leakage through the pores of the electrode. It may be noted at this stage that the initial potential of the outgoing interface in the experiments of Ferguson and Dubpernell was always positive and that this potential was shifted in the negative direction on cathodic polarisation of the ingoing interface. Further it was frequently found that anodic polarisation of the ingoing interface shifted the potential of the outgoing interface in the positive direction. In fact the permeability to anode polarisation appeared to be greater than the permeability to cathode polarisation. A negative potential on the outgoing interface has in fact never been observed with platinum. It has frequently been found, however, that the positive potential of the outgoing interface can be reduced by cathodic polarisation of the ingoing interface.

The first observation of a negative potential on the outgoing interface was made by Coehn and Baumgarten (32) on palladium membranes. This diffusion has more recently been investigated from the point of view of overpotential theory by Stout (58) and by Frumkin and Aladjalova (57). It was found

by Stout that the initial potential of a palladium electrode and the slope of the Tafel line (the overpotential-log current density relationship) were significantly interrelated and that this initial potential was dependent on the hydrogen concentration in the electrode. On the basis of this it was assumed that the slow stage of the electrochemical reaction lay in the recombination of the hydrogen atoms on the interface. It was found that the inside of palladium tubes would attain negative potentials when the outside was polarised cathodically. This potential was assumed to be caused by the increase in concentration of hydrogen due to the increase in the rate of reaction so that the electrode was behaving as if it were in equilibrium with a higher hydrogen pressure. The relation between the potential and the hydrogen content is obscure however. It was assumed that the potential was determined by the amounts of the alpha- and beta-phase in equilibrium. It is difficult to see how the potential of two phases in equilibrium with each other can vary with the amount of one of the phases present. Furthermore it is unlikely that the distribution of hydrogen atoms throughout the bulk of the metal during the determination of the concentration-potential relationship was that at equilibrium or in fact comparable with that at the working cathode.

Frumkin and Aladjalova also found a transfer of potential to the outgoing interface of membranes when the ingoing interface was polarised cathodically at fairly low currents (less than 0.0 amp). The change of potential on the outgoing interface was found to be equal to the slowly growing part of the overpotential on the ingoing interface. The potential of the outgoing interface was further found to be independent of the presence of acids or alkalis at the interfaces, whereas the overpotential on the ingoing interface showed a marked dependence on pH. Mainly on the basis of these experiments, it was concluded that the electrode was behaving as an equilibrium electrode, the diffusion not affecting the concentration distribution. The potential at the interfaces as opposed to the potential due to the electrochemical reaction was assumed to be independent of the nature of the solution and to be determined by the slow diffusion of hydrogen from the interface through the solution.

It is difficult to assess the validity of the interpretation in the absence of data on the effect of the environment of the interfaces on the diffusion kinetics or even the permeation rate. Measurements of the potential alone cannot give sufficient evidence to enable conclusions to be reached as to the nature

of the processes at the interfaces. Deviations from the observed relationships would be expected at higher current densities on the basis of the explanations put forward by Frumkin and Aladjalova. Furthermore it is evident that the results obtained disagree in several directions with those of other workers and with general experience in the diffusion field.

5. Measurement of the rate of permeation of membranes.

The majority of the measurements of the diffusion as such have been concerned with the determination of the rate of permeation of membranes. The change in pressure in the gas space on the outgoing interface of the membranes (a direct measure of the rate of diffusion) has been measured as a function of the conditions at the ingoing interface. The term membrane used is not strictly speaking justified since many of the measurements were carried out with finite and infinite cylinders. No error is introduced in this manner however, since the results are not sufficiently accurate to have been affected by a consideration of the geometrical configuration.

It has been found by many workers (8), (5), (12), (33), that the rate of electro-diffusion through iron membranes

is independent of the pressure of gas on the outgoing interface or over the solution on the ingoing interface. Pressures up to 300 atmospheres have been obtained on the outgoing interface of membranes with the ingoing interface cathodically polarised (33). On the strength of this information the determination of the rate of permeation by measurement of the change of pressure of a constant volume system may be considered valid.

Studies have been made of the effect of a wide variety of factors upon the rate of permeation and these will now be considered in turn.

Temperature.

The rate of permeation has always been found to increase with temperature. The only investigations carried out are for the permeation of iron either from the cathodically polarised interface or from the interface during dissolution in acid.

It was found by Bellati and Lussana (5) that the rate of permeation varied as the absolute temperature. The data of Winkelmann (8) indicate a variation with the temperature to a power greater than 5. Fuller found a marked temperature dependence of the rate of permeation from the interface

dissolving in acid. The clearest indication of the temperature dependence lies in the work of Borelius and Lindblom (30). These workers found that their data for the permeation of iron from the cathodically charged interface followed the usual temperature dependence of reaction rates ($e^{-b/T}$), between 25 and 97°C. The value found for the term b (4550) is very similar to the value (4700) found for diffusion at high temperatures from the gas phase. If the data of Edwards (27) for diffusion from the interface dissolving in hydrochloric acid are recalculated a very similar value for b (5050) is obtained. It is not valid, however, to conclude that the essential step in the diffusion processes is the same since we are here considering the steady rate of permeation through the membrane and the diffusion coefficient. The above temperature dependence may in fact consist largely of a term dependent on the endothermic dissolution of hydrogen in iron.

Current Density.

It was found by Bellati and Lussana (5) that the rate of permeation of iron varied directly as the current density at low current densities and more slowly at high current densities. Winkelmann (8) also found that the permeation varied less slowly than the current density. More recent workers have correlated

the rate of diffusion with the square root of the current density by analogy with the diffusion at high temperatures, where the permeation rate is found to be proportional to the square root of the pressure. Bodenstein (23) correlated the diffusion in this manner. The agreement appeared to be more satisfactory in the measurements made after decreasing rather than increasing the current density, which is reminiscent of the hysteresis of the permeation rate with increasing and decreasing current density observed in the iron-hydrogen system by Aten and Zieren (37) and by Borelius and Lindblom (30). A comparable relation was obtained between the logarithm of the permeation rate and the hydrogen overpotential. The similarity between the square root of the pressure and the square root of the current density is apparent from these results if it is assumed that the overpotential is governed by the concentration of hydrogen atoms on the interface.

Borelius and Lindblom also found a correlation between the permeation rate and the square root of the current density, in the temperature region 25 to 97°C.

It may be concluded that the process involved in the diffusion is the same at low as at high temperatures and that the current is equivalent to a very high pressure. In this case it was shown that $\bar{p} = 17000 \times \text{current density (amp.)}$

and at the highest current density observed the "pressure" at the ingoing interface was 750 atmospheres. On this simple view the pressure on the outgoing interface may well build up to very high values without affecting the rate of diffusion.

It may be noted that the data of Borelius and Lindblom, Bodenstein, and those of Aten and Zieren on unpoisoned electrodes all indicate that 0.1% of the atoms discharged diffuse through the electrode. The data of Edwards for the diffusion from the interface dissolving in acid give a higher value but comparison is difficult because the permeation rate varied over a factor of 8 in the acid concentration range considered.

Borelius and Lindblom found deviations from the proportionality of the permeation rate and the square root of the current density at low values of the current density, the permeation rate varying more rapidly than expected. Similar deviations were found by Bellati and Lussana (5). These deviations from a square root law together with the fact that the diffusion obeys the square root law up to such high pressure equivalents have assumed considerable importance in the consideration of the diffusion process. It is a matter of considerable difficulty to find an explanation for the fact

that the rate of permeation varies as the square root of the pressure up to very high pressures for the diffusion at high temperatures (61). In view of this fact the above experiments are important for they indicate that the permeation is pressure dependent to even higher pressure equivalents. The surface must be saturated with hydrogen at comparatively low pressures and clearly if the bulk of the metal within the ingoing interface is in equilibrium with the adsorbed layer the permeation rate should approach a constant value independent of the pressure. In order to explain the observed behaviour, some effect of the processes occurring at the interfaces on the diffusion must be postulated. The possible effects have been considered by Smithells (61), Wang (48) and Barrer (51). It would appear that in order to explain the pressure dependence of the diffusion up to high pressures and also the fact that high pressures of an inert gas have no effect on the diffusion some interface reaction as proposed by Wang must take place. In this treatment it was assumed that a molecule striking the surface leads to the immediate absorption of one atom the other atom being adsorbed on the surface. The more usual types of surface adsorption and desorption processes were also considered.

The deviations at low pressure have been ascribed (61) to the effect of partial coverage. It has been pointed out by

Barrer (54) that the temperature dependence of the deviations does not agree with such an explanation and that the behaviour may be explained in terms of a slow transfer from the ingoing interface into the bulk of the metal, coupled with a slow transfer from the bulk of the metal to the outgoing interface. This behaviour would lead to a considerable reduction of the concentration gradient within the metal and result in a complex dependence on pressure. It would appear that the deviations at low pressures or current densities may be partly if not largely caused by the presence of impurities in the metal (30) (55) or even the presence of depolarisers and that further experiments are required before the interpretation can be carried further.

On the basis of a slow transfer from the interface to the bulk of the metal there will clearly be an appreciable concentration discontinuity at the interface (51). In electrodiffusion the "pressure" may be expected to rise sufficiently high, or else the surface may be sufficiently activated, for the metal within the ingoing interface to become saturated. Under these conditions the permeation rate should become independent of the current density. This behaviour has been observed by Barrer on very active palladium membranes. (54). It was found that inactive electrodes showed the usual square

of permeation
root dependence/on the current density. As the activity of the electrodes is increased by alternate oxidation and reduction, the plot of the permeation rate against the square root of the current density increasingly bends away from the permeation rate axis and at a certain activity the rate of permeation becomes independent of the current density. It was found that for varying activity of the electrodes at constant current density the diffusion coefficient remained essentially constant by the method of evaluation used (21) (52). From the values of the permeation rates, it was found that as the activity of the electrodes decreased the concentration within the ingoing interface fell increasingly below the equilibrium value. It was assumed that under these conditions the slow transition from the interface to the bulk of the metal increasingly takes control, and that the method of evaluating the diffusion coefficient was independent of the extent of the interference by the interface.

Barrer showed that the data of Edwards for iron gave values for the diffusion coefficient that were very similar to those obtained from the data for cathodically polarised iron. The results indicated that there were only moderate deviations of the concentration within the interface from the equilibrium

value. For inactive electrodes this concentration was appreciably lower, indicating that here also the slow transfer across the ingoing interface was assuming increasing importance.

It is difficult to assess the validity of this group of experiments. The observations are very limited and the behaviour could not be reproduced for different electrodes. The current density ranges studied were too small to confirm the dependence of the rate of diffusion on the current density, particularly as the current density enters as a very low power. In the absence of data on the hydrogen overpotential of the electrodes used it is difficult to assess the condition or purity of the surface of the metals. The independence of the observed "diffusion coefficient" with respect to the permeation rate is surprising. The palladium lattice is known to show marked expansion (42) in the range of concentrations considered and to undergo a phase change. Under these conditions marked variations in the diffusion coefficient would be expected.

The small reduction of the concentration of hydrogen from the equilibrium value within the ingoing interface in the experiments with iron membranes is of interest in view of the fact that such high pressure equivalents of the current density have been found with iron and also experimentally observed on the outgoing interface. For palladium it has been shown that

the equilibrium concentration of hydrogen becomes limited at the high current densities at which the limiting permeation rate on active electrodes was observed. It would appear that the interface of the inactive electrodes must also have been completely covered at these current densities and that the continued dependence of the permeation rate on the square root of the current density could not be occasioned solely by a slow transfer from the interface to the bulk of the metal but rather by a mechanism as proposed by Wang (48). This is also indicated by the experiments with the iron membranes. The solutions of the diffusion equation for the radiation boundary condition used cannot give any information as to the nature of the interference at the interface. These equations can be expected to be obeyed only if the rate of transfer across the interface is proportional to the concentration difference at the interface, which would appear to be a very special case. A qualitative measure of the extent of the interference by the interface can however be obtained without reference to the nature of the process. It may be noted at this stage that any process will give a value for the "diffusion coefficient" and that the presence or absence of a bulk controlled diffusion must be assessed by comparing the experimental permeation rate-time curves with the theoretical expressions,

e.g., equation (21) below. The interference by slow interface processes will be further considered in the discussion.

Solution Factors.

Under this heading are considered the effect of additions to the solution and the use of different media. The first effect may be termed poisoning of the interface.

The effect of poisoning of the interface on the rate of permeation cannot be separated from the effect on the dissolution of hydrogen. It was found by Korber and Ploum (41) that on dissolution of iron in acid or on cathodic polarisation of iron the deposited hydrogen would only enter into the bulk of the metal in the presence of poisons in the solution. The hydrogen content of the metal appeared to be markedly affected by the presence of poisons. The impurities present in commercial iron were sufficient for dissolution in the bulk of the metal to occur. It is unlikely on the strength of this evidence that any data in the literature really refer to diffusion under pure conditions and it appears that the effects of poisoning referred to by other authors really refer to the poisoning of contaminated interfaces. The observations of Alexejew and Palukarov (29) are related to those of Korber and Ploum. These authors found that the

breaking stress of cathodically polarised iron wires was only affected in the presence of poisons (mercury and arsenic) in the solutions. (See also 18).

It was found by Fuller (19) that the rate of permeation of iron tubes was increased by applying a coating of another metal to the surface. Aten and Zieren (37), and Aten and Blokker (38) found a large increase in the rate of permeation through iron when the ingoing interface was poisoned by arsenic or mercury in acid or alkaline solutions. The effect first increased and then decreased with the poison concentration and was particularly marked at higher current densities. Under these conditions up to 30% of the deposited hydrogen diffused through the bulk of the metal. The permeation rate was found to be a linear function of the logarithm of the rate of hydrogen evolution rather than of the square root of the current density. Furthermore the ratio of the orders of the concentration appearing in the expressions for the permeation rate and the rate of hydrogen evolution was independent of the nature or amount of the poison. The clearest indication of some uniformity in the behaviour was obtained by Kobosew and Monblanova (46) who showed that the permeation rate was a single-valued function of the cathode potential. It is evident that

the diffusion is consistently affected by some interface factor. A further consideration of the results is of little value however, in the absence of data on the effect of the various treatments on the diffusion coefficient.

The effect of the medium itself on the permeation rate is related to these experiments. It has been frequently observed that the rate of permeation is lower in alkaline than in acid solutions. It was found by Aten and Zieren and by Aten and Blokker that the ratio of the orders of the concentration terms appearing in the expressions for the permeation rates and the rate of evolution of hydrogen was lower in alkaline than acid solutions. The data of Coehn (25) and of Coehn and Baumgarten(32) who attempted to relate the adsorption and permeation rate with the charge on the gas bubbles at the interface, may also in fact indicate that diffusion and dissolution is favoured by low pH. It is difficult to see how the charge on the gas bubbles could affect the permeation so markedly but on the views of Frumkin and Aladjalova on the nature of hydrogen overpotential on palladium such an effect is possible.

It was found by Edwards (27) that the rate of permeation (P) through iron, the ingoing interface of which was dissolving in acid, increased with the concentration of the acid (C)

according to the relation $P = kc^{+0.4167}$. The permeation rate was also found to vary with the nature of the acid. It is not clear, however, whether the results indicate a direct effect of the acid concentration on the permeation rate or whether the behaviour is controlled by the rate of dissolution of the iron in the acid.

The most direct investigation of the effect of the medium has been carried out by Kobosew and Monblanova (46). No effect on the permeation velocity through palladium of a variety of media on the outgoing interface (water, hydrogen, benzene, butyric acid) could be found. These media cover a wide range of viscosity, surface energy and dielectric constant and it is evident that the molecular forces at the outgoing interface have no influence on the diffusion process. It may be noted that any effect on the diffusion process due to bubble formation or to diffusion away from the interface is also thereby ruled out. Solutions of electrolytes were found to have a very marked effect on the permeation velocity when placed in contact with the outgoing interface. The effect appeared to be highly specific, no correlation with either the ionic charge on the ions or the ionic concentration being observed. The permeation rate was most markedly reduced in the presence of the potassium

ion, the reduction increasing with increasing concentration. It is unlikely that the effect can be attributed to poisoning since the permeation rate returned to its original value on replacing the ionic solution with water.

The results of Frumkin and Aladjalova (57) are difficult to reconcile with these observations. The potential behaviour at the ingoing and outgoing interfaces was explained by considering that the electrode contained a certain equilibrium concentration of hydrogen determined by the slow diffusion away from the electrode into the bulk of the solution. The presence of alkalis was found not to affect this part of the overvoltage but only a part, observed at the working cathode, and attributed to the electrochemical reaction. The potential of the outgoing interface and therefore presumably the rate of diffusion was found to be independent of the presence of acids or alkalis on the ingoing or outgoing interface. The results were not, however, supported by measurements of the rate of diffusion.

Kobosew and Monblanova also regarded the diffusion to be controlled by the interface and considered that the results could be explained on the basis of a change in the adsorption energy of hydrogen leading to a change in the rate of transfer

across the ingoing interface. The data of Frumkin and Slygin (47) on the anodic charging of platinised platinum may in fact substantiate such a picture. It is evident from the data that the strength of binding of hydrogen to platinum is markedly affected by anion adsorption and it may well be that the binding energy would be similarly affected by cation adsorption. It is impossible, however, to conclude that the binding strength alone is effective in altering the permeation rate without precise knowledge of the manner in which the diffusion kinetics are affected by the factors altering the permeation velocity.

Bulk factors.

Under this heading the manner in which factors affecting the bulk of the metal, affect the diffusion process, is considered.

The effect of the geometrical configuration has only been very rarely investigated, e.g., there is no comparison in the literature of the behaviour of slabs and rods. It was found by Aten and Zieren (37) that the plot of the permeation rate against $1/\text{thickness}$ showed positive deviations from linearity at low thicknesses. Slow processes at the ingoing interfaces would be expected to give negative deviations at small thicknesses. The manner in which this behaviour is linked to

poisoning is not clear, however, but it may be noted that the deviations decrease with decreasing arsenic concentration. It was found by Edwards (27) that for the dissolution of iron in acid the rate of permeation varied inversely with the thickness as would be expected on the basis of Fick's laws of diffusion. Frumkin and Aladjalova found the permeation rate through palladium to be independent of the thickness of the membrane.

Impurities in the electrode material and alloying have been frequently found to affect the rate of permeation. It was observed by Charpy and Bonnerot (12) that the hydrogen content of iron, after diffusion at high temperatures, was lowered for saturation both at high temperatures from the gas phase and at room temperatures by cathodic polarisation. A simultaneous removal of the impurities in the diffusing gas was observed. Borelius and Lindblom (30) found that the slope and to a certain extent the shape of the plot of permeation rate through iron against the square root of the current density was affected by the carbon content and by heating the metal. It was apparent that any treatment facilitating the accumulation of carbon at the grain boundaries hindered the diffusion. As against this observation, it was observed by

Edwards that the rate of permeation through a single crystal of iron was not different from the rate through the polycrystalline material. It would be premature to draw any conclusions as to the part the grain boundaries play in the diffusion process. It is probable, in fact, that the diffusion behaviour of pure iron has never been observed.

There are numerous observations in the literature that prolonged diffusion changes the diffusion characteristics and that heating the metal restores the original state. It is not clear, however, to what extent this may be caused by the removal of adsorbed poisons. Repeated oxidation and reduction or anodic and cathodic polarisation have been found to activate electrodes for the diffusion process. It has been considered that this treatment exerts some influence on the rate of transfer of hydrogen from the interface into the bulk of the metal but no study of the change of the interface with these treatments in relation to the diffusion process has been made.

The effect of alloying palladium with silver has been studied by Coehn and Baumgarten (32), who showed that the permeation rate of hydrogen through the alloys decreased with increasing silver content. As has been stated above, it appears that the dissolution of hydrogen exhibits a maximum

with increasing silver concentration and therefore the diffusion coefficient must show a marked reduction with increasing silver concentration. This is also apparent when the data for the charging of thin foils (Tamman and Nowack (20), Coehn and Jurgens (39)) are compared with those for the charging of thick foils (Kruger and Sacklowski(28), Coehn and Baumgarten (32)). It is evident that the thick foils were not under equilibrium during the charging process and that this is to be attributed to a falling diffusion coefficient. The diffusion of potentials (32) through palladium-silver membranes also indicates a falling diffusion coefficient with increasing silver content.

CONSIDERATION OF PREVIOUS WORK.

As has been repeatedly pointed out it is difficult to assess the validity of the conclusions from previous work in the absence of data on the diffusion kinetics. The main measurements of the diffusion have been those of the permeation rates. These are complex quantities even if it is assumed that the diffusion is controlled by the transfer through the bulk of the metal. It is impossible to assess the true effect of the interfaces, of temperature, poisoning etc. in the absence of data on the diffusion kinetics. It may be concluded that

the experiment design in previous work (insofar as this was carried out to interrelate the diffusion and electrochemical kinetics) was inadequate to demonstrate the deduced relationships.

Apart from this, the experimental technique of previous workers, with the possible exception of that of Frumkin and Aladjalova was, in all probability, inadequate. It was evident that a thorough investigation would have to be carried out under the stringent conditions of purity etc. shown to be necessary by recent measurements in electrochemical kinetics.

Experimental conditions and choice of system in the present experiments.

It was clear from the above considerations that it would be necessary to avoid all poisoning of the electrode either by the solution or any material used to seal in the electrode and any form of depolarisation. In the light of recent experiments, it is an easy matter to prepare pure solutions and the manner of preparation and the experimental technique necessary are indicated in the experimental section. Depolarisation by anodic or cathodic depolarisers could be avoided by also carrying out the experiments in an appropriate inert atmosphere. It became evident during the course of the experiments that it was necessary to guard against electrical depolarisation in certain types of measurements. Precautions were therefore

taken to guard against electrical leakage and valve potentiometers were employed to measure potential changes.

The choice of electrode system was limited by several considerations. In addition to measurements of the dissolution of hydrogen in wires, it was desired to conduct experiments with membrane electrodes since important conclusions could be reached by the comparison of such systems. In order to carry out such experiments it was necessary to obtain leak-tight seals. Although a variety of sealing materials was investigated, it was found that the systems were invariably poisoned either by the sealing material itself or because of the impossibility of cleaning the system effectively. It was clear, therefore, that the metal would have to be chosen so that the electrode could be sealed directly into glass, and subsequently cleaned by the methods employed for the rest of the apparatus. The choice was further limited since it was desired to investigate the permeability under anodic and cathodic conditions, (necessitating an inert electrode material) in a metal, in which the dissolution was known to proceed endothermically at high temperatures since such systems show a more regular temperature dependence than systems with an exothermic dissolution of hydrogen. Of all the systems known to show

permeability to hydrogen at high temperatures, platinum appeared to be the most obvious choice. It was found that this could be sealed directly into glass without the use of intermediate metals or solders, and furthermore a wide range of conditions of the interfaces could be effectively investigated.

Choice of Set Up and Boundary Conditions.

It appeared desirable to extend the observations of previous workers in several directions in the light of modern views on electrochemical kinetics and the complexity of diffusion phenomena. In a complete investigation of the kinetics of diffusion the main concern must necessarily be an investigation of the extent to which the diffusion is actually controlled by the transmission through the bulk, by slow stages at the interfaces, and to what extent concentration terms affect the diffusion coefficient. Three general methods of approach are possible. First the effect of geometrical configuration on the rate of sorption, desorption or transmission can be investigated, and the extent to which the observed quantities obey the predictions from Ficks laws of diffusion can be observed. Secondly, a comparison of the rates of sorption, desorption and transmission, best

characterised by the concentration terms entering into the derived expressions, should give information as to the presence of slow interface reactions and their location. Thirdly, a comparison of the energies of activation of the rates of permeation and of the diffusion coefficients should show to what extent the diffusion step is controlled by the transmission through the bulk. The effect of concentration terms on the diffusion coefficient can best be estimated by investigating the systems over a range of boundary conditions. Although the solutions of Fick's laws will only be very approximately obeyed if the diffusion coefficient varies with the concentration, a semi-quantitative picture can be built up.

The experiments were accordingly divided into the following sections:-

1. It was decided to investigate whether there was any diffusion of cathodic potential and to what extent the build up of potential on the outgoing interface could be correlated with the potential at the ingoing interface and rate of deposition of hydrogen.

2. The diffusion of anodic potential was investigated in an attempt to correlate the potential change with the measured diffusion coefficient and the concentration-potential relationships.

3. Quantitative measurements were made of the diffusion coefficient according to the methods developed by Daynes(21) and by Barrer (52). The conditions at the ingoing interface varied through a range of anodic potentials, the reversible hydrogen potential, to about $-0.1v$. The outgoing interface was maintained at a potential at which according to the experiments indicated in Section 2 above there was no hydrogen on the interface. Rates of permeation, in the steady state were also recorded.

4. The rates of dissolution and desorption of hydrogen as a function of time were measured on wires, over a range of anodic potentials. Diffusion coefficients were obtained as a function of the anodic potential and the equilibrium concentrations for adsorption and desorption were compared with those obtained from 3. above.

The experiments in 2, 3, and 4 above were carried out over a range of temperatures.

GENERAL THEORETICAL CONSIDERATIONS.

For the experiments outlined above, it is necessary to consider the solution of Fick's laws of diffusion for the slab and the rod. For the membrane only the region $0 < x < l$ will be considered and for the wire the infinitely long rod will be treated

in the cylindrical co-ordinate system. In this end effects will therefore be neglected. Further, for the membrane we shall mainly deal with the amount of material crossing the interface $x=0$ as a function of time with various boundary conditions at the interface $x=l$ and shall not be further concerned with the concentration distributions since these are not determinable. For the wire also we shall not concern ourselves with concentration distributions and only deal with the amounts crossing the interface $r=a$ as a function of time.

For the membrane we shall be concerned with both Fick's first and second law of diffusion. The first law can be stated in the form:

$$P = -D \frac{\partial c}{\partial x} \quad (1)$$

and the second in the form:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (2)$$

where D is the diffusion coefficient, P the permeation rate, and C the concentration.

From equation (1) the diffusion coefficient can only be obtained if the concentration gradient is known, or the concentration if the diffusion coefficient is known. Since the concentration gradient could not be directly measured in the present experiments, the diffusion coefficients were evaluated

from the second law and the concentration within the ingoing interface derived from the first law by substitution. We can solve equation (2) in one of two forms; either to give the concentrations as a function of distance and time or as the amount of material which has crossed the interface $x=0$ as a function of time. Again the first alternative has to be ruled out since the concentration distribution within the metal cannot be determined in the present type of experiment. Accordingly the solution used for the evaluation of the diffusion coefficient was that for the total amount which has diffused across the interface $x=0$ as a function of time. Various other solutions were also used to interpret the potential changes on the interface $x=0$ during the charging of the ingoing interphase ($x=l$) and to check the extent to which the system obeyed Fick's laws of diffusion. These solutions and their application are indicated below.

The solution of equation (2) can be approached in one of two ways; classically it can be deduced most conveniently from Fourier's Integral by the use of Fourier's transform.

Alternatively the solutions can be obtained by the use of the Laplace Transformation in conjunction with a table of transforms or the Inversion Theorem for the Laplace Transformation.

The second method, as will be seen below, in conjunction with various expansions and the use of tables of transforms gives useful solutions which are rapidly convergent for small values of time. Since the solutions deduced from Fourier's Integral can be equally readily obtained from the Laplace Transformation by the use of the Inversion Theorem we shall only indicate the manner of obtaining the solutions by this method.

If the concentration C is a function of the time t and the space variables x, y, z then the Laplace Transform is the integral

$$L[c(x, y, z, t)] = \bar{c} = \int_0^{\infty} e^{-pt} c(x, y, z, t) dt \quad (3)$$

p being a number whose real part is positive and large enough to make (3) convergent. \bar{c} is a function of p and x, y, z .

Further we shall need certain theorems governing the transforms.

$$L\left[\frac{\partial c}{\partial t}\right] = pL(c) - c_0 \quad (4)$$

$c_0 = \lim_{t \rightarrow 0} c$, c_0 being a function of x, y, z .

$$\text{for } \int_0^{\infty} e^{-pt} \frac{\partial c}{\partial t} dt = [e^{-pt} c]_0^{\infty} + p \int_0^{\infty} e^{-pt} c dt$$

$$\text{II. } L\left[\frac{\partial^n c}{\partial x^n}\right] = \frac{\partial^n \bar{c}}{\partial x^n} \quad (5)$$

$$\text{or } \int_0^\infty e^{-pt} \frac{\partial^n c}{\partial x^n} dt = \frac{\partial^n}{\partial x^n} \int_0^\infty e^{-pt} c dt$$

$$\text{III } L\left[\int_0^t c(t') dt'\right] = \frac{1}{p} L[c] \quad (6)$$

$$\text{for } \int_0^\infty e^{-pt} dt \int_0^t c(t') dt' = \left[\frac{e^{-pt}}{p} \int_0^t c(t') dt' \right]_0^\infty + \int_0^\infty e^{-pt} c dt = \frac{\bar{c}}{p}$$

We may consider the slab $0 < x < l$ with no transfer of material at $x=0$, initial concentration within the slab and on the interfaces zero, and $x=l$ maintained at constant concentration C for $t > 0$.

We can apply the Laplace Transformation to Fick's second law

$$\frac{\partial^2 c}{\partial x^2} - \frac{1}{D} \frac{\partial c}{\partial t} = 0, \quad 0 < x < l; \quad c=0, t \geq 0, \quad x=0$$

$$c=C, t > 0, \quad x=l$$

Multiplying by e^{-pt} and integrating with respect to t from 0 to ∞

$$\int_0^\infty e^{-pt} \frac{\partial^2 c}{\partial x^2} dt - \int_0^\infty e^{-pt} \frac{\partial c}{\partial t} dt = 0 \quad (7)$$

we obtain from theorems I and II

$$\frac{d^2 \bar{c}}{dx^2} - \frac{p \bar{c}}{D} = 0 \quad (8)$$

$c_0(x)$ being zero. The partial differential equation (2) is thus

reduced to the ordinary differential equation (8). Equation (8) is usually referred to as the subsidiary equation.

Applying the same process to the boundary conditions we obtain

$$\begin{aligned} \frac{d\bar{c}}{dx} &= 0, \quad x = 0 \\ \bar{c} &= \frac{C}{\rho}, \quad x = l \end{aligned} \quad (9)$$

Solving equation (8) with these boundary conditions we obtain the Laplace Transform c of the solution of the problem.

In the above case the solution is: (60)

$$\bar{c} = \frac{C \cosh qx}{\rho \cosh ql}, \quad q^2 = \frac{\rho}{D} \quad (10)$$

To derive c from \bar{c} we have to use the Inversion Theorem. For small values of time an alternative procedure is useful giving a rapidly converging series for c . (60)

We have

$$\begin{aligned} \bar{c} &= \frac{C \cosh qx}{\rho \cosh ql} = \frac{C(e^{qx} - e^{-qx})}{\rho e^{ql}(1 - e^{-2ql})} \\ &= \frac{C}{\rho} [e^{-q(l-x)} + e^{-q(l+x)}] \sum_{n=0}^{\infty} (-1)^n e^{-2nql} \\ &= \frac{C}{\rho} \sum_{n=0}^{\infty} (-1)^n e^{-q[(2n+1)l-x]} + \frac{C}{\rho} \sum_{n=0}^{\infty} (-1)^n e^{-q[(2n+1)l+x]} \end{aligned} \quad (11)$$

Using a table of transforms we obtain

$$c = C \sum_{n=0}^{\infty} (-1)^n \operatorname{erfc} \frac{(2n+1)l-x}{2\sqrt{Dt}} + C \sum_{n=0}^{\infty} (-1)^n \operatorname{erfc} \frac{(2n+1)l+x}{2\sqrt{Dt}} \quad (12)$$

This equation will be used to interpret the charging curves of the outgoing interface described in Results: sections (3) and (4).

A further case which will be needed in the main body of the work is the solution for $0 < x < l$ with zero initial concentration, $x=0$ maintained at zero and $x=l$ at constant concentration C for $t > 0$.

The solution in this case is: (60)

$$\bar{c} = \frac{C \sinh qx}{p \sinh ql} \quad (13)$$

In this case we shall not be interested in the concentration changes but in the total quantity Q of material which has crossed the plane $x=0$ from the time $t=0$ to the time $t=t$ i.e.

$$Q = D \int_0^t \left[\frac{\partial c}{\partial x} \right]_{x=0} dt \quad (14)$$

Applying theorem III

$$\bar{Q} = \frac{DCq}{p^2 \sinh ql} \quad (15)$$

To solve this problem we have to use the Inversion Theorem. This states that

$$c(t) = \frac{1}{2\pi i} \int_{\gamma-i\infty}^{\gamma+i\infty} e^{pt} \bar{c}(p) dp \quad (16)$$

where p is complex. γ is taken to be so large that all

singularities of $\bar{c}(p)$ lie to the left of the line $(\gamma - i\infty, \gamma + i\infty)$. Since the above argument is not rigid it is strictly speaking necessary to verify that the solution of the problem satisfies the differential equation and the boundary conditions. This can be performed on the contour integral (16) but will not be proved here.

In the problems dealt with here $\bar{c}(p)$ is a single valued function of p with a row of poles along the negative real axis. The solution in form of the contour integral can therefore be put into real form by completing the contour by a circle of radius R not passing through any pole of the integrand. In the present problems the integral over the circle vanishes in the limit as $R \rightarrow \infty$, and in the limit the line integral is equal to, by Cauchy's theorem, $2\pi i$ times the sum of the residues at the poles of its integrand.

In the above case we therefore have:

$$Q = \frac{DC}{2\pi i} \int_{\gamma - i\infty}^{\gamma + i\infty} \frac{e^{pt} q dp}{p^2 \sinh ql} \quad (17)$$

The integrand has a double pole at $p=0$ of residue $\frac{1}{l} \left[t - \frac{l^2}{6D} \right]$ and at those values of p which make $\sinh ql = 0$ ie

$$q = \frac{n\pi i}{l}, \quad p = -\frac{n^2 \pi^2 D}{l^2}, \quad n=1, 2, 3, \dots \text{ etc.}$$

of residue

$$e^{-\frac{n^2 \pi^2 D t}{l^2}} \cdot \frac{n\pi i}{l} \frac{p^2 \frac{d}{dp} \left[\sinh l \sqrt{\frac{p}{D}} \right]}{p^2} \Big|_{p = -\frac{n^2 \pi^2 D}{l^2}}$$

ie

$$\frac{2l}{D\pi^2 n^2} (-1)^n e^{-\frac{Dn^2 \pi^2 t}{l^2}}$$

so that

$$Q = \frac{DC}{l} \left[t - \frac{l^2}{6D} - \frac{2l^2}{D\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} e^{-\frac{D\pi^2 n^2 t}{l^2}} \right] \quad (18)$$

For large values of t the exponential terms tend to zero and (21)

$$Q = \frac{DC}{l} \left[t - \frac{l^2}{6D} \right] \quad (19)$$

ie. equivalent to a steady flow for a time $t - l^2/6D$. By measuring the time delay in establishing the steady state and equating to $l^2/6D$ we obtain D . (52)

This method was used to obtain diffusion coefficients as a function of the concentration at $x=1$. In the present experiments the concentration terms were assumed to be constant if the interface potential was constant and the total amount diffused was calculated from the total charge that had crossed the interface $x=0$ as a function of time. The more general case (54) with initial concentration C_0 ; $C=C_1$, $x=0$, $t > 0$; $C=C_2$, $x=1$, $t > 0$; was not used since the experimental conditions would have made the measurements ambiguous.

The time lag in approaching the steady state was calculated in the following manner. Values of the rate of transition P across the interface $x=0$ were plotted against the time t . The total amount Q which has diffused across this interface is then the area under the curve P, t . If the time intercept required is denoted by t_2 and the time at which the permeation reaches the final stable value P_1 is t_1 at which the total permeation is Q_1 then we may write for (19)

$$Q = P_1 t - P_1 t_2$$

and at the point P_1 , t_1 we have

$$\frac{Q_1 - P_1 t_1}{P_1} = -t_2$$

Multiplying the numerator and denominator by t_1 we have

$$t_2 = \frac{[P_1 t_1 - Q_1] t_1}{P_1 t_1} = \frac{l^2}{6D} \quad (20)$$

Here $P_1 t_1$ is the area enclosed from $t=0$ to $t=t_1$ and $P=0$ to $P=P_1$ while $P_1 t_1 - Q_1$ is the difference between this and the area not enclosed by the curve $P-t$. Assuming that the area is proportional to the weight of the graph paper we can cut along the $P-t$ curve and weigh the separate pieces of paper and then multiply t_1 by the area ratio indicated by (20). By equating to $l^2/6D$ we obtain D .

Treating equation (15) in the same manner as equation (10) i.e. expanding in a series the terms obtained by expressing $\sinh ql$ as negative exponentials, and then using a table of transforms, we obtain the total amount which has diffused across the interface $x=0$ from time $t=0$ to $t=t$

$$Q = 4D^{1/2} C t^{1/2} \sum_{n=0}^{\infty} \text{ierfc} \left(\frac{(2n+1)l}{2\sqrt{Dt}} \right) \quad (21)$$

We can use this series, again rapidly converging, to check to what extent the system is actually obeying Fick's laws of diffusion and the above boundary conditions by comparing the experimental value of Q with the value obtained from equation (21) with the experimental values of C and D .

A test of the extent to which the system is obeying Fick's laws has already been indicated for a range of experimental conditions in equation (12). The range of factors in such a test is very large however and simpler comparisons of the theoretical and experimental behaviour can be obtained using the system under the boundary conditions of equation (21). The test of the total quantity diffused is not very sensitive however and the nature of the deviations is not immediately apparent. A better comparison is obtained by using the experimental and theoretical values of the rate of transition as a function of time.

We have

$$DL \left[\frac{\partial c}{\partial x} \right] = D \frac{dc}{dx} = \frac{DCq \cosh qx}{n \sinh ql}$$

$$D \frac{\partial c}{\partial x} = C \left[\frac{D}{\pi t} \right]^{\frac{1}{2}} \sum_{n=0}^{\infty} e^{-\frac{[(2n+1)l-x]^2}{4Dt}} + C \left[\frac{D}{\pi t} \right]^{\frac{1}{2}} \sum_{n=0}^{\infty} e^{-\frac{[(2n+1)l+x]^2}{4Dt}}$$

at $x=0$

$$D \left[\frac{\partial c}{\partial x} \right]_{x=0} = 2C \left[\frac{D}{\pi t} \right]^{\frac{1}{2}} \sum_{n=0}^{\infty} e^{-\frac{(2n+1)^2 l^2}{4Dt}} \quad (22)$$

This expression will be applied in the results.

In the experiments described in Results: section 2 two elementary tests of the extent to which the system was obeying Fick's laws were carried out, mainly as a check of the applicability of the experiment design. In this test we consider the region $0 < x < l$ with initial concentration C_0 . The interface $x=0$ is maintained at C_0 for $t > 0$ while the interface $x=l$ is discharged at a rate Q . The rates of change of potential with different discharge rates can then be compared. The subsidiary equation for this problem is

$$\frac{d^2 \bar{c}}{dx^2} - \frac{\rho}{D} \bar{c} = -\frac{C_0}{D}$$

with boundary conditions

$$\bar{c} = \frac{C_0}{\rho}, \quad x=0, \quad t > 0$$

$$D \frac{d\bar{c}}{dx} = \frac{Q}{\rho}, \quad x=l, \quad t > 0$$

the solution is

$$\bar{c} = \frac{C_0}{\rho} - \frac{Q \sinh qx}{D \rho q \cosh ql}$$

which for small values of time may be put in the form

$$c = C_0 - \frac{2Qt^{\frac{1}{2}}}{D^{\frac{1}{2}}} \left[\sum_{n=0}^{\infty} (-1)^n \operatorname{ierfc} \frac{(2n+1)l-x}{2\sqrt{Dt}} - \sum_{n=0}^{\infty} (-1)^n \operatorname{ierfc} \frac{(2n+1)l+x}{2\sqrt{Dt}} \right]$$

and at $x=l$ we have

$$c = C_0 - \frac{2Qt^{\frac{1}{2}}}{D^{\frac{1}{2}}} \left[\sum_{n=0}^{\infty} (-1)^n \operatorname{ierfc} \frac{2nl}{2\sqrt{Dt}} - \sum_{n=0}^{\infty} (-1)^n \operatorname{ierfc} \frac{2(n+1)l}{2\sqrt{Dt}} \right] \quad (23)$$

This expression cannot be applied in an analysis of the charging curves owing to its complexity. We may note that the decrease in concentration at any time t is proportional to the discharge rate Q . If the potential time curves on the outgoing interface are determined for a range of values of Q , the concentrations at equal potentials on the different potential time curves can be compared.

A similar useful comparison can be obtained by using the rates of change of concentration on the outgoing interface as a function of the discharge rate of this interface. We have

$$L \left[\frac{\partial c}{\partial t} \right] = \bar{c} - C_0 = \frac{-Q \sinh qx}{Dq \cosh ql}$$

and at small values of time on the outgoing interface

$$\left[\frac{\partial c}{\partial t} \right]_{x=l} = -\frac{Q}{D} \left[\frac{D}{\pi t} \right]^{\frac{1}{2}} \left[\sum_{n=0}^{\infty} (-1)^n e^{-\frac{n^2 l^2}{Dt}} - \sum_{n=0}^{\infty} (-1)^n e^{-\frac{(n+1)^2 l^2}{Dt}} \right] \quad (24)$$

The rate of change of concentration and hence potential after a given time t should therefore be proportional to the discharge rate Q .

We may now consider the solution of the diffusion equation for the cylinder radius a for the case of constant surface concentration C for $t > 0$. This solution was used by Eyring(53)

to study the diffusion of hydrogen from the gas phase into platinum at high temperatures. A similar set up has been used in the present experiments the rate of transition across the interface being characterised by the current flowing into the cylinder.

This problem can again be most easily treated by the Laplace Transformation. No assumption need be made as to the possibility of expanding the initial distribution in terms of a Fourier Bessel series and the coefficients of the series are readily obtained. Strictly as before the solution must be verified but this will not be carried out here.

We have to solve

$$\frac{\partial^2 c}{\partial r^2} + \frac{1}{r} \frac{\partial c}{\partial r} - \frac{1}{D} \frac{\partial c}{\partial t} = 0 \quad 0 \leq r < a, t > 0 \quad (25)$$

for the conditions $c=C, r=a, t > 0$.

The subsidiary equation is

$$\frac{d^2 \bar{c}}{dr^2} + \frac{1}{r} \frac{d\bar{c}}{dr} - q^2 \bar{c} = 0 \quad (26)$$

$$q^2 = \mu/D \quad \text{with} \quad \bar{c} = C/\mu, \quad r=a.$$

This equation is satisfied by the Bessel function $I_0(qr)$ and $K_0(qr)$. The latter tends to infinity as $r \rightarrow 0$ and must be excluded.

Hence

$$\bar{c} = \frac{C I_0(qr)}{\mu I_0(qa)} \quad (27)$$

Using theorem II and writing P for the rate of transition at $r=a$

we have

$$\bar{P} = D \left[\frac{d\bar{c}}{dr} \right] = \frac{DC_0 I_1(qa)}{\rho I_0(qa)}$$

and hence

$$P = \frac{DC}{2\pi i} \int_{\gamma-i\infty}^{\gamma+i\infty} e^{\rho t} \frac{q I_1(qr) d\rho}{\rho I_0(qa)} \quad (28)$$

The integrand is a single valued function of ρ and the contour can again be completed by the circle of radius R . The zeros of $I_0(qa)$ are at $\rho = -D\alpha_n^2$ where α_n are the roots of $J_0(\alpha_n a) = 0$ $N=1, 2, 3, \dots$ Using the fact that

$$I_1[z e^{\pm \frac{1}{2}\pi i}] = e^{\pm \frac{1}{2}\pi i} J_1[z]$$

we see that

$$\begin{aligned} \left[\rho \frac{d}{d\rho} I_0(qa) \right]_{\rho = -D\alpha_n^2} &= \left[\frac{1}{2} qa I_1(qa) \right]_{q = i\alpha_n} \\ &= -\frac{1}{2} a \alpha_n J_1(a\alpha_n) \end{aligned}$$

and hence the residue at the pole $\rho = -D\alpha_n^2$

$$= \frac{2 e^{-D\alpha_n^2 t} \alpha_n J_1(a\alpha_n)}{a \alpha_n J_1(a\alpha_n)}$$

Therefore we have by Cauchy's theorem

$$P = \frac{2CD}{a} \sum_{n=1}^{\infty} e^{-D\alpha_n^2 t} \quad (29)$$

at the point $r=a$.

This system affords an easy means of evaluating both D and C from the experimental data. We may calculate a calibration curve with assumed values of C and D which we may term C_t and D_t and obtain

$$P_t = \frac{C_t D_t}{a} \sum_{n=1}^{\infty} e^{-D_t \alpha_n^2 t_t}$$

We can plot the value of P_t for any value of t_t on double logarithmic paper. Similarly we can plot the experimental values of P_e as a function of t_e

$$P_e = \frac{C_e D_e}{a} \sum_{n=1}^{\infty} e^{-D_e \alpha_n^2 t_e}$$

Taking the x-axis of the logarithmic paper as the time coordinate we see that the shape of the P_t t_t and the P_e t_e curves are only determined by the magnitude of the product Dt . By displacing either curve we can adjust them so that they fit together and obtain the time t_t corresponding to the point t_e . At this point

$$D_e t_e = D_t t_t \quad (30)$$

and D_e is obtained. As at this point the magnitude of the series is the same we have

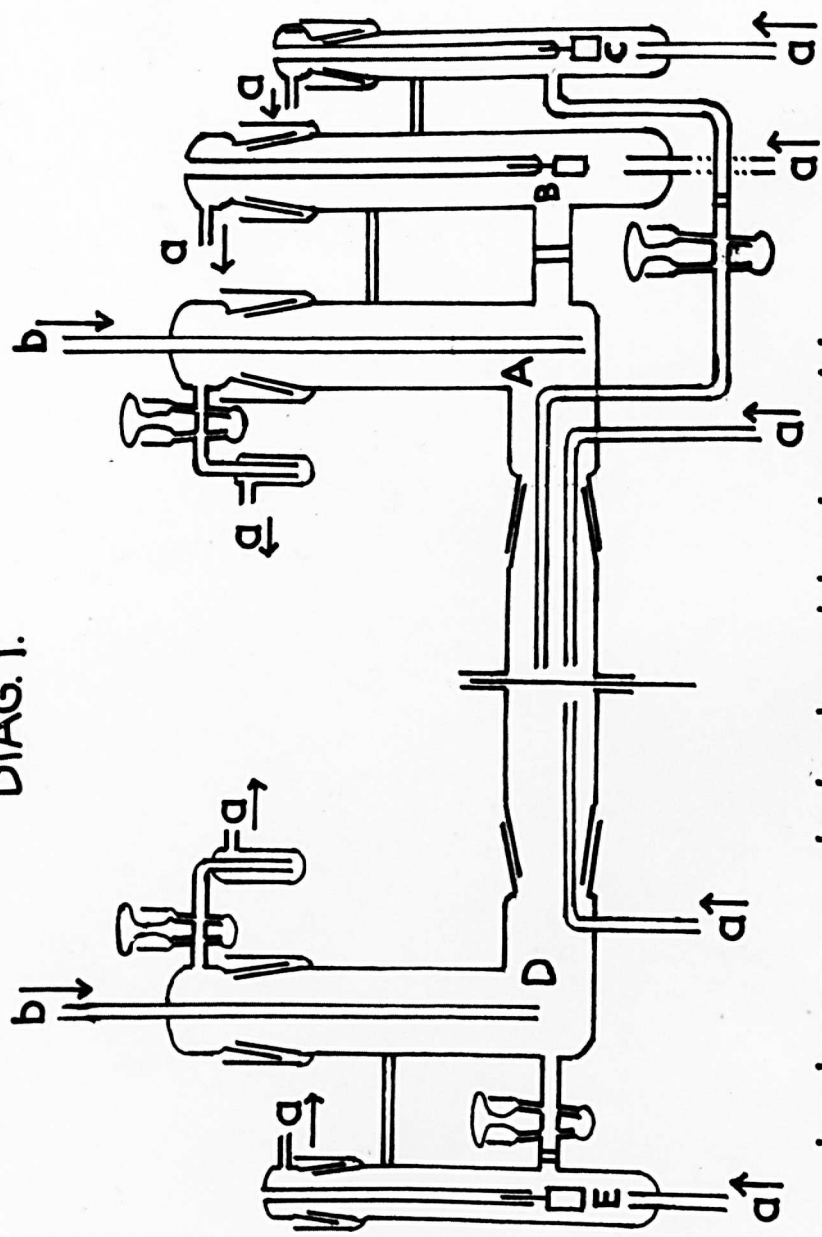
$$\frac{P_e}{C_e D_e} = \frac{P_t}{C_t D_t} \quad (31)$$

and C_e is obtained. The fitting of the curves can best be

accomplished by plotting the results and the calibration curve on separate sheets of thin paper and adjusting the sheets over an illuminated pane of glass.

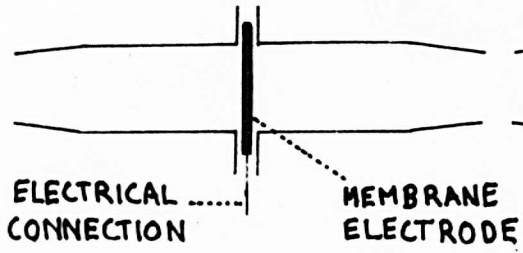
The above relations have all dealt with the analysis of Fick's laws on the basis of a diffusion process controlled entirely by the bulk. More complicated relationships are found when interference by the interfaces occurs. The diffusion equation in combination with slow interface processes can be conveniently solved by the methods used in the conduction of heat with radiation boundary conditions. The applicability of slow interface processes to the present system will be considered in the discussion.

DIAG. I.

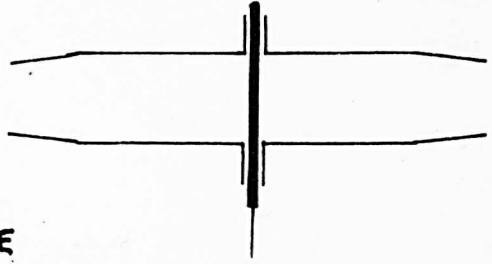


a hydrogen b hydrochloric acid

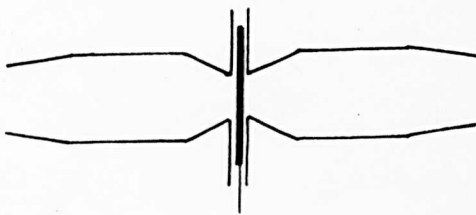
DIAG. 2.



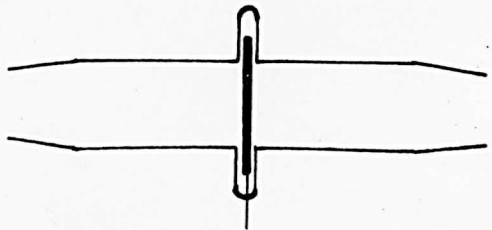
DIAG. 3.



DIAG. 4.



DIAG. 5.



EXPERIMENTAL DETAILS.

Electrode Design.

Wire electrodes.

The electrodes used in the experiments described in Results: section 5 were cut from platinum wire of radius 0.0175 cm. and sealed into soda-glass quill tubing.

Membrane electrodes.

A variety of electrode designs was used. In the preliminary experiments on the transfer of cathodic potential carried out with cells 1 and 2 various seals with cements were investigated. Platinum membranes 0.001 in. thick were sealed between ground-glass flanges in the manner indicated in diags. 2 to 4. The electrical lead was attached to the membrane in the area lying between the ground-glass flanges. With cell 1 a number of experiments were carried out with the flanges attached directly to the bulk of the apparatus. This system was found to be unsatisfactory as the strain involved resulted in the introduction of leakage in spite of a variety of clamping devices. This system was accordingly replaced by the system actually shown in diag. 1. This enabled the electrode system to be clamped without strain on both sides of the membrane.

The sections containing the electrode compartments could then be slid on to the electrode mounting. This type of mounting was then also used with cell 2.

The area of the electrode in the flange system used with cell 1, was of the order of 4 sq. cm. With this system the sealing properties of a range of greases, resins, and inorganic cements were investigated. The seals were found to be unsatisfactory and the electrodes were extensively poisoned as was shown by measurements of the hydrogen overpotential.

The area of the electrode in the flange system used with cell 2 was of the order of 1.5 sq. cm. With the system depicted in diag. 4 the electrode area could be reduced to 0.3 sq. cm. thus enabling higher current densities to be obtained. A range of thermoplastic polymers, waxes, and solutions of various polymers was used for sealing. The most satisfactory seals were obtained with solutions of polystyrene, which was found to have a strong adhesion to both platinum and glass.

All the above sealing materials were found to poison the electrode surface, as was shown by measurements of the hydrogen overpotential. As was stated in the Introduction, it appeared that, since in other systems the diffusion was found to be extremely sensitive to poisons, it was necessary to use

completely clean surfaces in this case. Attempts were therefore made to produce satisfactory electrodes by sealing directly into glass. These could be cleaned in a manner similar to that used for the rest of the apparatus and would yield unambiguous results.

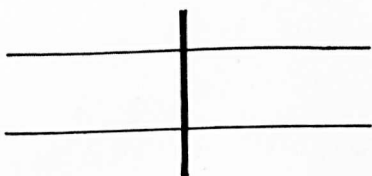
It was considered that satisfactory seals could be made with thin platinum membranes on the Housekeeper pattern using Pyrex glass. In the type illustrated in diag. 5 Pyrex glass tubes were flanged and attached to the joints. The platinum disc was then placed between the flanges and these were sealed together so as to overlap the edge and to cover some part of the platinum surface and the electrical connection to the membrane. The glass was pressed into contact with the platinum and sometimes a slight vacuum was maintained on the inside of the glass tubing to facilitate the adhesion of the glass and platinum. Although these electrodes were found to be initially leak-tight according to chemical tests (hydrochloric or sulphuric acid in contact with one interface, silver nitrate or barium chloride solution with the other, over a period of up to 48 hours) they usually broke down after a period of 1 to 7 days, i.e., during the duration of the experiment. This type of system was therefore abandoned. These electrode systems were used in combination with both

cell 1 and cell 2.

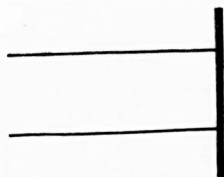
Various attempts were made to seal the platinum into HH and W1 glasses (made by the General Electric Company) as intermediates to Pyrex but these attempts were unsuccessful. It was considered that a soft glass would have to be used. Lead glass was found to give a very powerful adhesion and very satisfactory seals could be made. Pronounced greying of the platinum in the area of the seal was found, however, presumably owing to contamination by lead. These types of seals were therefore abandoned and efforts were concentrated on producing satisfactory soda-glass seals.

Seals with soda-glass along the lines of the Housekeeper seal described above could not be used as too much strain was introduced and the platinum could not be held firmly enough between the flanges to make uniform rotation in the blowpipe flame possible. A similar seal was tried with a small flange and with the disc protruding beyond the edge of the glass. The system was rotated mechanically with the disc horizontal. An electric furnace was built round the rotating tubes and the area of the seal was heated with two fine oxy-coal-gas flames. Slight distortions occurred, however, and the lower tube thickened while the upper tube became thinner so that the final result although leak tight was very weak mechanically.

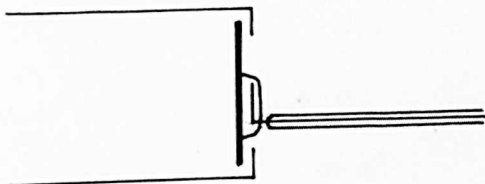
DIAG. 6.



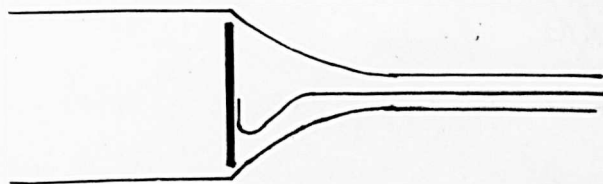
DIAG. 7.



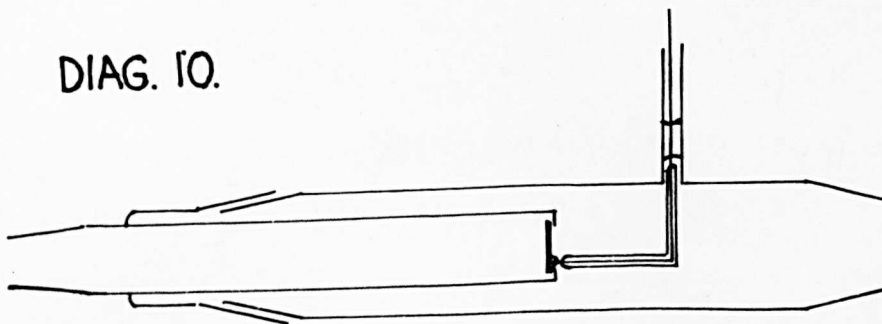
DIAG. 8



DIAG. 9.



DIAG. 10.



From the mechanical point of view the seal shown in diag. 6 which has been frequently employed for certain alloy-glass seals was found to be more satisfactory. It was considered that seals of this type would be more free from leakage and that attachment of an electrical lead wire would not interfere with the seal. It was found, however, that in spite of careful annealing these seals broke off after some time at the glass-metal boundary. The tubes were ground flat and polished and very carefully cleaned, as it was thought that unevenness or dirt could weaken the seal, but this produced no marked improvement. Seals where only one face of the platinum was sealed to the glass as shown in diag. 7 were found to be most satisfactory mechanically but still showed a tendency to develop leakage after a period of days. It was concluded that in order to produce satisfactory seals it would be necessary to grip the edge of the platinum disc and that the seal would have to be mounted in a manner as free from strain as possible. The type of seal shown in diag. 8 was found to be most satisfactory in this respect. Electrical connection was made to the centre of the foil and the area where the wire was attached to the foil was coated with glass to avoid any irregularity in diffusion caused by mechanical

interference with the membrane. The lead-in wire was covered with glass and taken through the outer tube as shown in diag. 10. In this way the electrode system was kept free from strain and was in fact found to be free from leakage according to chemical tests over a period of weeks. This type of electrode was used for the remaining experimental work described in Results: sections 1 to 4.

Two methods were used for producing seals of this type. In the first, glass tubing was first thinned and blown into a thin test tube end, the centre of which was then blown out, and the rim heated so as to form a platform on which the disc could rest. The disc with the electrical connection attached was then dropped on to the platform and sealed into position. In this manner excessive accumulation of glass on the edge of the platinum was avoided. At the end of the sealing process, the area where the wire was attached to the membrane and the wire itself were coated with glass. In the second method, glass tubing was pulled down as shown in diag. 19 and the disc with electrical connection attached sealed in. The pulled down section was then thinned and blown off and the wire-disc connection and wire coated with glass as before. It was found unnecessary to anneal the electrodes. The electrodes were then

attached to the mounting as shown in diag. 10, and the electrical connection sealed.

The electrodes prepared in this manner were used in combination with cells 2 and 3, in the experiments described in Results: sections 1 to 4. The electrodes used in the experiments described in Results: section 1 in combination with cell 2 were used in the mounting indicated in diag. 10 while in the experiments described in Results: sections 2 to 4, using cell 3, the mounting was as shown in diag. 11.

Cleaning of Apparatus.

All glassware was cleaned for several hours (usually overnight) before each experiment with a 1:1 mixture of AR sulphuric and nitric acids. This was followed by four washings with tap water and then tap water was allowed to flow through the apparatus overnight. Parts containing sintered glass discs were not cleaned with running water because they collected suspended particles sufficiently large not to pass through the sintered plate. The electrode mounting and the electrodes were not washed with tap water but only with distilled and then conductivity water.

After being washed with tap water overnight, the apparatus was washed three times with distilled water and then three times with conductivity water. Conductivity water was then allowed

to stand in the apparatus for several hours and usually overnight, the complete cleaning process usually taking two days.

In those experiments described in Results: sections 2 to 5, where extremely small quantities of solution were placed in contact with the outgoing interface of membrane or wire electrodes, it was necessary to remove all water from the section of the apparatus near the electrodes in order to avoid concentration changes and interference from any dissolved oxygen in the conductivity water. These parts were accordingly dried with purified acetone. AR acetone was fractionated, the fraction boiling between 56.2 and 56.5°C being collected. It was then treated with acid potassium permanganate solution, alkaline silver nitrate solution, and potassium carbonate, being fractionated after each treatment, and finally again fractionated. A long column packed with Fenske rings was used in the fractionation and a low take-off rate was used.

Platinum electrodes used for pre-electrolysis of the solutions were cleaned in the same way as the experimental electrodes except that they were heated in an alcohol flame before the final washing with conductivity water. Platinised platinum electrodes (prepared by the method of Ellis (62)), used

as reference or as non-polarisable cathodes, were left immersed in conductivity water between the experiments and were washed repeatedly (ca. 12 times) with conductivity water before use.

All sections of the apparatus that could be detached and tap keys etc. which could be lifted out were washed separately during the cleaning process. Connecting bridges for gas supply were washed with the sulphuric acid - nitric acid cleaning mixture which was not left in contact with the glass for any length of time and then with tap, distilled, and conductivity water. Periodically these bridges were also cleaned in the manner described for the rest of the apparatus.

Gas Purification.

Nitrogen and Hydrogen used in the experiments described below were purified in the following manner:-

Hydrogen.

Cylinder gas was passed through silica gel and then magnesium perchlorate in order to dry it; then through a furnace filled with Hopcalite and maintained at 120°C to remove any carbon monoxide; from there over soda-lime to remove carbon dioxide and then over palladised asbestos (5%) maintained at 400°C to remove any oxygen. The gas was then again dried by

passing through silica gel and further purified by passing through one trap filled with charcoal, and then two glass spirals cooled in liquid nitrogen.

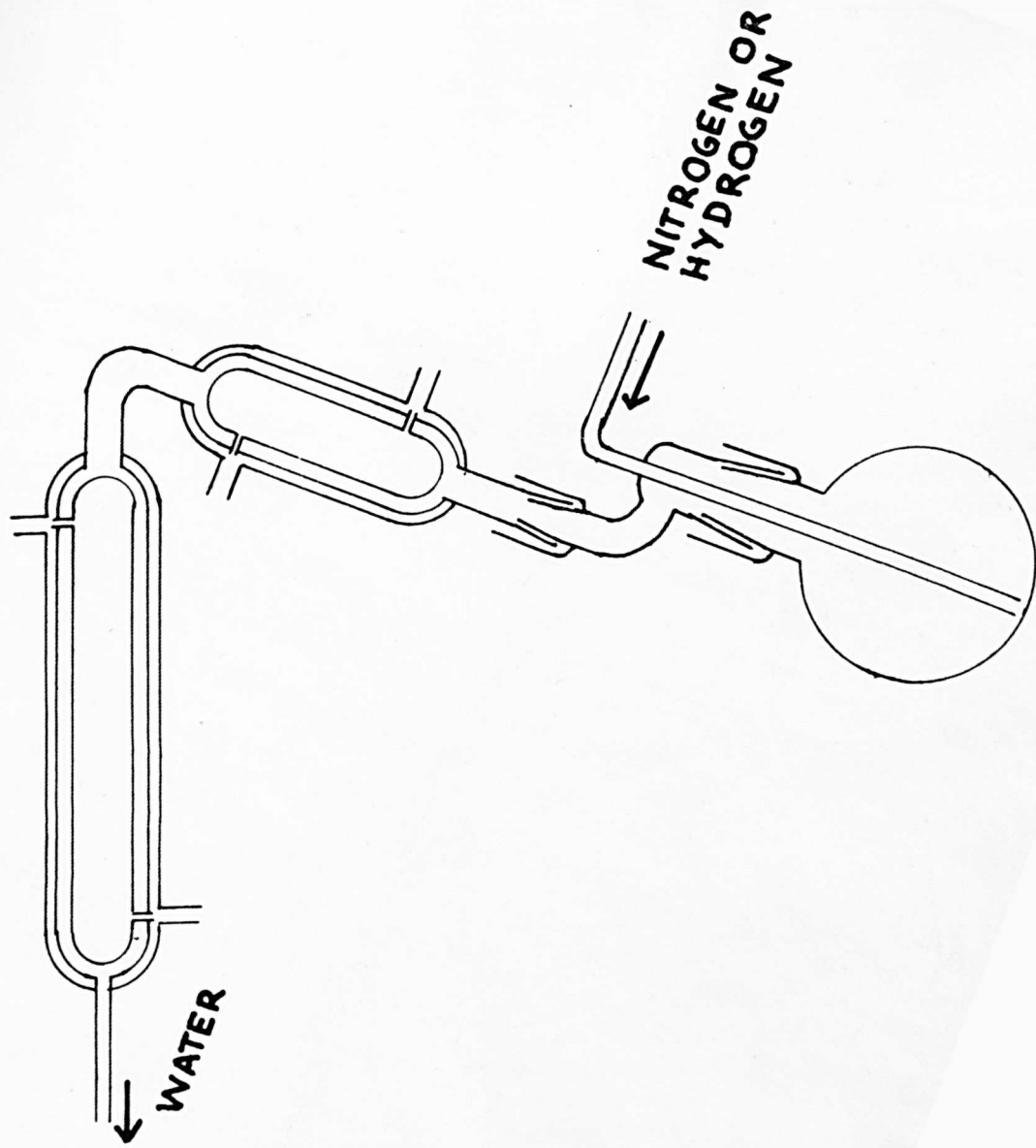
Nitrogen.

Cylinder gas was bubbled through a solution of sodium hydrosulphite in 10% potassium hydroxide solution, containing 1.5% of indigo carmine as indicator, in order to remove the bulk of the oxygen. As this solution gave off small quantities of hydrogen sulphide, the gas was then passed through alkaline potassium plumbite solution. The solutions were contained in sintered-glass bubblers. The gas was passed over silica gel and then through a trap cooled in solid carbon dioxide-alcohol mixture in order to dry it. The last traces of oxygen were removed by passing the gas over copper gauze heated to 600°C. Finally the gas was passed through two traps cooled in liquid nitrogen.

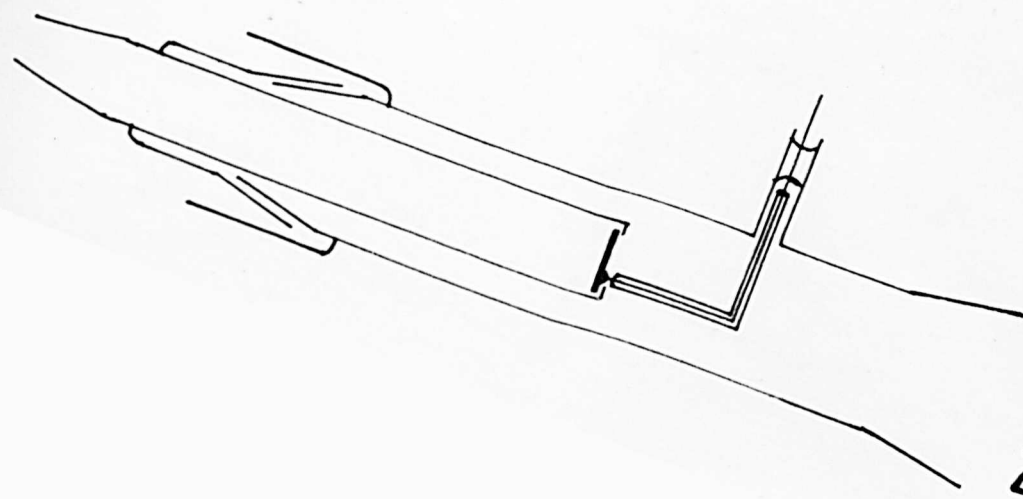
In the experiments described in Results: sections 4 and 5, the gases were also passed through a pre-heater and pre-saturator containing conductivity water in order to avoid cooling in the experimental cell during the experiment.

The gas trains described above were made throughout of Pyrex glass except the furnace containing the palladised asbestos which was made of soda-glass. The silica gel tubes used to dry the gas streams were contained in electric

DIAG. 12.



DIAG. 11.



furnaces and could be heated by these when required.

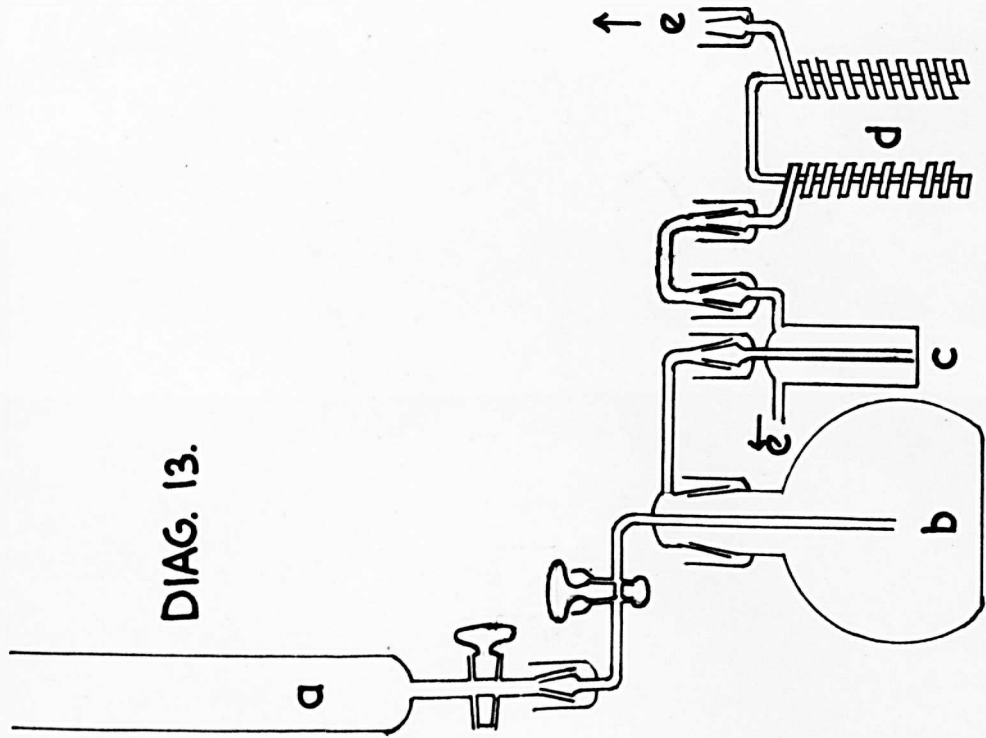
The gas trains were provided with mercury safety valves.

Preparation of Solutions.

In the experiments described below, normal solutions of hydrochloric acid prepared in an atmosphere of nitrogen or hydrogen were used. The conductivity water used in the preparation of the solution was refluxed in a purified gas stream (nitrogen or hydrogen) for a period of six or more hours in order to remove any dissolved oxygen. The conductivity water was then distilled in the gas stream into the appropriate solution preparation vessel, the first fraction being rejected. The solution preparation vessels had previously been evacuated and filled three times with the appropriate gas. The water distillation apparatus is shown in diag. 12.

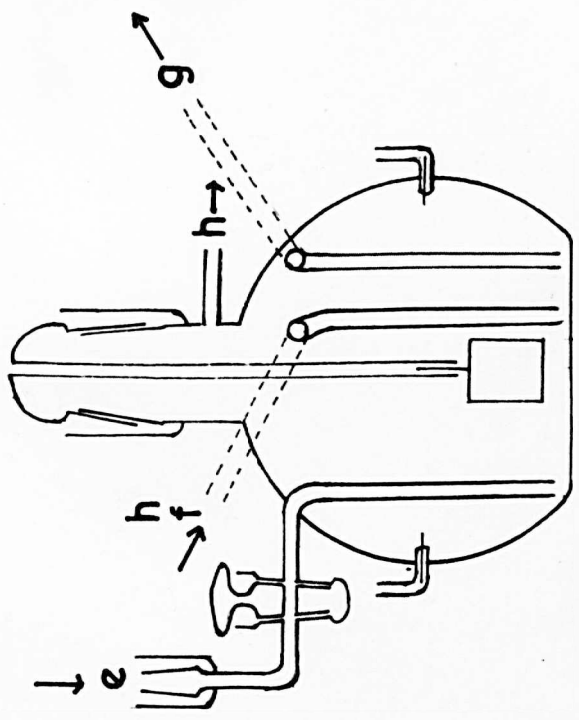
Hydrogen chloride gas was then passed into the water until the concentration reached one normal. The concentration was determined conductrimetrically with a Mullard "Magic Eye" conductivity bridge, a frequency of 1000 cycles per second being used. The solution was stirred with a stream of hydrogen or nitrogen. The hydrogen chloride gas was prepared by dropping AnalaR sulphuric acid on to AnalaR

DIAG. 13.



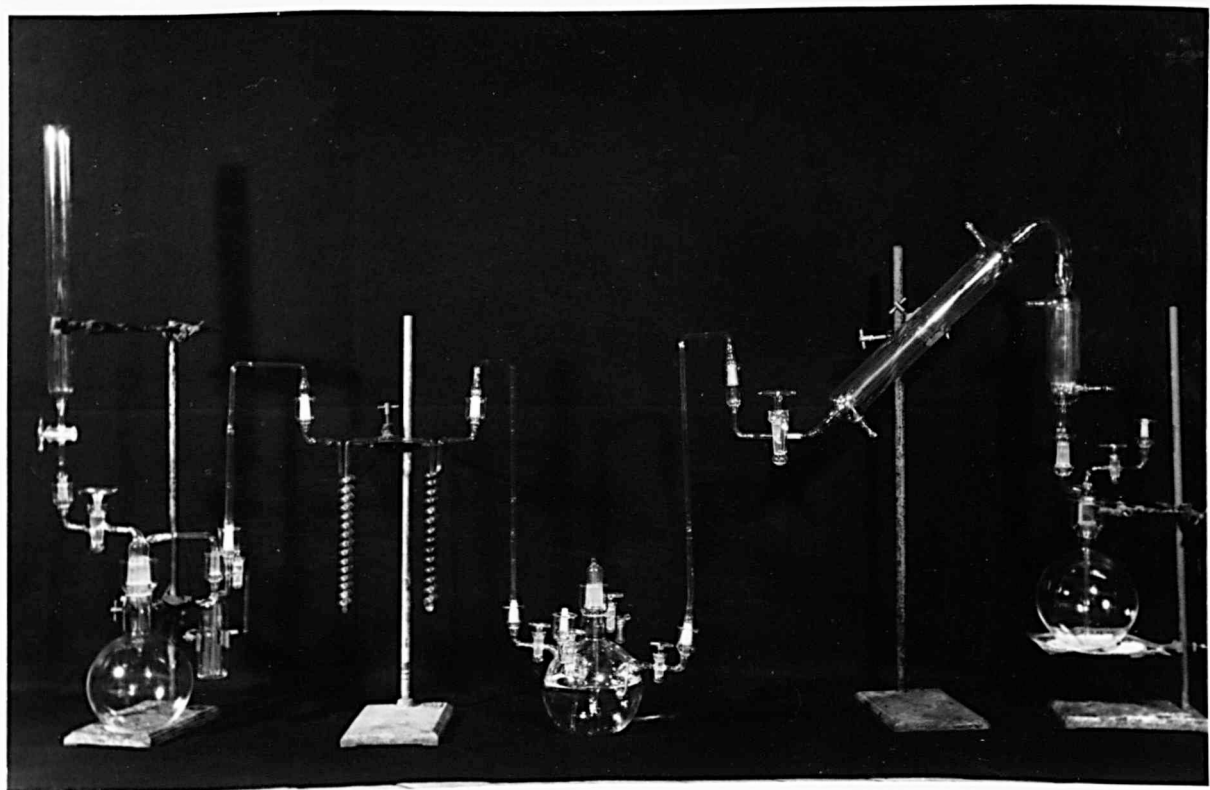
a sulphuric acid
 d spiral traps
 g hydrochloric acid

DIAG. 14.



a ammonium chloride
 b bubbler
 c hydrogen chloride
 d water
 e nitrogen

Diag. 15.



ammonium chloride in the apparatus shown in diag. 13. The gas was passed through two traps cooled in a mixture of solid carbon dioxide and alcohol. Before starting generation on the gas, the generating train was evacuated and filled three times with hydrogen or nitrogen, whichever was appropriate.

All taps and joints shown in diags. 12 and 13 were provided with solution seals in order to reduce the access of atmospheric oxygen into the apparatus.

The solutions prepared in a hydrogen atmosphere were pre-electrolysed for a minimum period of 12 hours with a current of 20 milliamp. and a cathode area of 10 sq. cm. A subsidiary platinum cathode was used in the appropriate solution preparation vessel in conjunction with an external platinum anode, which was separated from the main bulk of the solution by a closed tap and sintered disc. The solution was pushed out of contact with the subsidiary cathode before interrupting the pre-electrolysis. During the pre-electrolysis the solutions were stirred with a stream of hydrogen. The pre-electrolysis ensured that any impurities which might be deposited at the cathode during the course of the experiments were removed beforehand.

Solutions prepared in a nitrogen atmosphere were not pre-electrolysed, because this would have introduced hydrogen into

the solution. These solutions were left in contact with a large area of platinum (10 sq. cm.) overnight (cf.(38)) while being stirred with a stream of nitrogen.

Diag. 15 indicates the general layout of the solution preparation apparatus.

Apparatus Design and Experimental Procedure.

Cells 1 and 2.

For the experiments on the transfer of cathodic potential, two essentially similar cells were used. The main difference lay in the size, the first cell requiring ca. 1 litre and the second ca. 200 ml. of solution for an experiment. It was found that the first cell, being large, introduced strain into the electrode systems Diag. 1.

The electrode systems used with the two cells have been indicated above. Both cells consisted essentially of a cathode compartment A, the cathode being one interface of the membrane electrode, an anode compartment B and a reference electrode compartment C on the ingoing interface of the membrane. In the middle section were the various forms of electrode mounting described above.

The anode compartment B was separated by a sintered disc from A. C was separated from A by a sintered disc in cell 1

and also in cell 2 when hydrogen electrodes were used as reference electrodes; an additional tap (closed during the experiments) was interposed in certain of the experiments with cell 2 when calomel reference electrodes were used.

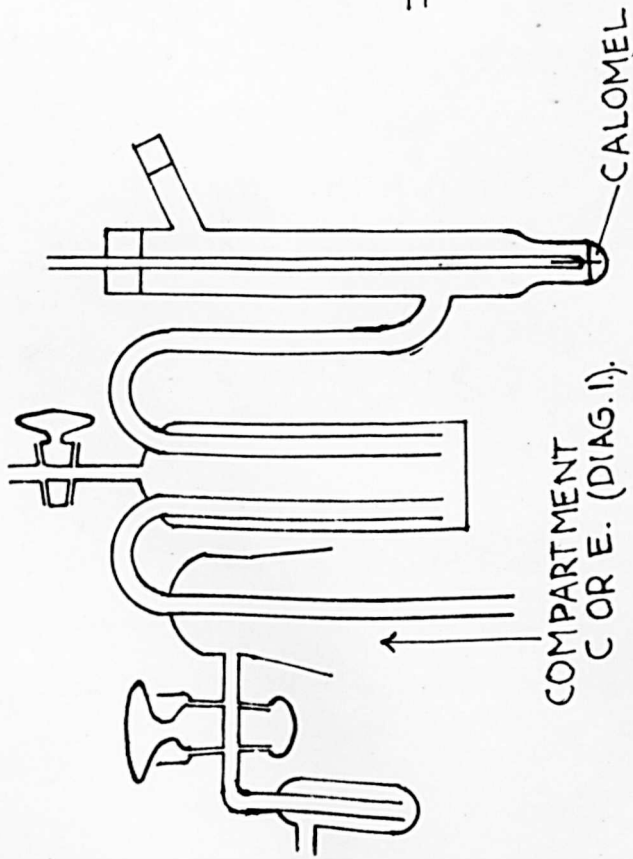
Compartment C was connected to the polarised ingoing (cathodic) interface by means of a Luggin capillary to avoid the inclusion of any resistance drop in the measured potential.

On the outgoing (nonpolarised) side of the membrane were a compartment D and a reference electrode compartment E. In the first apparatus, E was separated from D by a sintered disc and also connected by a Luggin capillary to the outgoing interface. In the second apparatus a tap was again included but the capillary was left out since there was no resistance drop on the non-polarised side. Hydrogen could be passed through any of the electrode compartments and also over the surfaces of the membrane electrode.

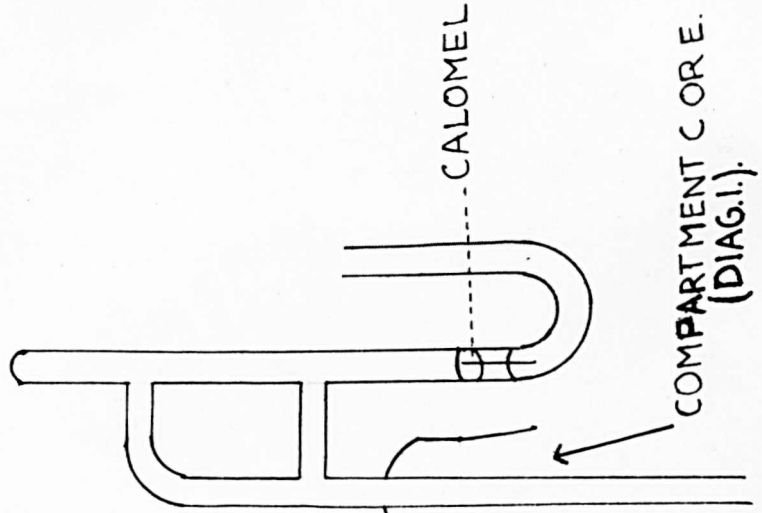
All taps and vertically placed joints were provided with solution seals to prevent the diffusion of oxygen into the cell. The horizontally placed joints were kept moist by contact with the solution in the cell. The apparatus was made of Pyrex glass.

Normal hydrochloric acid was prepared as indicated above

DIAG. 16.



DIAG. 17.



in the solution preparation vessel shown in diag. 14. An external anode compartment was placed on the hydrogen chloride gas connection and the solution pre-electrolysed overnight using an internal cathode. The cell was then evacuated 3 times and filled with hydrogen in order to remove air, and the hydrochloric acid distributed to the cell through the connectors.

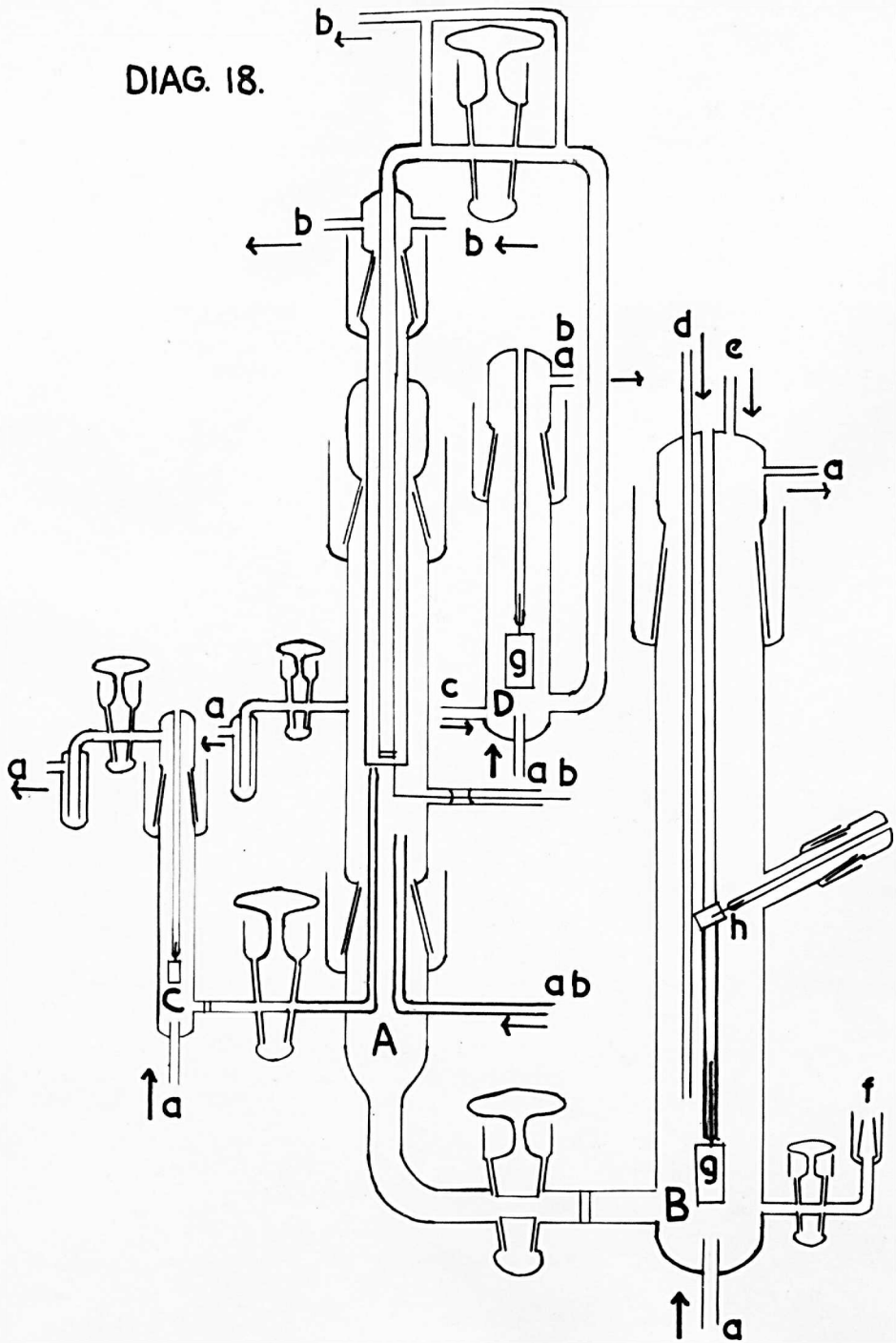
Two types of calomel electrode, diags. 16 and 17, were used. That shown in diag. 17 was found to be more satisfactory since it could be filled without contact with the atmosphere, and the solution had no tendency to run back into the cell.

In these experiments (Results: Section 1) the ingoing interface of the electrode was polarised over a range of current densities, the solution being stirred with hydrogen, and any potential changes on the outgoing interface were measured with reference to the reversible hydrogen potential. The solution at this interface was also stirred with hydrogen.

Cell 3.

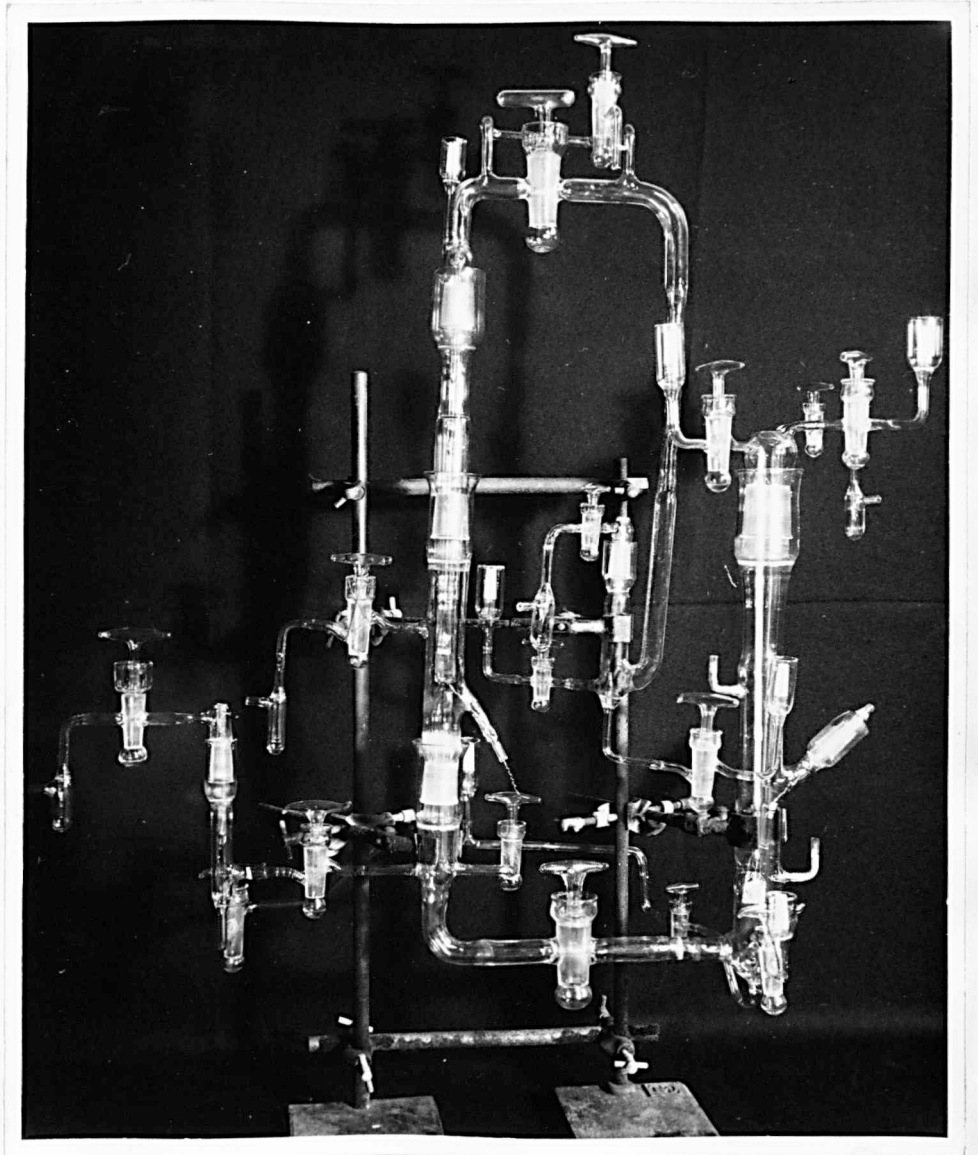
For the experiments on the transfer of anodic polarisation a horizontal membrane electrode was used. Two systems were used on the outgoing interface of the membranes. In the first, the potential was taken with reference to a glass electrode in

DIAG. 18.

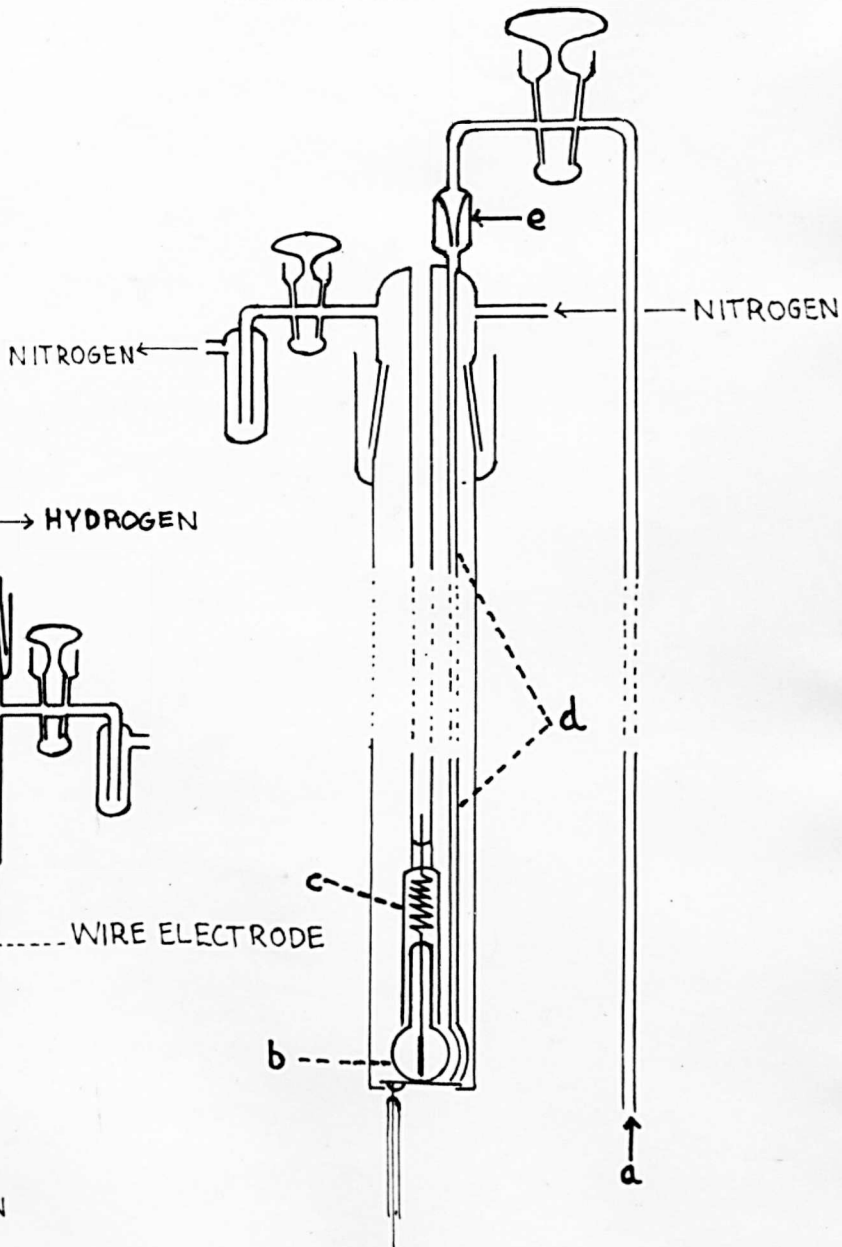


- a hydrogen
- b nitrogen
- c hydrochloric acid
- d hydrogen chloride
- e water
- f external anode
- g non-polarisable cathode
- h pre-electrolysis electrode

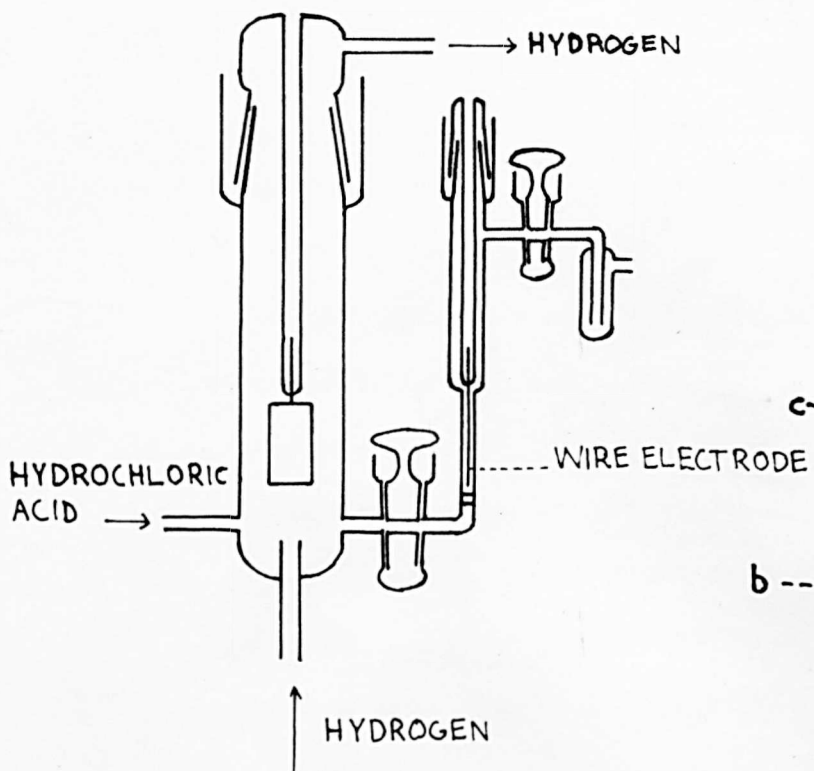
Diag. 19.



DIAG. 20.



DIAG. 21.



contact with a drop of solution on the interface and, in the second, with reference to a hydrogen electrode connected through a capillary to the outgoing interface. A thin film of solution was placed between the membrane and a fine sintered disc sealed into the end of this capillary.

The main apparatus (cell 3) used with both these methods was the same. (Diag. 18 and 19). As before it consisted of a cathode chamber A, one face of the membrane being the cathode and an anode chamber B separated by a tap and sintered disc. A reference electrode compartment C was connected to the polarised interface by a Luggin capillary as before via a closed tap and sintered disc. The apparatus was made of Pyrex glass. All the electrode compartments could be stirred with hydrogen.

The glass electrode set up is shown in Diag. 20. The tube a was directly connected to the solution preparation vessel Diag. 14. The electrode bulk b was pushed into contact with the membrane by a platinum spiral along a guide tube c. Hydrochloric acid was pushed up from the solution preparation vessel and a drop formed by means of the dropper e. The drop then ran down the capillary d and part was delivered to the glass electrode and formed a thin layer of solution between this and the membrane.

The set up with the capillary is shown in Diag. 18.

Hydrochloric acid was pushed into contact with the membrane through the reference electrode compartment D and the capillary. By adjusting the pressure over the outgoing interface a thin film of solution could be left in contact with the membrane. A tap was placed in the capillary bridge so that the membrane could be isolated from the solution in compartment D.

The hydrochloric acid solution for the section of the apparatus on the polarised side of the membrane was prepared in the anode compartment E in the manner described above. The solution was then pre-electrolysed using an internal cathode and an external anode. As before the anode compartment was evacuated and filled with hydrogen three times before the solution preparation. The solution for the outgoing interface, was prepared in the solution preparation vessel Diag. 14, in a nitrogen atmosphere since hydrogen would have acted as a depolariser. The solution was left overnight in contact with a sheet of platinum of area 10 sq. cm. while being stirred with a stream of nitrogen. The solution was then placed in contact with the electrode, either directly with the glass electrode via e (Diag. 20) or via the electrode compartment D and the capillary bridge (Diag. 18). The space A and the parts of the apparatus on the non-polarised side of the membrane were

evacuated and filled with nitrogen four times. Section A was not filled with hydrogen since the difference in pressure across the membrane might have broken it or at least introduced uncertainty as to the tightness of the seal.

The ingoing interface of the electrode was alternately polarised cathodically and anodically at a current density of 10 milliamp. per sq. cm., the solution at the interface being stirred with hydrogen. The change of the potential of the outgoing interface with time was measured with a pH meter with either the glass or the hydrogen electrode as reference. The experiments were carried out at room temperature which was recorded.

Anodic and cathodic currents in the range 1 microamp. to 10 milliamp. were obtained with electrical circuit 1, in the range 0.001 to 1 microamp. with electrical circuit 2. (see below).

The results of these experiments are given in Results; Sections 2 and 3.

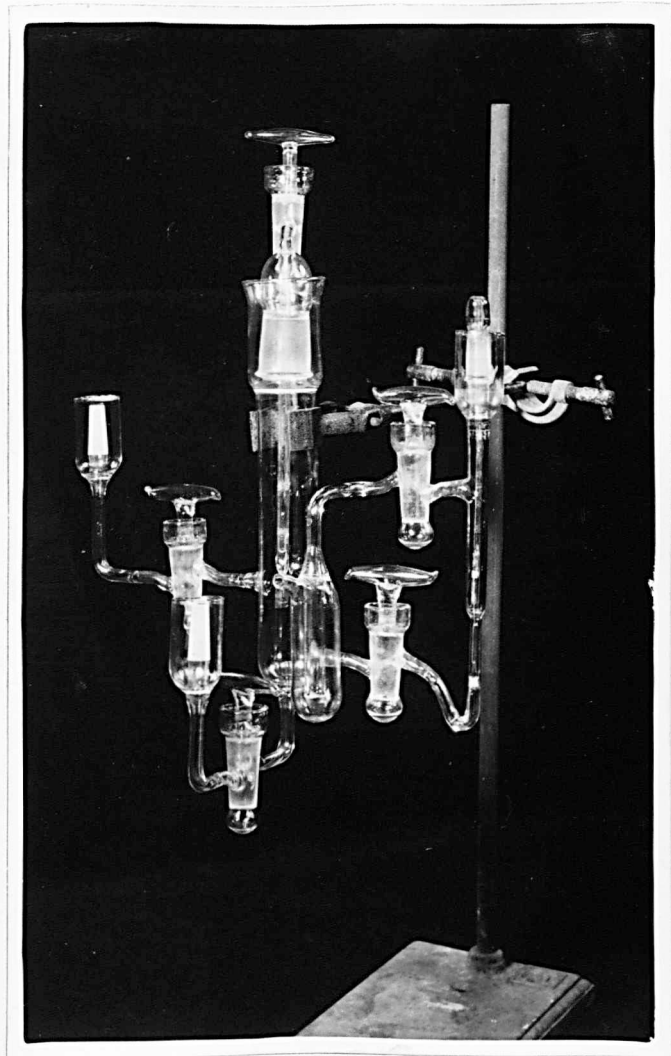
It became apparent during the above experiments that depolarisation by diffusion of hydrogen through the solution into the gas space covering the outgoing interface was a more important factor than depolarisation by diffusion into the solution. An attempt was made to derive the rate of diffusion through the membrane by comparing the potential

changes observed with and without small subsidiary currents applied between the reference electrode in D and the membrane. It was considered that a more satisfactory manner of investigating the system would be to maintain the outgoing interface at constant potential and to measure the change in the current necessary to maintain this potential as a function of the conditions on the ingoing interface. Under these conditions, depolarisation by the solution could be maintained at a constant, measureable, level. For these experiments it was necessary to reduce the resistance of the connection from the reference electrode compartment D to the outgoing interface of the membrane from the order of 10,000 ohms in the system described above to an order of 100 ohms to avoid a large potential drop through the connecting solution. A wide bridge was made containing a coarse sintered disc sealed into the end of the connection. With the electrode interface covered by about 1 cm. of solution, the resistance of the bridge was about 300 ohms. As the maximum current through the bridge was of the order of 1.5 microamp. the error in the potential drop at the outgoing interface during any observation did not exceed 0.5 millivolt, which represents a negligible change in the hydrogen concentration of the interface.

The experimental technique was similar to that described above. The apparatus was placed in an air thermostat. The outgoing interface was maintained at a potential of +1270mv. at 20°C, +1280mv. at 30°C. and +1290 mv. at 40°C., a non-polarisable hydrogen electrode being used as cathode. The ingoing interface was alternately discharged to the above potentials, a non-polarisable hydrogen electrode being used in compartment B, and then maintained at potentials of +1100, +900, +700, +500, +300, and +100 mv. versus the non-polarisable electrode. The change of current with time with the outgoing interface at constant potential was measured. Measurements were also made with the ingoing interface at the reversible potential (obtained by bubbling hydrogen over the interface or using small cathodic currents), and at an overpotential of 100 mv. (by using a cathodic current density of 20 milliamp. per sq. cm.).

Charging curves were also obtained, the potential of the outgoing interface being measured as a function of time and the ingoing interface being maintained at +100 mv. (at which there appeared to be the maximum hydrogen concentration within the interface). From the current-time variation curves on the

Diag. 22.



outgoing interface described above it was possible to evaluate the diffusion coefficient as shown in the introduction, and the concentration of hydrogen within the ingoing interface assuming that Fick's laws of diffusion were obeyed.

Electrical circuits 3 and 4 (described below) were used as the source of constant potential on the outgoing and ingoing interface respectively.

The results are given in Results: Section 4.

Cell 4.

The apparatus used for the experiments on the diffusion into wires is shown in Diag. 21. It consisted of a non-polarisable hydrogen electrode in the compartment A and a platinum wire in the capillary B, this wire being the experimental specimen. The wire was separated from A by a sintered disc and closed tap. It was arranged to lie in the middle of the capillary, the radius of which was chosen so that the minimum volume of solution was required. The length of wire used was 3 cm., radius 0.0175 cm. The wire was sealed into soda-glass, the rest of the apparatus being made of Pyrex glass.

In these experiments the amount of hydrogen dissolving

in the wire was measured as a function of potential and from the current-time curves the diffusion coefficient and equilibrium concentration were evaluated as a function of the potential.

The technique used was similar to that described above. The hydrochloric acid was prepared in a nitrogen atmosphere in the solution preparation vessel (Diag. 14) the apparatus filled with nitrogen, and the cell filled with acid so as to fill the capillary etc.

The wire was first discharged to the potentials indicated above and then successively charged to the potentials +1100, +900, +700, +500, +300, and +100 mv. without intermediate discharge. The change of current with time was measured, the end current remaining after there was no further change in current being taken as zero. The difference between this current and the actual readings was assumed to be the rate of dissolution at any one time. Certain discharge curves were also taken in which the order of applying the potentials was reversed. The potential applying circuit 3 (described below) was used as the source of constant potential.

The results are given in Results: section 5.

Electrical Circuits.

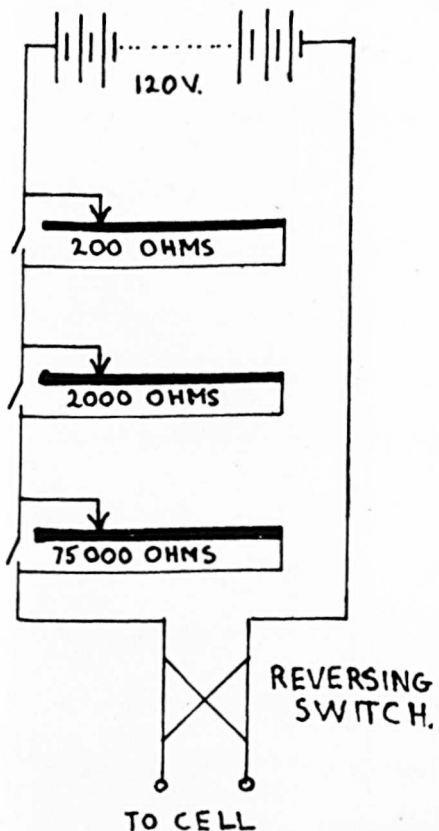
All parts of the experimental cell and the electrical circuits were insulated from earth by either Perspex sheets or blocks of paraffin wax.

Electrical connections were made by means of screened, Polythene-insulated, single strand, copper wire, "Co-ax". In the experiments described in Results: Sections 1, 2, and 3, the switches were mounted on a Perspex panel. Ceramic-insulated, silvered switches were used to separate different parts of the electrical circuits. These were found to tarnish in the atmosphere until they developed an appreciable resistance when closed. Therefore switches and dial resistances were mounted in a closed Perspex box. Wood and Paxolin, the more usual switchboard insulators, were found to leave appreciable leakage currents. Ordinary toggle switches were used where a very high insulation resistance was not required.

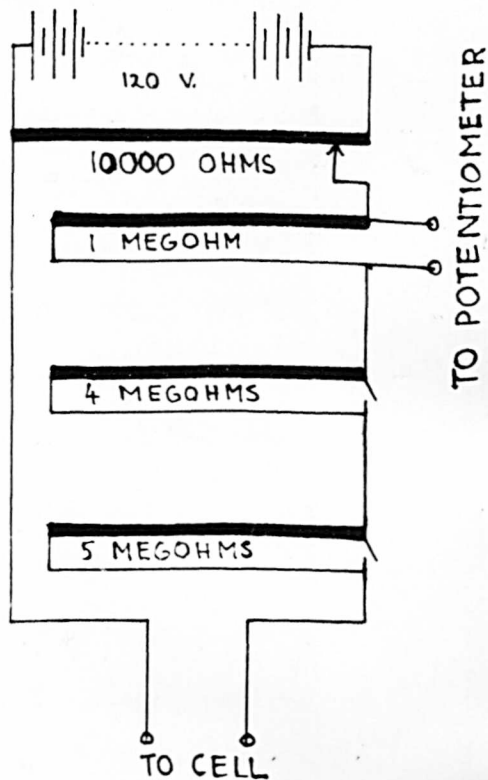
Circuit 1.

Cathodic and anodic polarising currents in the range 1 microamp. to 10milliamp. used throughout these experiments were obtained by using three progressively increasing resistances which could be by-passed at will. A reversing switch was included to enable instantaneous changing from cathodic to

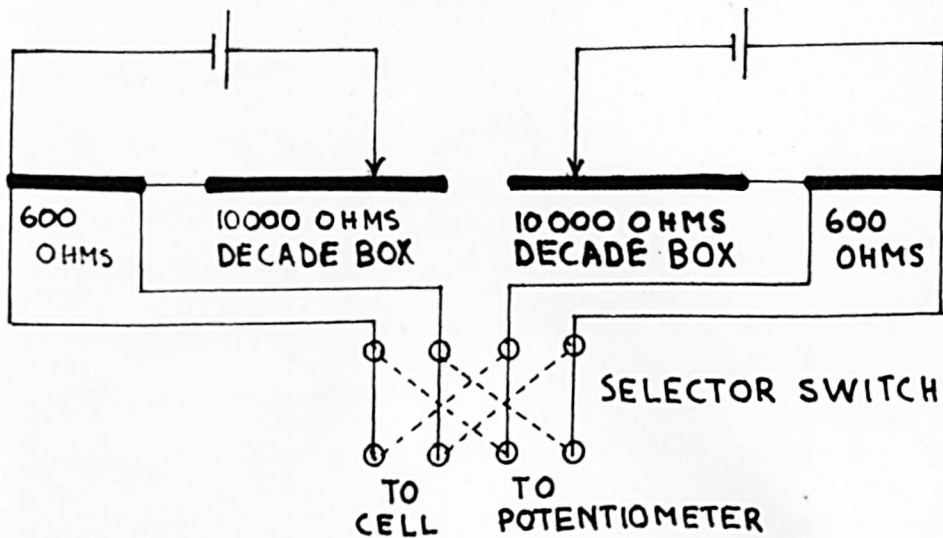
DIAG. 23. CIRCUIT 1.



DIAG. 24. CIRCUIT 2.



DIAG. 25. CIRCUIT 3.



anodic conditions. To minimise any alteration in the current due to the potential drop in the cell, high tension batteries, 120 Volts. were used as the source of current. (Diag. 23)

Circuit 2.

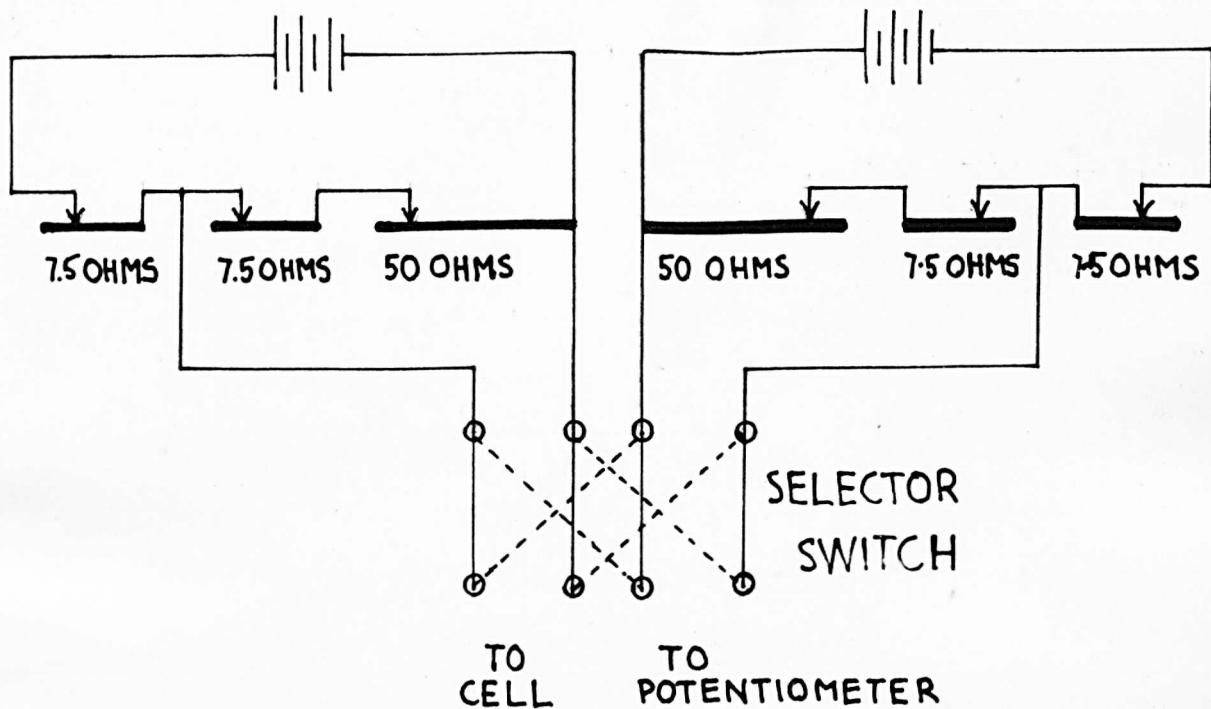
To obtain the stable small currents in the range 0.001 to 1 microamp. in the experiments described in Results: Section 3, a high tension battery was used in combination with a potential divider and a stable, fixed resistance (10 to 100 megohms).

Diag. 24. The fixed high resistances were maintained in sealed glass tubes containing silica gel.

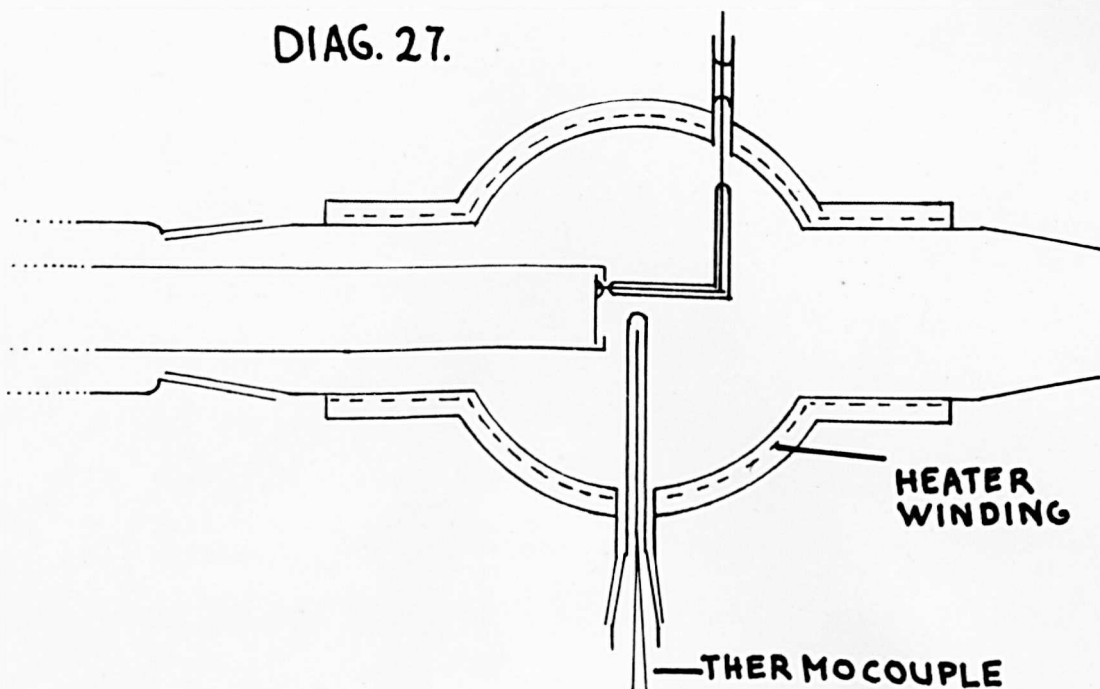
Circuit 3.

The fixed small voltages (up to 1290 mv.) applied to the outgoing interface of the membrane and the wire electrodes, as described in the experiments in Results: Sections 4 and 5, were obtained from a potential dividing circuit with a non-inductive 600 ohm. resistance in combination with a non-inductive decade resistance box as shown in Diag. 25. Two such circuits were used and were connected to a multi-selector switch so that either circuit could be adjusted or applied instantaneously to the cell independently of the other. Two-volt accumulators were used as the source of e.m.f.

DIAG. 26. CIRCUIT 4.



DIAG. 27.



Circuit 4.

Two similar circuits were used for applying the controlled potentials to the ingoing interface of the membranes as described in Results: Section 4. The potential dividing circuit consisted of three resistances as shown in Diag. 26; six-volt accumulators were used as the source of e.m.f. The total resistance of these circuits was 65 ohms. It was necessary to maintain a higher current in the potential dividing circuits for the polarisation side, as much larger currents flowed through the cell on this side of the membrane owing to the presence of hydrogen in the solution.

Current Measurement.

The current in polarising circuit 1 was measured with a Cambridge multi-range microammeter. The current in the stable high resistance circuit 2 was determined by measuring the potential drop along a standard 10 megohm resistance with a valve potentiometer. The current in the potential applying circuit 3 was measured by either a medium sensitivity or a high sensitivity galvanometer selectable at will. The first was a standard Tinsley instrument, sensitivity 108mm. microamp., period 2 seconds, resistance 730 ohms. To measure a range of currents a common shunt was provided for this and the high sensitivity instrument. To avoid over-critical damping in the

Tinsley instrument, which had to measure currents that were varying fairly rapidly, a standard variable resistance was included in series with it. The second galvanometer, which was used for measuring small currents in the experiments with wires described in Results: Section 5, was a standard Gambrell instrument. This instrument had a non-linear calibration and values of the currents had to be obtained by comparison with known currents. The sensitivity was of the order of 10,000 mm./microamp. at one metre, the resistance 2108 ohms. The period washigh but still sufficiently low compared with the rate of current variation to enable satisfactory current-time variation curves to be built up as described in Results: Section 5. By means of these two instruments the current could be measured over a range of 10,000.

Potentiometers.

For the experiments described in Results: Section 1, a Mullard "Magic Eye" potentiometer and a Tinsley microvolt potentiometer were used. It was found that for certain systems these instruments drew too large a current and a Cambridge pH meter was used instead. In this way depolarisation by electrical currents was avoided. For the experiments described in Results: Section 2, a G.E.C. type pH meter was substituted and used for the remaining experiments.

Thermostats.

The heaters and saturators used in the gas purification trains to adjust the temperature and water content of the gases above the solutions in the experimental cell were contained in the usual type of water thermostat. The water was stirred with a double paddle and the temperature was maintained constant with a fixed background and a variable control heater. The control heater was actuated by a toluene regulator in combination with a hot wire vacuum switch.

The cells used in the experiments described in Results: Sections 4 and 5 were contained in an air thermostat. This was constructed with double walls of asbestos with a $\frac{3}{4}$ inch gap between the walls. The connecting tubes for the gas streams, water, etc. were led through small holes in the top of the tank. Taps, etc. on the experimental cell were manipulated through small doors in the front of the tank. The front section could be completely removed for assembly of the apparatus. The air space in the thermostat was directly heated. An adjustable background heater was used in combination with a variable control heater controlled by a sensitive toluene regulator with hot wire vacuum switch. The toluene regulator was shielded from direct heating by means of baffles. For work at 20°C. and also sometimes at 30°C. a background cooler was used. This consisted of a widely wound coil of lead tubing through which water could

be circulated. The air space was stirred directly by means of a high speed fan.

With this thermostat the air temperature could be maintained constant to within ± 0.2 at 20, ± 0.3 at 30, and ± 0.5 at 40°C . over the whole of the thermostat and somewhat better throughout the working space. The temperature in the region of the electrodes, which was frequently recorded during the experiments, remained constant to within $\pm 0.1^{\circ}\text{C}$.

EXPERIMENTAL RESULTS.

1. Experiments on the transfer of cathodic potential.

As stated above the first aim of the preliminary experiments was the investigation of the presence or absence of a transfer of cathodic potential.

In the initial stages of this work an attempt was made to find an inert sealing material that would not poison the electrode but would enable the electrode to be sealed in without leakage. In conjunction with apparatus 1 a variety of materials were tried. Greases (e.g., Apiezon, silicone grease), apart from poisoning the electrode, were found to be unsatisfactory as they lacked the necessary rigidity. Various cements, e.g., silicone cements, silicone rubber and commercial sealing compounds were found to poison the electrodes heavily.

In conjunction with apparatus 2 a variety of waxes, e.g., picein, and solutions of polymers, e.g., polymethylmethacrylate, polystyrene were employed. With all the above materials except polystyrene it was found that when a satisfactory seal had been achieved, there was no transfer of negative potential when the ingoing interface was polarised cathodically, even though the ingoing interface was heavily poisoned. It was frequently found that with these poisoned

systems the potential of the outgoing interface with the ingoing surface unpolarised fell below the reversible hydrogen potential. On cathodic polarisation of the ingoing interface, the potential of the outgoing interface eventually reached the reversible hydrogen potential, indicating that, if there were any diffusion, this was too small to produce a cathodic shift on the outgoing interface, i.e., the permeation rate was less than that corresponding to a cathodic current of 10^{-3} amp./cm².

When electrodes sealed in with polystyrene were used, similar results were obtained. This sealing material, which was found to have a very strong adhesion to both glass and platinum was used to construct electrodes of small surface area, flanges being used, as illustrated in Diag. 4. With this system it was possible to attain higher current densities in the apparatus used. At the same time the volume of solution on the outgoing interface was reduced so as to produce conditions as favourable as possible for the observation of diffusion of negative potential. It was found with this set up that extremely erratic values of the potential of the outgoing interface were recorded, the potential following very largely the reading set on the potentiometer. Intermittent contact with the potentiometer gave more negative values than permanent contact,

but the potential of the outgoing interface remained on the positive side of the reversible hydrogen potential. It was evident that the potentiometer together with the deactivating influence of the polystyrene was depolarising the electrode, and that the rate of diffusion was smaller than 10^{-6} amp., the current taken by the potentiometer when on balance.

In order to avoid this electrical depolarisation a pH meter employing a current of 10^{-14} amp. when on balance was substituted for the potentiometer. When this system was used, it was found that very negative potentials (up to $-1.25v$) were attained on the outgoing interface. This negative potential was independent of the current density but was different for different electrodes and depended on the time for which the electrode had been used.

It was evident that the experiments would have to be carried out with every precaution being taken to avoid depolarisation and poisoning in order to decide as to the presence or absence of a diffusion of negative potential.

When the Housekeeper type seal of the platinum into Pyrex described above was used, observations were confined to one current density for each electrode. The outgoing interface was stirred with hydrogen and adopted the reversible hydrogen

potential. The potential could be measured to within 0.1mv. with respect to a calomel electrode. The small potential shifts that were observed at high current densities (10^{-2} amp/cm.²) were of the order of the ohmic resistance drop in the connection to the membrane, this resistance drop being included in the measured potential. In some of the experiments a larger build up of potential was observed after a long period of time; in some experiments a decay of potential on the outgoing interface after interrupting the cathodic current flowing into the ingoing interface could be followed with a Tinsley microvolt potentiometer over a range of about 3 mv. In these latter experiments the hydrogen overpotential on the ingoing interface was high and so the electrodes were presumably poisoned. It appears possible that on poisoned electrodes there may be a small potential shift but it seems difficult to attribute any significance to such small changes. Further, as stated above, the efficiency of this type of seal was doubted since larger increases of potential were only observed with electrode systems that were afterwards shown to have broken down resulting in leakage.

Further experiments were therefore made with electrodes sealed into glass in a variety of ways. The system finally decided upon was that shown in Diags. 8 and 9. Further

precautions were taken to avoid poisoning of the membranes by mercury from the calomel electrodes. It had been observed that after long experiments mercury could be detected in the region of the electrode by electrolysing the solution on to a copper wire and "spot testing" the dissolved deposit with cuprous iodide. This diffusion of mercury (presumably as dissolved mercurous chloride) had the effect of making the potential of the outgoing interface unsteady on decay of the current on the ingoing interface, the potential falling below the reversible value. On further cathodic polarisation of the ingoing interface the potential of the outgoing interface regained the reversible value. To avoid this deactivation the design of calomel electrode shown in Diag. 17 was used and closed taps were interposed between the reference electrode compartments and the membrane electrode. The calomel electrodes were cleaned separately between each experiment. When these precautions were taken no deactivating influence after long polarisations could be detected.

With this type of system it was found that there was no diffusion of negative potential up to current densities of 10^{-1} amp./cm.². The small potential shifts observed were proportional to the current and were in fact equal to the product of the current and the independently measured resistance of the

lead-in connection.

Various experiments were carried out in order to ascertain whether any increase in the rate of diffusion obtained by poisoning the ingoing interface would produce any negative potential on the outgoing interface (which was under the same stringent conditions as before, i.e., free from poisoning). Acridine and arsenic were the poisons employed. No negative potential was observed on the back of the electrode and so presumably the increase in the rate of diffusion was insufficient to be detected in this manner. No direct measurements were made in the later experiments Results: Sections 3 and 4 of the experimental work to confirm the effect of poisons on the rate of diffusion, but ample evidence was obtained that poisoning, which occurred inadvertently during the course of the experiments, did in fact increase the rate of diffusion.

The electrodes as used above would, according to other workers, have a strongly adsorbed layer of oxygen on the surface. Further, as found by Oatley (63) and Eggleton (64) for iron, such layers can exert a marked blocking influence for the passage of hydrogen from the bulk of the metal to the surface. Similar blocking effects were in fact found in the later sections of the experimental work. (Results: Section 4.). It has further been

observed by various workers that heating in hydrogen, or alternate oxidation and reduction, or anodic and cathodic polarisation activates membranes for diffusion. The effects of these various pre-treatments were therefore investigated.

The ingoing and outgoing interfaces were polarised cathodically and anodically at current densities up to 10^{-3} amp/cm.² This treatment, although later found (Results: Sections 2 to 4) to increase the rate of diffusion and to produce more reproducible values of the permeation rates, did not increase the rate of diffusion sufficiently to produce negative potentials on the outgoing interface.

The electrodes were pre-heated in oxygen and then hydrogen in a special cylindrical furnace (Diag.27) for 12 hours at 490°C; no measureable effect was observed.

It was again found that if the potential of the outgoing interface fell below the reversible hydrogen potential during the experiments then cathodic polarisation of the ingoing interface restored the potential to the reversible value. If hydrogen stirring was stopped on the outgoing interface, and the ingoing interface was polarised anodically, then the potential of the outgoing interface could be made to fall to +700 mv. over a period of 48 hours. Further, by passing oxygen through the solution on the outgoing interface the potential could be

altered at will to about +150mv. Cathodic polarisation of the ingoing interface caused the potential to return gradually to the reversible value.

It was thought that more pronounced potential changes might be observed in solutions of different pH. The hydrochloric acid on the outgoing interface was accordingly replaced by normal potassium chloride. It appeared that in these solutions the platinum attained the reversible hydrogen potential with difficulty. The potential of the outgoing interface with hydrogen stirring and the ingoing interface at the reversible potential was about +600mv. Cathodic polarisation of the ingoing interface reduced this positive potential and the extent of reduction appeared to be dependent on the current density. Up to current densities of 6×10^{-1} amp./cm² the outgoing interface did not, however, attain the reversible potential.

It was concluded that there was no diffusion of negative potential, and that if any part of the negative potential observed at platinum cathodes is to be attributed to the electromotive activity of hydrogen, then the rate of diffusion in a system with stringent purification is too small to shift the potential into cathodic regions. Furthermore, various

activating and poisoning treatments of the ingoing interface did not increase the rate of diffusion sufficiently to produce a negative potential on the outgoing interface.

It was apparent, however, that hydrogen was diffusing and that further information on the diffusion might be gained by investigating the transfer of potential on the anodic side of the reversible potential. The results of experiments on this permeability are given in the next two sections. From the observations on the systems there described it was possible to develop a quantitative study of the diffusion kinetics of hydrogen through platinum at ingoing interface potentials in the range +1280 to -100 mv. The results of these experiments are given in Results: Sections 4 and 5.

2. Experiments on the transfer of potential on the anodic side of the reversible potential.

Experiments with the glass electrode as reference.

In order to investigate the transfer of potential on the anodic side of the reversible hydrogen potential, it was decided to set up membrane experiments and to polarise the ingoing interface of the membranes with anodic and cathodic currents and measure the potential changes on the outgoing interface.

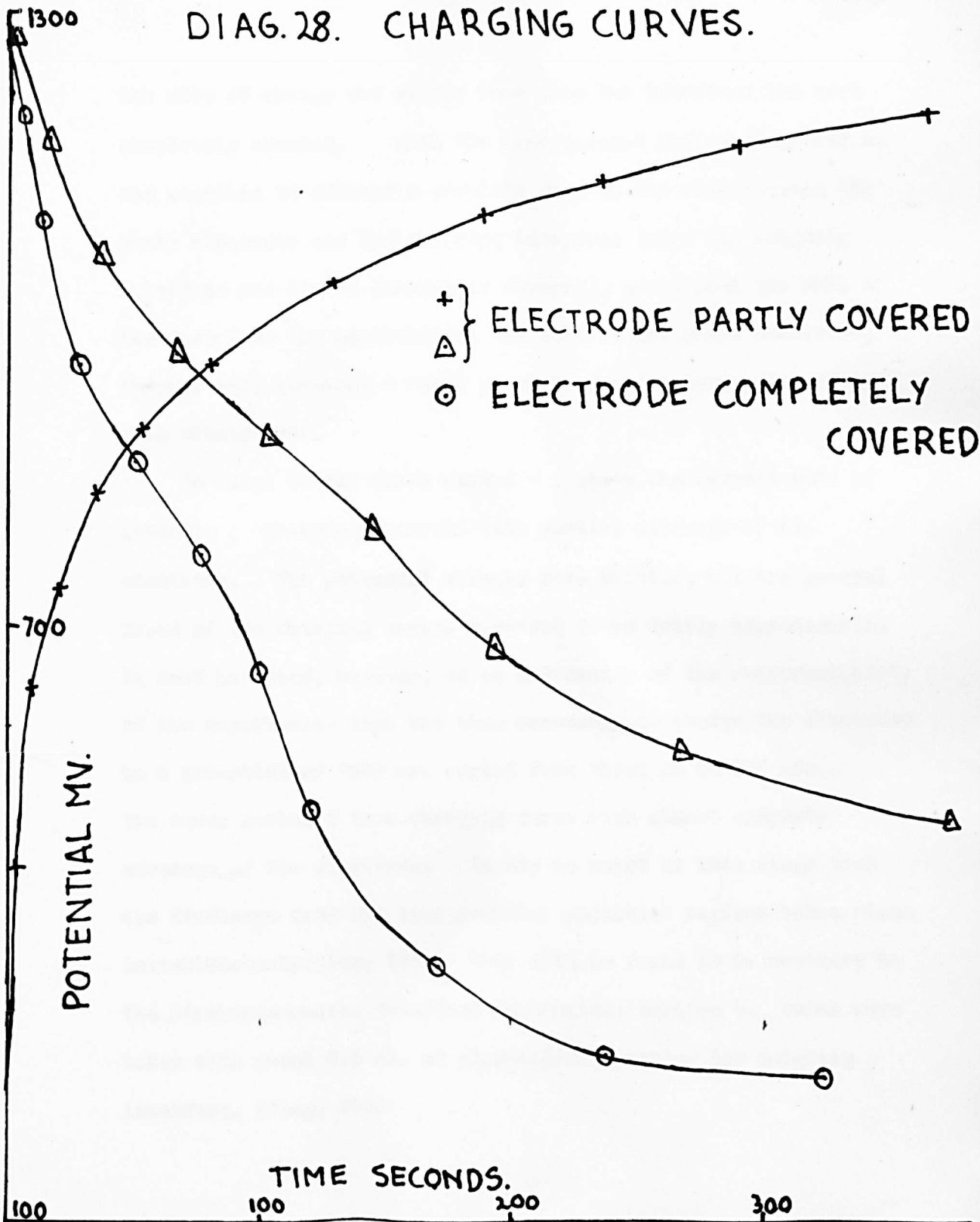
In order to minimise the effect of depolarisers, it was considered

necessary to keep the amount of solution covering the outgoing interface as small as possible, so that as far as possible only the charging of the interface would be observed. The set up and experimental details have been described above.

It was found that with the ingoing interface cathodically polarised the potential of the outgoing interface would reach about +150mv. but never attain the reversible hydrogen potential. In the light of subsequent experiments, this may be attributed to the fact that there is a maximum in the concentration-potential curve at about +100mv. At the time it was considered that at such potentials the outgoing interface attained a state of equilibrium, the amount of hydrogen diffusing through the electrode (which would decrease with decreasing positive potential of the outgoing interface) being balanced by the hydrogen lost by diffusion through the solution.

On anodic polarisation of the ingoing interface it was found that the outgoing interface would reach a potential of +1290mv. It was found, however, that both for cathodic and anodic charging the rate of change of potential varied very much from experiment to experiment and also on repetition during each experiment. Furthermore, it appeared to be dependent on the amount of solution covering the outgoing interface. Contrary to expectations it was found that with a small amount of electrolyte

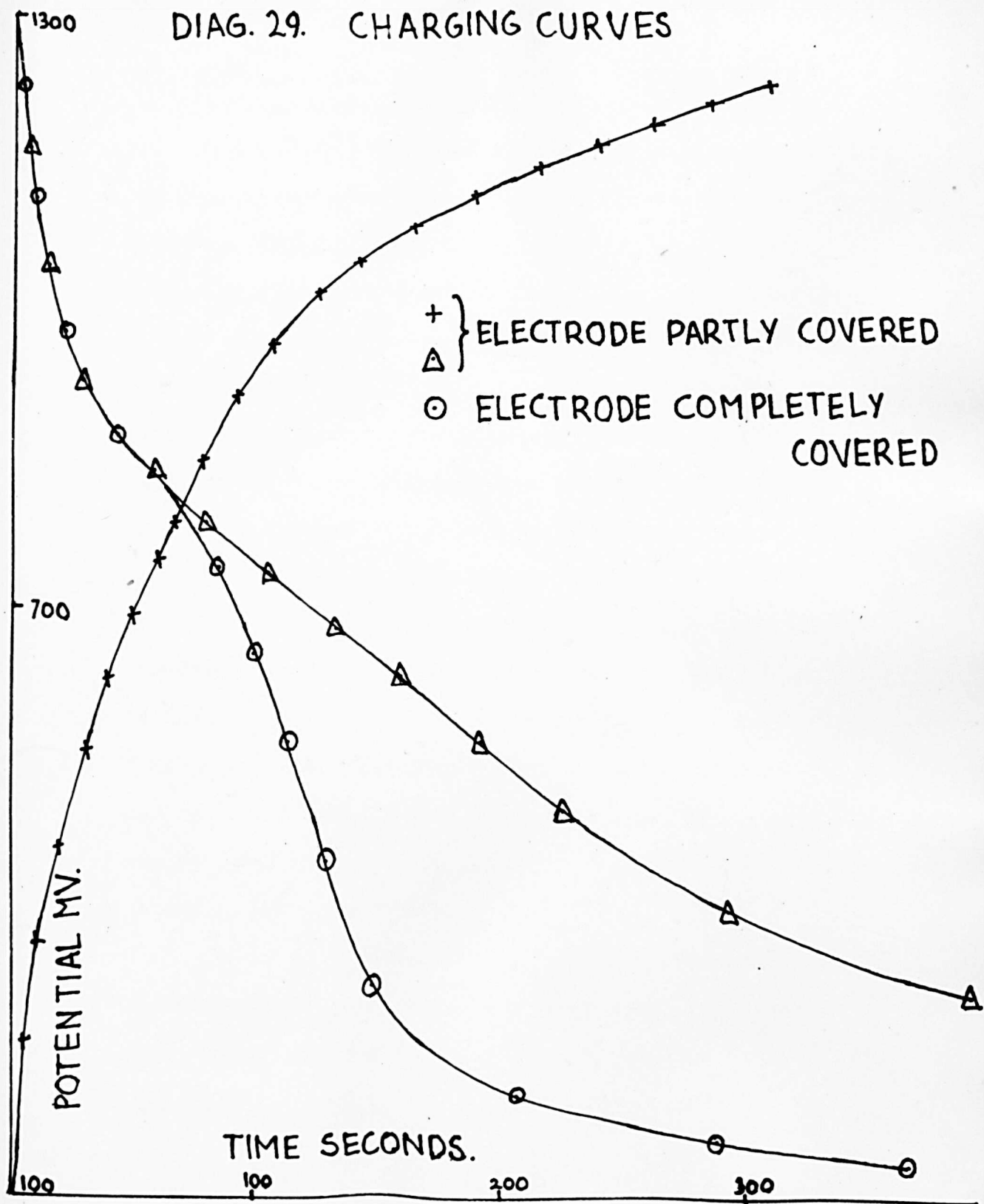
DIAG. 28. CHARGING CURVES.



the rate of charge was slower than when the interface was more completely covered. With the experimental set up described it was possible to deliver a complete drop to the area between the glass electrode and the outgoing interface (when the outgoing interface was almost completely covered), or to push the bulk of the drop into the capillary at the side of the glass electrode, thereby only covering a small portion of the outgoing interface with electrolyte.

In Diag. 28 the curve marked + , shows the largest rate of cathodic charging observed with partial coverage of the electrode. The potential changes were erratic, but the general trend of the charging curves appeared to be fairly reproducible. It must be noted, however, as an indication of the reproducibility of the experiments that the time necessary to charge the electrode to a potential of +200 mv. varied from about 10 to 100 min.. The curve marked 0 is a charging curve with almost complete coverage of the electrode. It may be noted at this stage that the discharge from the less positive potential regions takes place instantaneously (Diag. 28). This will be found to be contrary to the discharge curves described in Results: Section 3., which were taken with about 0.5 ml. of electrolyte covering the outgoing interface. (Diag. 30).

DIAG. 29. CHARGING CURVES



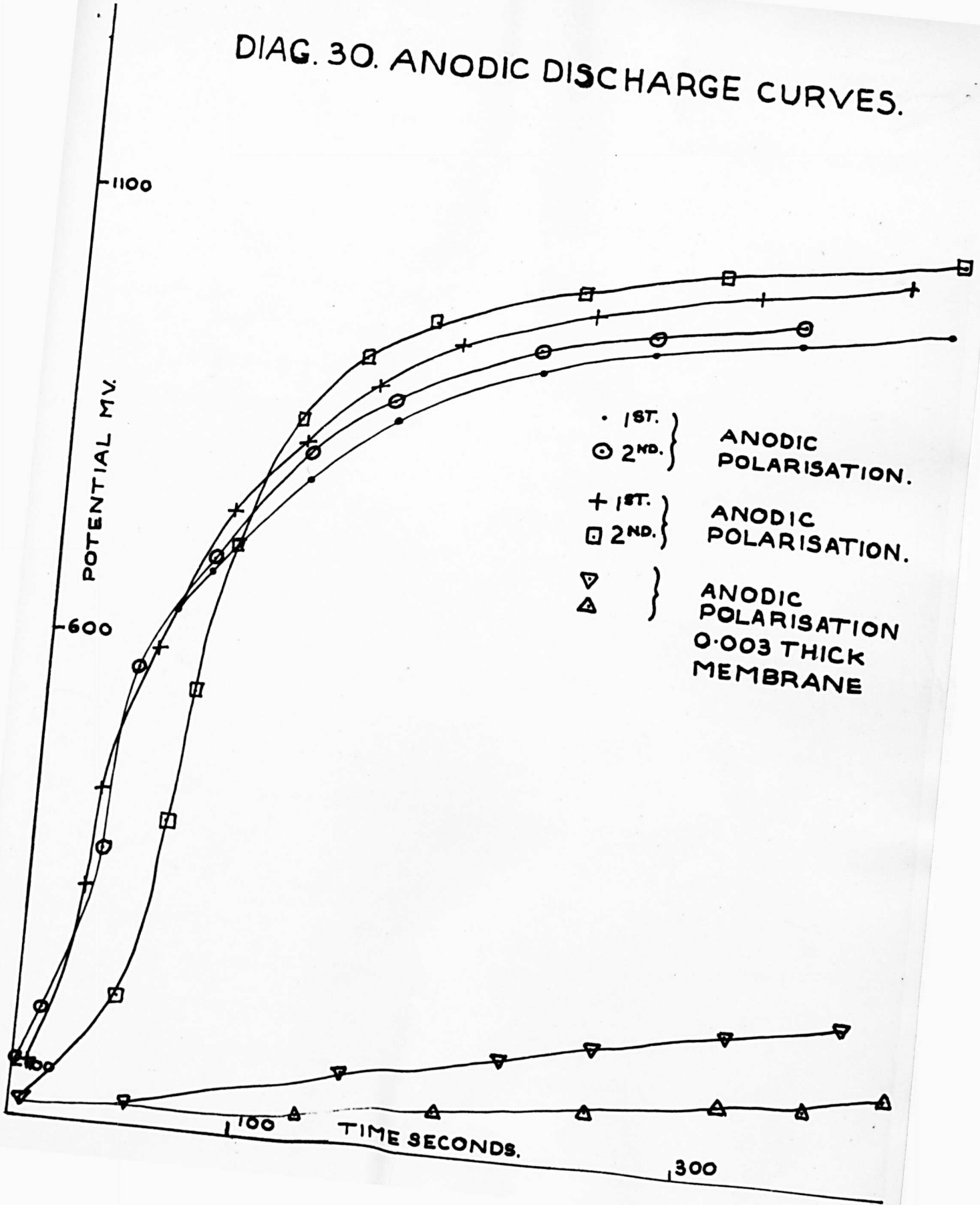
3. Experiments with sintered disc and capillary connection from the outgoing interface to a hydrogen electrode.

It was thought that the anomalous result of the variation of the rate of change of potential with coverage of the outgoing interface observed in the previous section might have been connected with the high resistance between the glass electrode and the partly covered interface. It was therefore decided to measure charging curves with a low resistance connection from the outgoing interface to a reference electrode. The experimental set up described above was suitable, giving a resistance of about 39,000 ohms, whose value moreover, could be checked at the completion of each experiment.

This experimental set up had the further advantage that the charging rate or steady potential of the outgoing interface could be examined with application of different boundary conditions to this interface by polarising through the capillary connection to the hydrogen electrode. The scope of the systems available for study was thereby extended and it was possible to make preliminary measurements of the diffusion kinetics.

It was again found, as in the experiments described in the previous section, that the rate of change of potential was dependent on the coverage of the outgoing interface. In Diag. 29 are given two charging curves, one for low coverage.

DIAG. 30. ANODIC DISCHARGE CURVES.



(marked +) and one for high coverage (marked @) of the electrode. It was possible to cover almost completely the outgoing interface with one drop of electrolyte by suitably adjusting the sintered disc over the electrode.

The charging curves obtained in this manner, i.e., with complete coverage were in fair agreement with those given in the previous section under the same conditions. In Diag. 30 discharge curves are shown which were taken with the outgoing interface covered by ca. 0.5 ml. of electrolyte. The spacing of the discharge curves gives an indication of the reproducibility during each and between different experiments.

The shape of the cathodic charging curves indicated that there was an increase in the amount of dissolution of hydrogen with decreasing potential at ca. +850 mv. The discharge curves also showed a decreasing potential change with time but as the rate of change of potential did not again increase at more positive potentials it was considered that the decreasing rate of discharge in these potential regions was largely due to the diffusion of depolariser up to the electrode surface. The difference in shape of the discharge curves in Diags. 30 and 29 at small positive potentials indicated that if the electrode was covered with appreciable volumes of electrolyte (ca. 0.5ml.) then there would be depolarisation of the electrode interface at

small positive potentials. This was substantiated by measurements of the discharge of electrodes 0.003 in. thick. The initial part of the discharge curves obtained with two different electrodes is shown in Diag. 30. According to the considerations of Nernst and Lessing the time of attainment of equal potentials should vary as the square of the thickness of the electrodes, if there is no exchange of hydrogen with the solution. It was found that the discharge of the thicker electrodes to +900 mv. took of the order of 6000 seconds as opposed to the expected 1000 seconds. It was evident that there was appreciable exchange between the electrode and the solution. It may be noted at this stage that the method of Nernst and Lessing is unsuitable for testing the obedience of Fick's laws of diffusion with this thickness range of electrodes. It was further considered that the slow change in potential observed with partially covered electrodes in the experiments described above could be attributed to depolarisation by diffusion through the solution into the gas space above the outgoing interface. On the basis of these charging curves it was considered that the cathodic charging curves gave the potential-time variation with the least interference by depolarisation. Deviations from true charging would only occur at high values of the time. Accordingly in the further interpretation of the potential-time

variation described below the cathodic charging curves were used.

The most interesting result of these experiments lay in the fact that the outgoing interface could be discharged to very positive potentials by removing hydrogen at the ingoing interface of the membrane. It was evident that whatever secondary processes were occurring at these positive potentials, e.g., oxygen deposition as has been so frequently suggested, the primary process lay in the removal of hydrogen. Further, it was clear that if hydrogen was in fact electromotively active on the positive side of the reversible potential then the concentration and diffusion coefficient could be related to the potential by setting up systems with suitable boundary conditions.

It was considered that measurements in both the steady and non-steady state could be made by either measuring the rate of change of potential of the outgoing interface, a constant current passing into this interface, the ingoing interface being at a constant potential, or by measuring the change in current necessary to maintain the outgoing interface at constant potential, the ingoing interface also being at constant potential. In the first group of measurements it was possible to apply a current to the outgoing interface smaller or larger than the largest rate of permeation. In the first case the potential would alter until it reached a value between the most positive and the most negative obtained in

the charging curves described above. In the second case a charging curve more rapid than the above charging curves could be obtained and the potential would tend to reach more positive or more negative values than could be obtained by charging through the membrane alone. In practise the subsidiary current on to the outgoing interface was interrupted when the potential of this interface reached the limiting values obtainable without the subsidiary current.

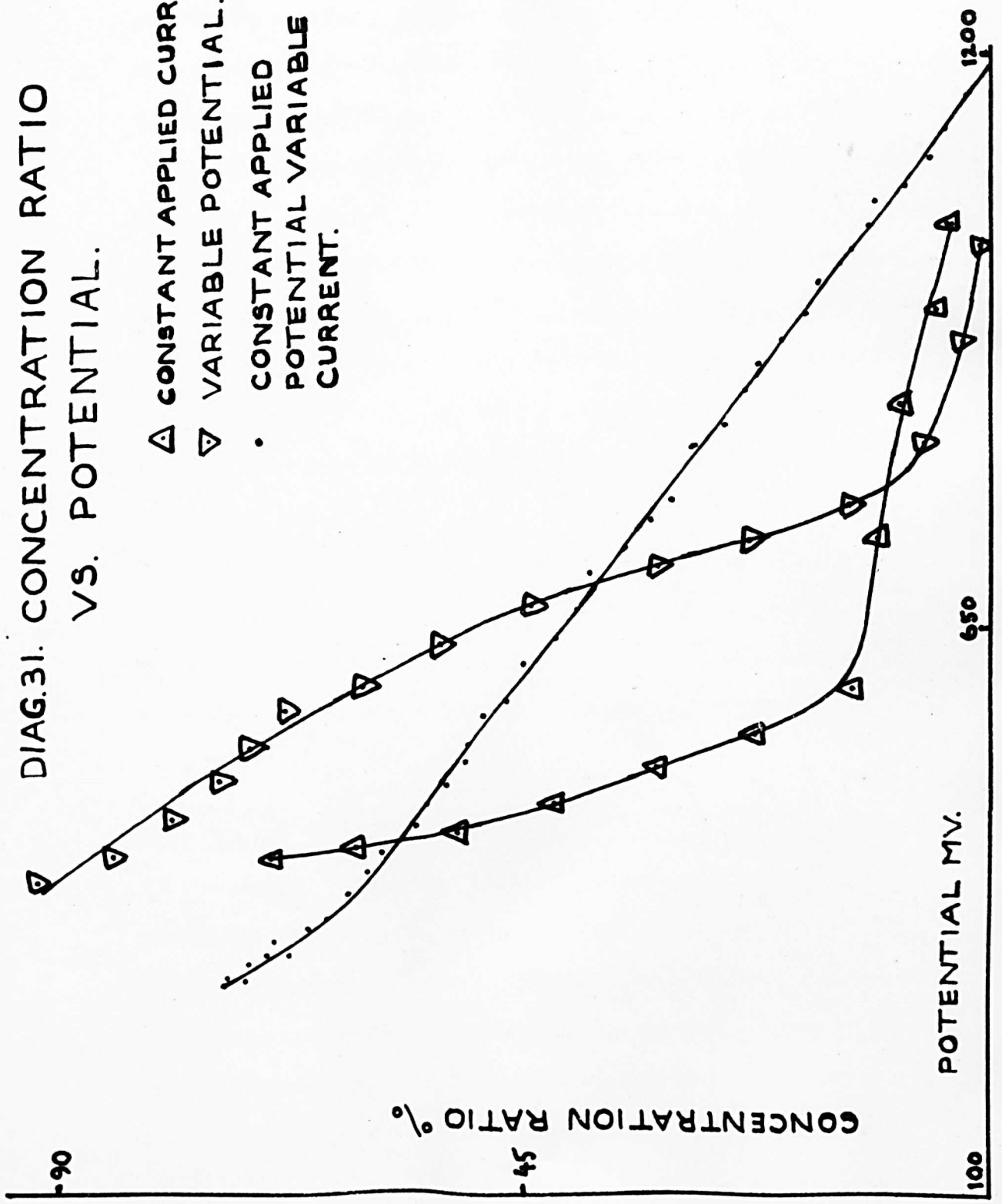
Measurements of the change of potential with currents on the outgoing interface smaller than the maximum rate of permeation.

It was considered that the potential of the outgoing interface would change until it reached the potential at which the rate of permeation in the steady state was equal to the current. By carrying out the experiments with a range of currents a potential-permeation rate curve could be built up.

In these experiments the ingoing interface was polarised anodically, and the outgoing interface cathodically using circuit 2. With a partially covered interface it was possible to follow the permeation rate to about +400 mv. with currents up to 3×10^{-8} amp. Assuming the diffusion coefficient to be independent of the concentration, the concentration ratio (selecting a given potential as 100% covered) at any other potential is given by the ratio of the permeation rates at these potentials. The results of two

DIAG.31. CONCENTRATION RATIO
VS. POTENTIAL.

- △ CONSTANT APPLIED CURRENT.
- ▽ VARIABLE POTENTIAL.
- CONSTANT APPLIED POTENTIAL VARIABLE CURRENT.

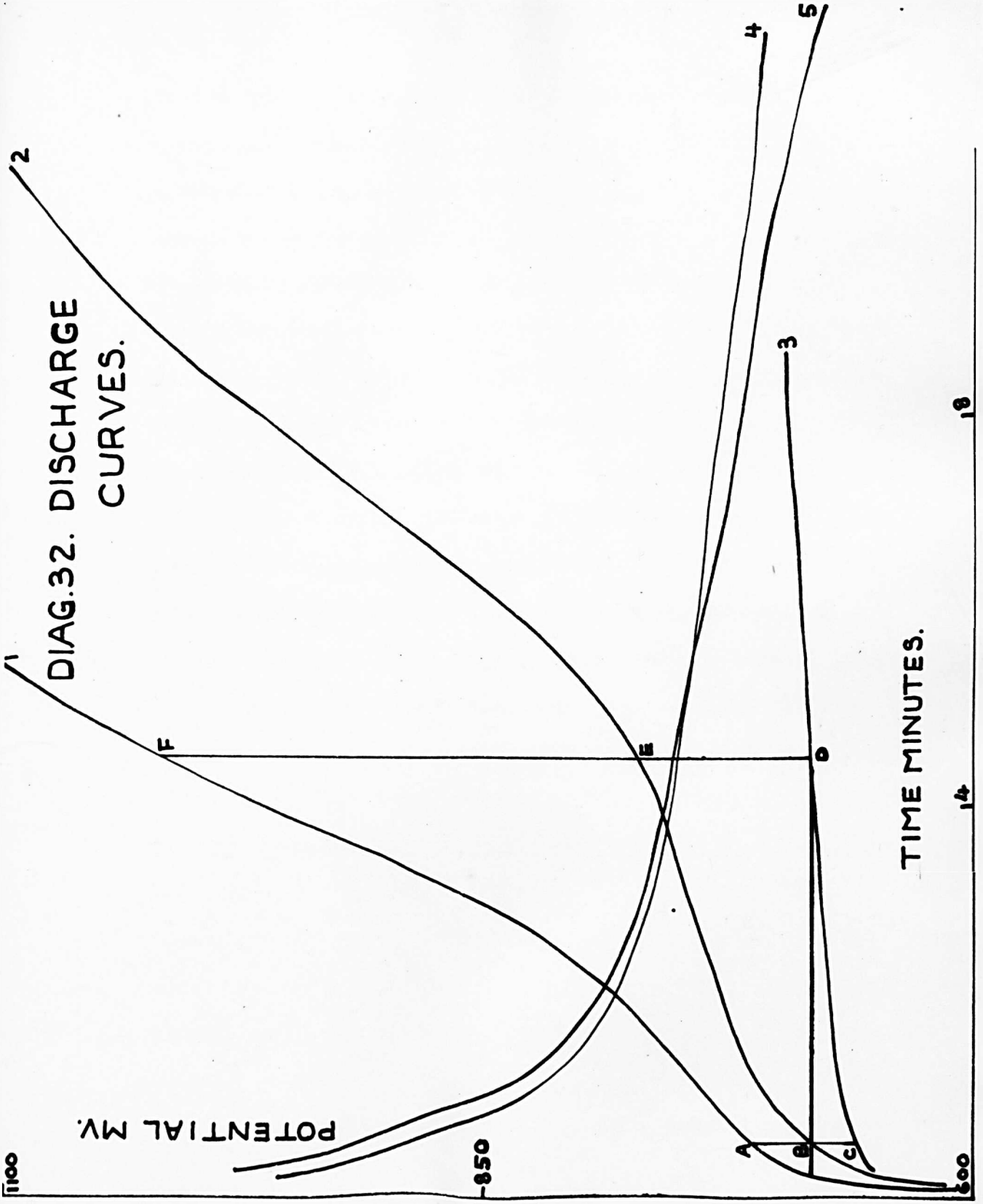


experiments are given in Diag. 31 where the concentration as a percentage of that at +380mv. is plotted against the potential. The curves are marked Δ and ∇ .

It was found that the potential varied for a very long time after the current had been altered and therefore equilibrium measurements could not be easily taken in this manner. With the above assumptions the results indicate a marked increase in the dissolution of hydrogen at about +700 mv. The corresponding charging curves in Diag. 29 do, in fact bend off in this potential region. Owing to the variation of the charging curve with coverage of the electrode it was considered doubtful that this represented a real effect. The complexity of the theoretical expressions for this type of system (equation 23) made it difficult to interpret the results in the non-steady state. For these reasons measurements on this system were abandoned.

Measurements of the change of potential with currents on the outgoing interface larger than the maximum rate of permeation.

In these experiments an anodic current was passed into the outgoing interface, the ingoing interface being polarised cathodically, so that the electrode would discharge completely. The outgoing interface was partially covered so that the current was small enough to ensure that the ohmic resistance drop in the solution connection was negligible and



therefore that the true potential of the outgoing interface was measured. In this system, only the non-steady state could be measured. Equation 23 was again applicable. Owing to the complexity of the solution it was considered that the most direct way of testing Fick's laws lay in the comparison of the potentials, and the rates of change of potential at fixed time intervals on different discharge curves obtained with a range of fixed anodic currents applied to the outgoing interface.

In Diag. 32 the curves marked 1, 2, and 3 correspond to fixed discharge rates in the ratio 5:2:1. The curves marked 4 and 5 represent cathodic charging curves after interrupting the polarisations marked 1 and 2. As has been stated above the concentrations on the outgoing interface after any time t , should be in the ratio of the fixed depolarisation currents that is, 5:2:1. A line is drawn in Diag. 32 to cut the curves 1, 2 and 3 at the points A, B and C. If now a line is drawn parallel to the time axis through the point B, to meet the curve 3, in the point D, and if the concentration of the interface is assumed to be determined only by the potential then the concentration at the point D is taken as two arbitrary units. If another line is drawn parallel to the potential axis to cut the curves, 1, 2 and 3 in the points F, E and D, the concentration at these points should be 10, 4, and 2 arbitrary units. Clearly then, if the system is

obeying the boundary conditions, the point E should lie below the point A. This is not so, and it is apparent that the discrepancy becomes larger, the larger the value of time at which the first line AC is placed.

This deviation from Fick's laws of diffusion for the above charging curves is more readily seen if the rate of change of potential de/dt after any time t , for the three curves 1, 2, and 3 is considered. As has been shown, these rates should be in the ratio of the fixed depolarisation currents. It is seen therefore, that (de/dt for curve 1): (de/dt for curve 2) for example, should be a constant and equal to 2.5. The actual values are indicated in the table below :-

Time	de/dt for curve 1	de/dt for curve 2	$\frac{de/dt \text{ for curve 1}}{de/dt \text{ for curve 2}}$
minutes	mv./sec.	mv./sec.	
1	0.714	0.555	1.29
2	0.78	0.302	2.59
3	1.57	0.272	5.75
4	1.79	0.334	5.34
5	1.36	0.52	2.61

Clearly the system was not conforming to the equation deduced. A number of reasons other than the non-obeyance of Fick's laws

could explain these deviations, e.g., the capacity of the interface for adsorption of hydrogen. A more precise investigation of the obedience of Fick's laws along these lines appeared difficult however owing to the mathematical intricacy of the solutions.

It appeared necessary to obtain more quantitative information on the diffusion coefficient so that Fick's laws could be tested by comparison of concentration-potential, and potential-time curves. In this way a test could be carried out absolutely, rather than by comparison. It was considered that data on the kinetics of diffusion could be evaluated more readily by maintaining both the in and outgoing interface at constant concentration.

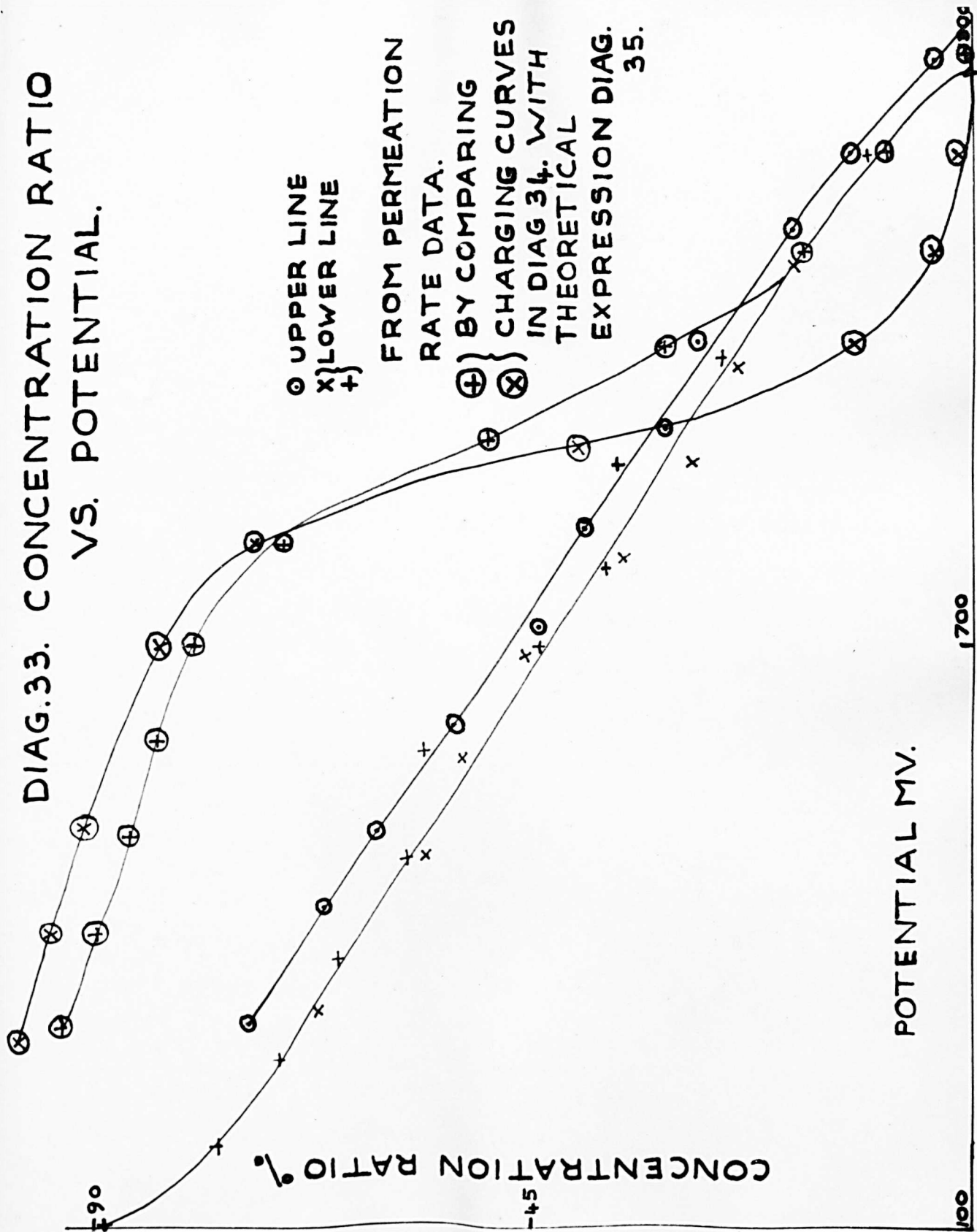
Measurements of the currents on the outgoing interface necessary to maintain this interface at constant potential.

In order to maintain the outgoing interface at constant concentration a constant potential was applied between this interface and a non-polarisable electrode with circuit 4 as described above. The current on the outgoing interface was measured as a function of time. The electrode was completely covered with electrolyte and the measured potential of the cell was corrected for the ohmic resistance drop in the solution connection. The ingoing interface was polarised cathodically and the outgoing interface was maintained at various positive

potentials, the current in the steady state being measured. Taking the surface at +1,280 mv. to be virtually free from hydrogen, and denoting the permeation rate at this potential by P and the permeation rate at any other potential by p, then assuming the diffusion coefficient to be independent of the concentration, the concentration at the latter potential is given by $100(1 - p/P)\%$ where the concentration at the ingoing interface is 100%. This quantity is plotted against the potential in Diag. 31, marked.

This system suffered from the disadvantage that the resistance of the solution connection from the outgoing interface to the non-polarisable electrode was too high, and because of this the potential of the outgoing interface altered as the current approached the steady state. It was thus not possible to measure the approach to the steady state at constant concentration at the outgoing interface. It was decided to lower the resistance of the bridge connection to the order of 100 ohms. This would make the ohmic resistance drop negligible and thus the potential of and therefore concentration at, the outgoing interface would remain constant. Equation 19 for the analysis of the non-steady state could therefore be applied, and the diffusion coefficient evaluated. The expected value of the diffusion coefficient was of the order of 10^{-7} cm./sec.². (as shown by a consideration of the

DIAG. 33. CONCENTRATION RATIO VS. POTENTIAL.



POTENTIAL MV.

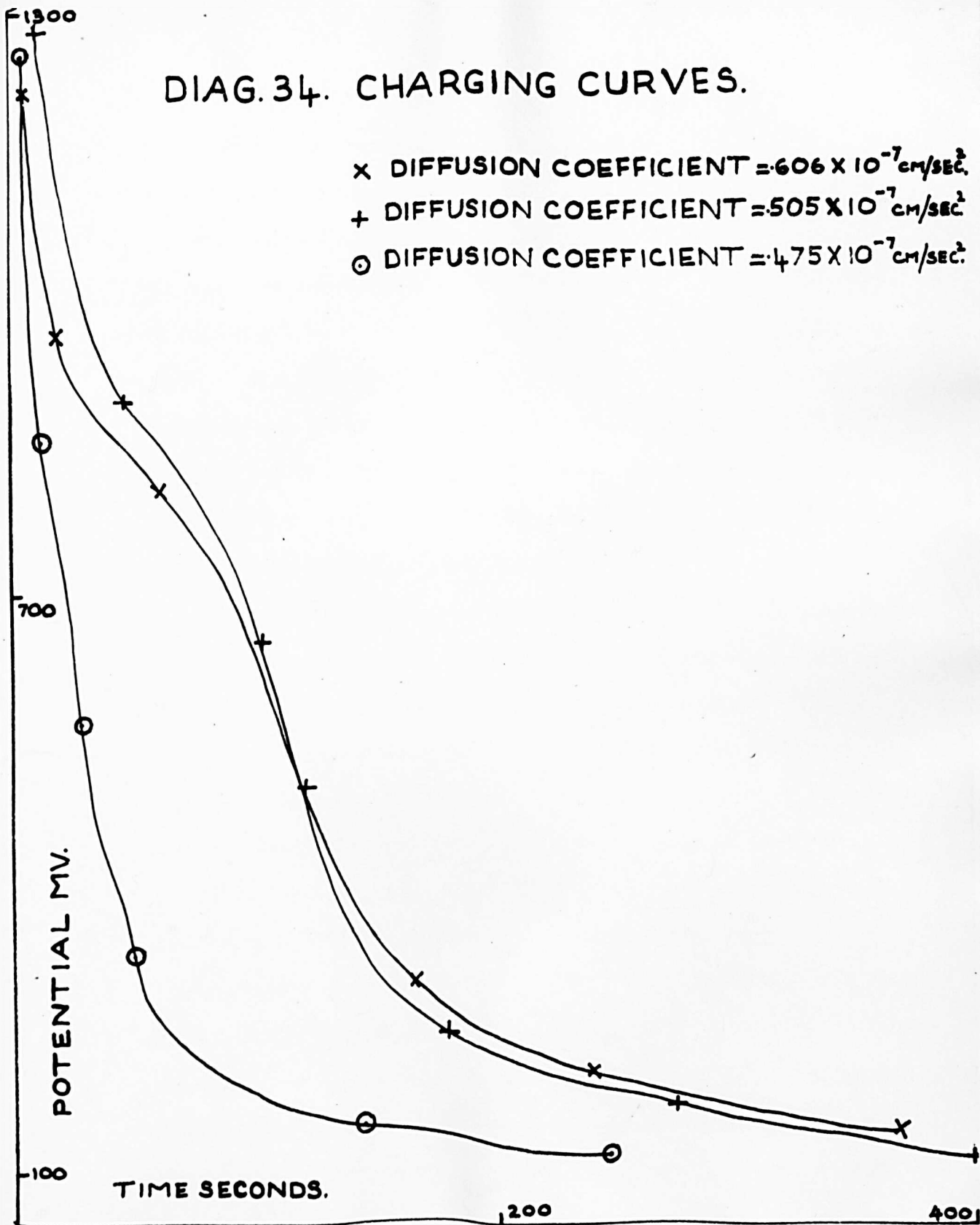
90

45

1700

DIAG. 34. CHARGING CURVES.

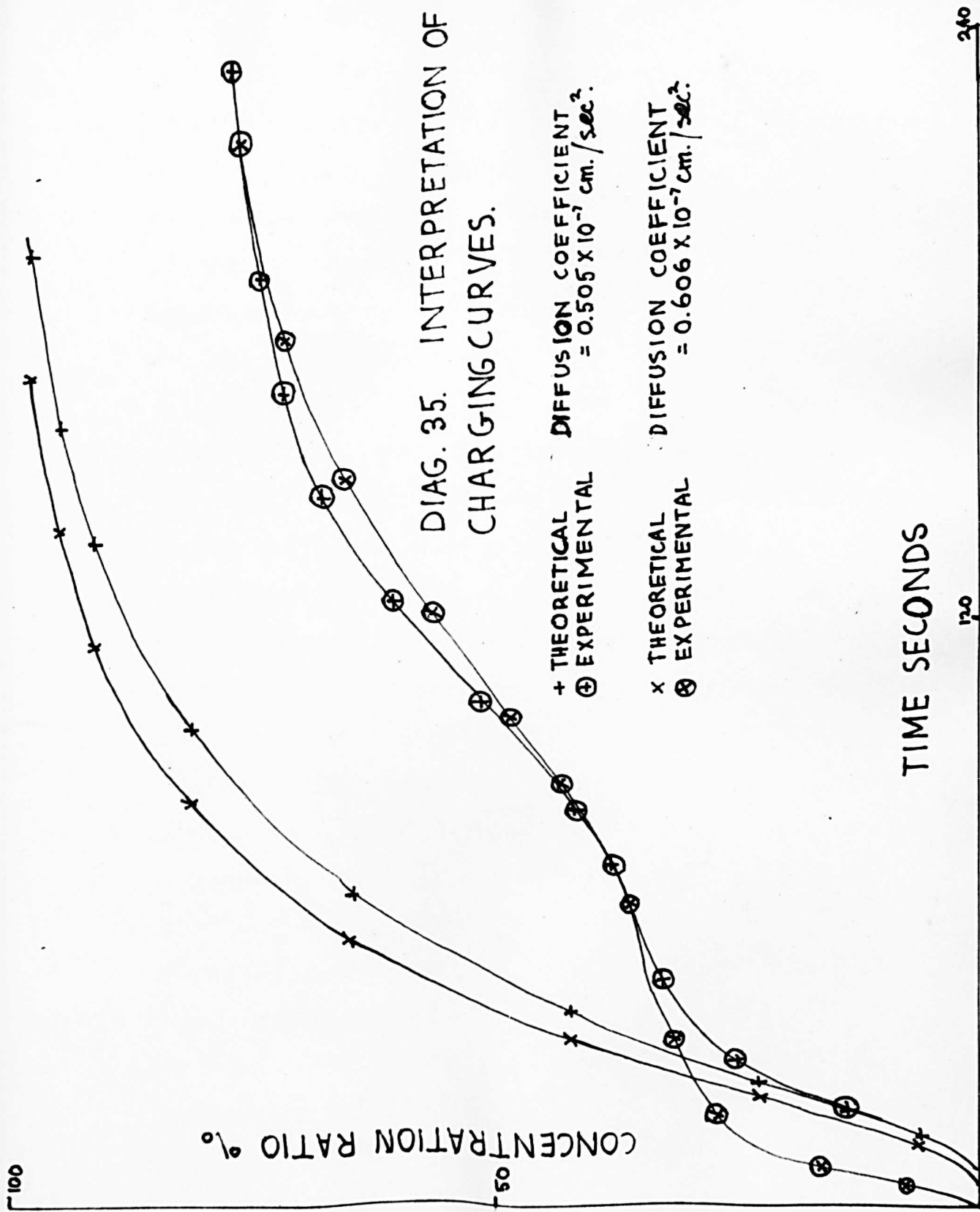
- x DIFFUSION COEFFICIENT = $606 \times 10^{-7} \text{ cm}^2/\text{SEC}^2$
- + DIFFUSION COEFFICIENT = $505 \times 10^{-7} \text{ cm}^2/\text{SEC}^2$
- o DIFFUSION COEFFICIENT = $475 \times 10^{-7} \text{ cm}^2/\text{SEC}^2$



shape of the charging curves). The expected time intercept was therefore of the order of 10 secs. for foil 0.001 in. thick, a suitable value in this method.

The diffusion coefficient was assumed to be independent of the concentration, and was determined with the outgoing interface at +1280 mv. the ingoing interface being polarised at 0.01 amp./sq.cm. The concentration ratio as a percentage of the concentration at the ingoing interface was again assumed to be given by $100(1 - p/P)\%$. (See above). This quantity is plotted against the potential in Diag. 33, for two runs marked + and x. The values of the diffusion coefficient for the two runs are shown on diag. 34. The results were similar to the results obtained with the high resistance solution connection between the outgoing interface and the non-polarisable reference electrode. The scatter of the points was attributed to stray depolarisation currents which were included in the value of the rate of permeation measured in this method.

Using these results it was possible to test Fick's laws of diffusion under the conditions of the experiment, i.e., for the boundary conditions chosen. From the value of the diffusion coefficient evaluated above the ratio of the concentration on the outgoing interface to that at the ingoing interface as a function of time for the boundary condition $dc/dx=0, x=0$ was calculated. (Equation 12.). Charging curves (marked x and +) Diag. 34 were



taken after the determination of the diffusion coefficient and from these in conjunction with the values of the concentration ratio as a function of potential (Diag. 33) experimental values of the concentration ratio as a function of time could be derived. The experimental and theoretical values for the two experiments are compared in Diag. 35.

It was apparent that the system was either not obeying Fick's laws of diffusion or else deviating from the chosen boundary conditions. Since the experimental points fell below, and in fact levelled out below the theoretical curves it was thought that exchange with the solution was the most likely reason. Consideration of an experiment in which the permeation rate, owing to poisoning, was larger by a factor of 10 than in the above experiments, substantiated this point of view. The concentration ratio (marked Diag. 33) was very similar to that in the above experiments while the charging curve (marked in Diag. 34) was more rapid. As the diffusion coefficient was lower than in the above experiments, the only reason for the more rapid charging lay in the higher permeation rate which was thought to lower the comparative effect of the depolarisation. Consideration of the charging curves (see Section 3) also indicated that depolarisation by the solution of the electrode interface was interfering in the measurements.

The possibility that the diffusion coefficient was a function of the concentration could not, however, be ruled out. The most immediate effect of such a variation would be to alter the concentration potential curve. To illustrate the effect of such a departure the charging curves, Diag. 34, were compared to the theoretical expression in Diag. 35, and the resulting values of the concentration ratio were plotted against the potential in Diag. 33 (curves marked \oplus and \otimes). The shape of these curves was more in accord with the measurements of potential at constant current described above, than those given by the expression $100(1 - p/P)$. The divergence of the results obtained by these two methods could not, however, be readily explained. It was accordingly decided to determine the diffusion coefficient over the whole range of concentration and thereby to obtain a more accurate measure of the concentration potential curve, and further to take the measurements independently of depolarisation by the solution. In order to achieve this the outgoing interface was maintained at the same potential throughout the experiment while the potentials to be investigated were applied to the ingoing interface. The results of these measurements are given in the next section.

4. Measurements of the approach to the steady state of permeation.

The general considerations have been outlined above. The manner of evaluating the results has been given in the Introduction (equation 19). The electrical circuits designated 3 and 4 were applied to the outgoing and ingoing interfaces and the apparatus used was that in the previous section.

The outgoing interface was maintained throughout these measurements at +1270, +1280, and +1290 mv. at 20, 30, and 40°C respectively which were the least positive potentials according to the anodic charging curves at which there was no hydrogen on the interface. The ingoing interface was at first discharged at the same potential. When the current flowing into the outgoing interface had become constant, a less positive potential was applied to the ingoing interface (from +1100 to -100 mv.). The current on the outgoing interface then approached a higher steady value and the approach to the steady state represented the approach to the steady state of diffusion. In fact the potentials on the ingoing and outgoing interfaces and the current flowing into the outgoing interface represented respectively, constant and zero concentration on the ingoing and outgoing interfaces, and the quantity of material crossing the outgoing interface per unit time.

With this technique the measurements could be taken independently of depolarisation, since the outgoing interface was

maintained at the same potential throughout the experiment (i.e., the rate of depolarisation was constant) and the currents measured represented the difference between the depolarisation current + rate of permeation and the depolarisation current. Depolarisation at the ingoing interface did not affect the validity of the measurements because the potential and therefore the concentration of hydrogen at the ingoing interface was maintained constant for each particular experiment.

The permeability varied considerably from experiment to experiment and further during the experiment itself. Accordingly the minimum value at each temperature was taken. This minimum was invariably found to be the first set of determinations in each run.

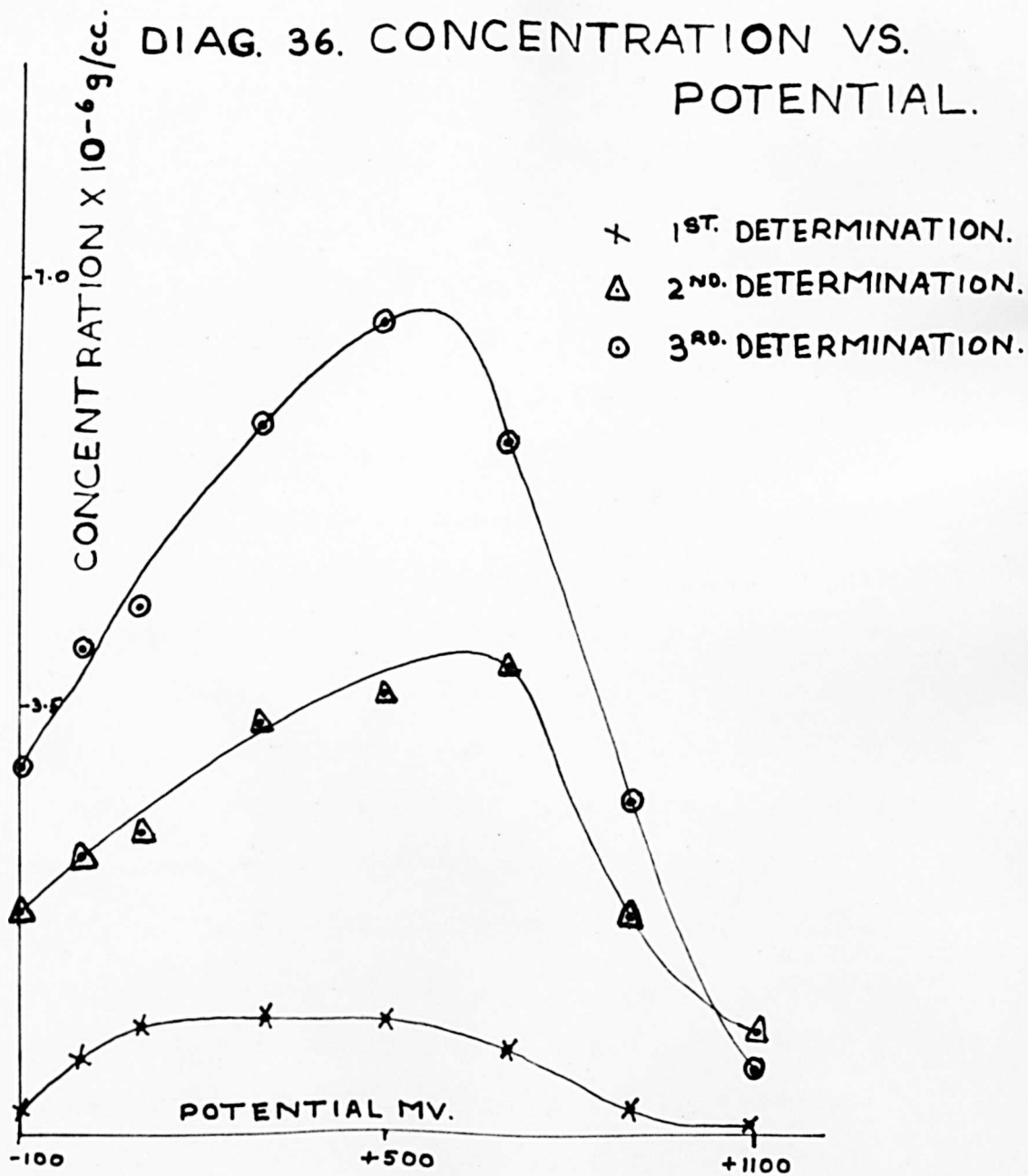
It was found that an initial application of +100 mv. to the ingoing interface gave an erratic approach to the steady state on the outgoing interface although subsequently the approach to the steady state at this and other potentials was regular. With the ingoing interface initially at +100 mv. there was a considerable time lag before any diffusion occurred. It appears likely that this was caused by a blocking effect of strongly adsorbed oxygen on the outgoing interface to hydrogen coming from within the metal. This was substantiated by the fact that there appeared to be no hindrance to hydrogen entering platinum through a similar surface in the

experiments described in Results: Section 5. Similar blocking effects have in fact been observed by Oatley (63) on platinum and by Eggleton (64) with nitrogen on iron. Furthermore, there are independent observations that indicate that there is a strongly adsorbed layer of oxygen on platinum surfaces left exposed to the atmosphere for some time.

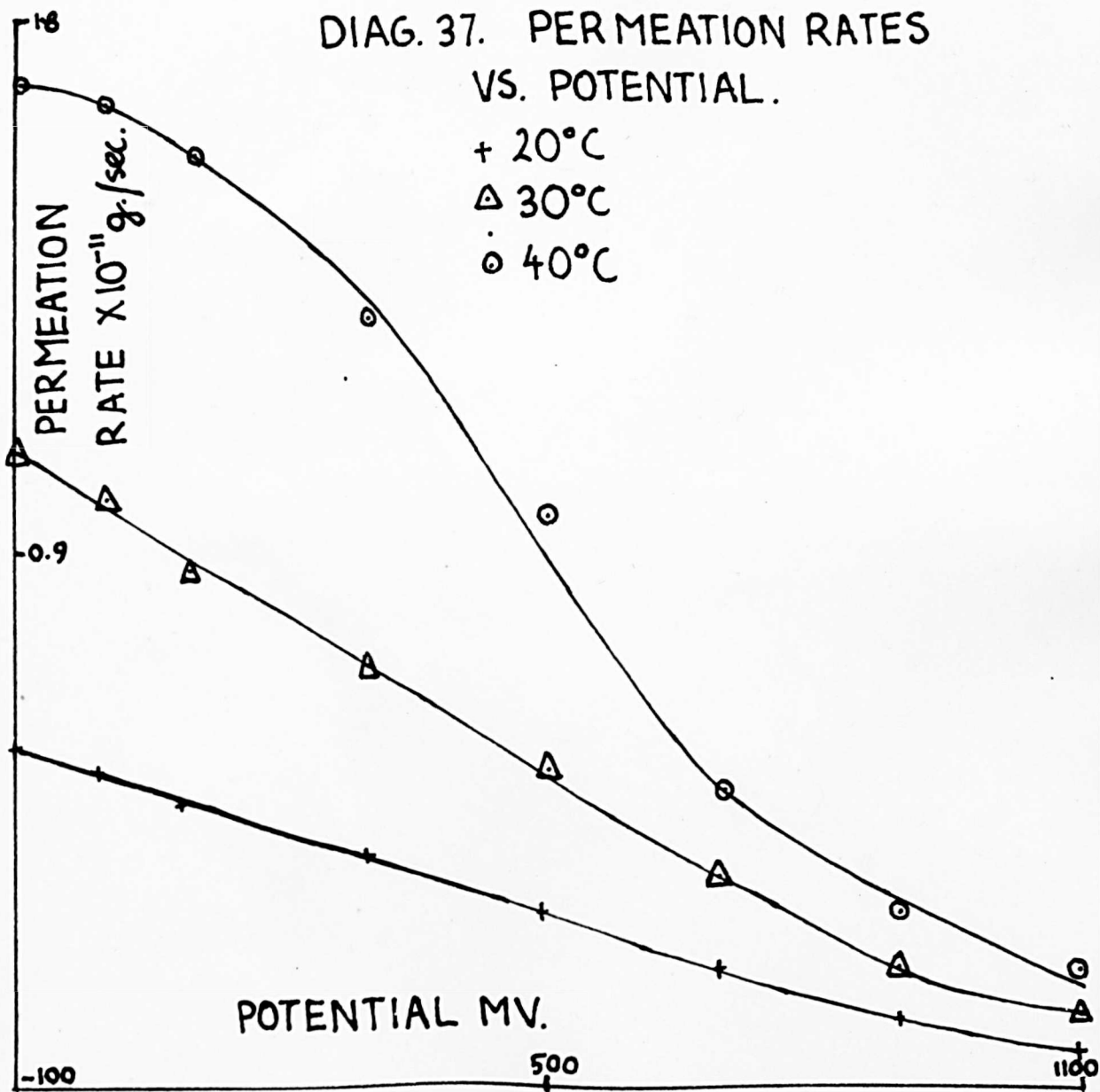
In order to obtain reproducible conditions, a potential of +100 mv. was applied to both interfaces before the actual measurements for 30 minutes and both interfaces were then discharged until the current in the circuit on the outgoing interface no longer showed any variation, i.e., no hydrogen came out of the platinum membrane. After this treatment, the approach to the steady state was entirely regular and so presumably this treatment was adequate in removing the oxygen layer. The surfaces were then in a condition analogous to the freshly reduced surfaces frequently found to be most active by other workers. The potential of +100 mv. was chosen since it represented the most negative potential which could be applied to the outgoing interface without introducing appreciable quantities of hydrogen into the solution and it appeared that at this potential there is a maximum in the hydrogen concentration within the platinum interface (see below).

The extent to which the concentration of hydrogen within the ingoing interface altered on successive determinations is indicated

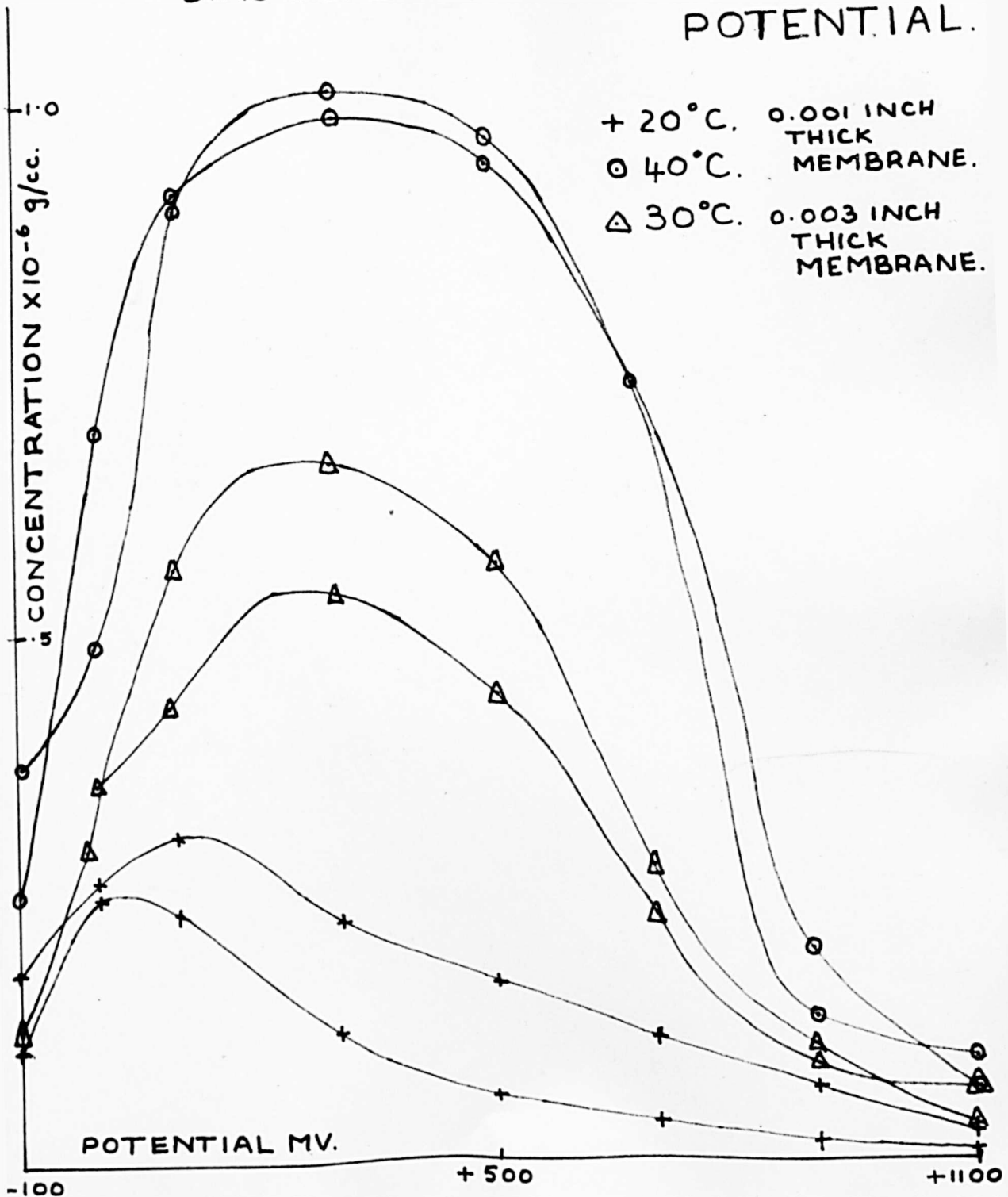
DIAG. 36. CONCENTRATION VS. POTENTIAL.



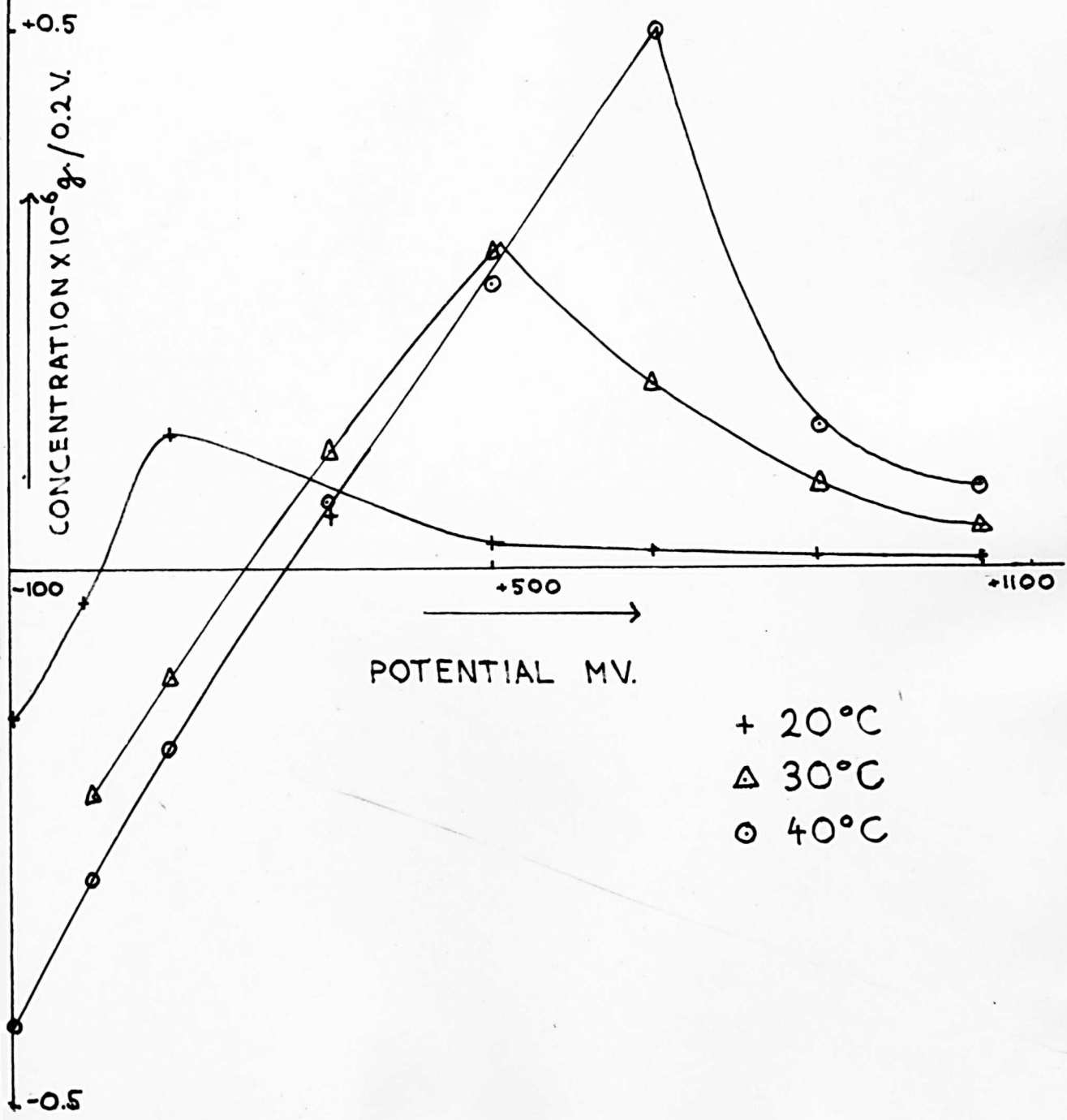
DIAG. 37. PERMEATION RATES
VS. POTENTIAL.



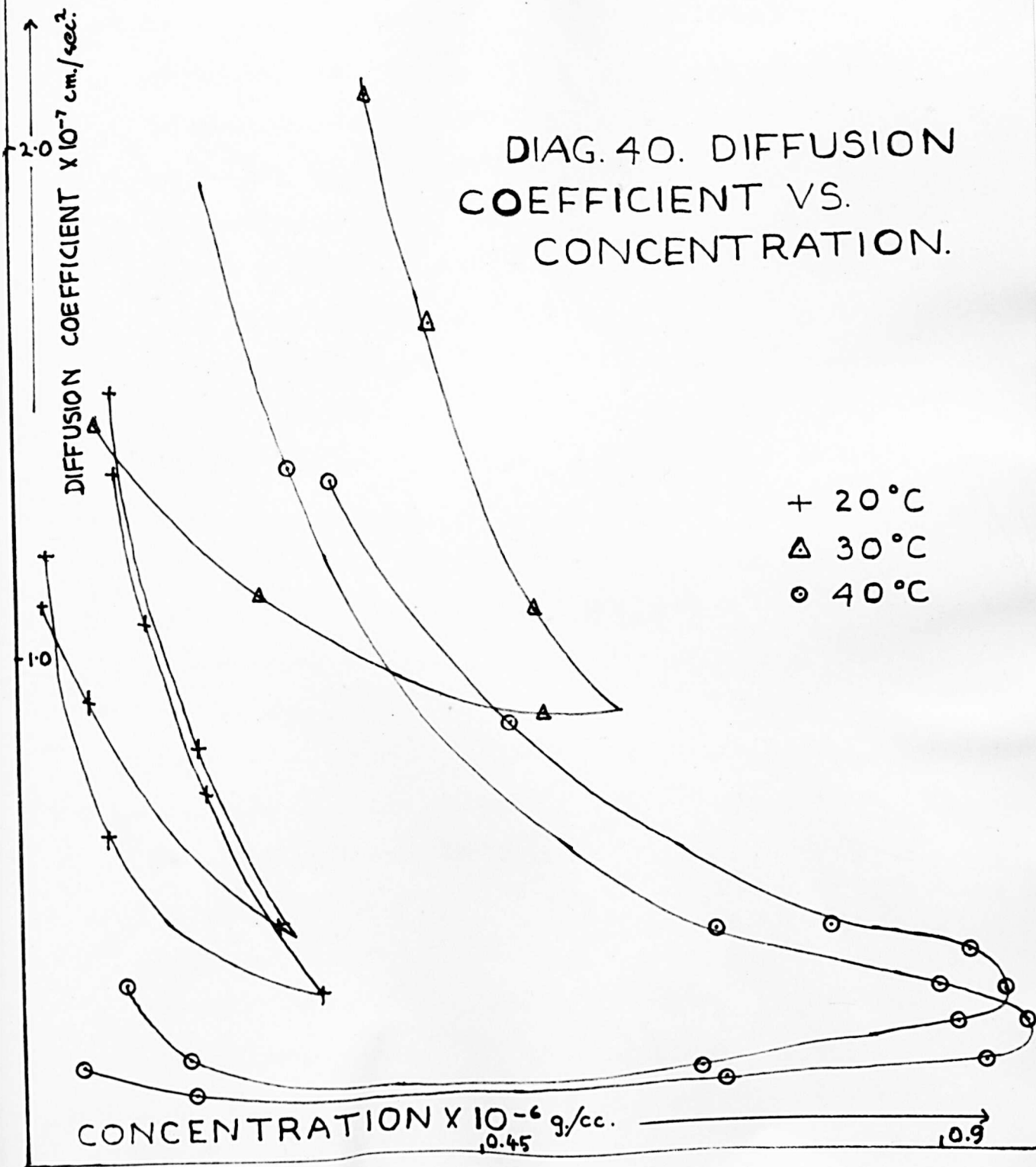
DIAG. 38. CONCENTRATION VS. POTENTIAL.



DIAG.39. CHANGE OF CONCENTRATION WITH POTENTIAL VS. POTENTIAL



DIAG. 40. DIFFUSION COEFFICIENT VS. CONCENTRATION.



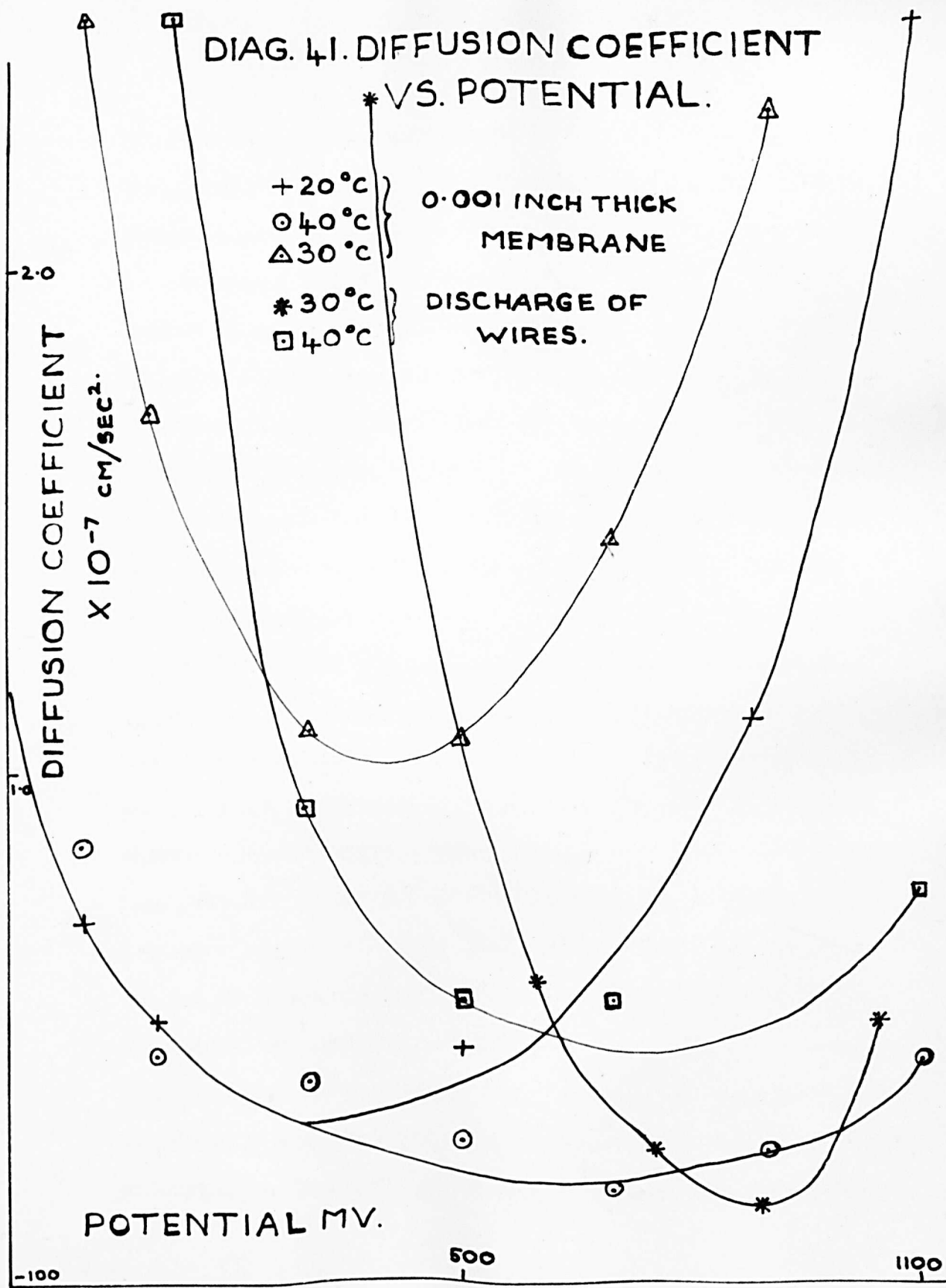
in Diag. 36. Measurements were made by applying successively more negative and then more positive potentials to the ingoing interface a saturation at +100 mv. being interposed as above between each set of determinations to maintain the activity of the interfaces. It was, however, found that the activity did not fall off even without a repetition of the saturation.

In Diags. 37 and 38 the rate of permeation and the concentration within the ingoing interface are plotted against the potential for experiments at 20 and 40°C on 0.001" thick membranes and at 30°C. for 0.003" thick electrodes. Repeated attempts were made to obtain reproducible results at 30°C. on 0.001" membranes in two groups of experiments with two sets of platinum foils from different batches. Reproducible results could not be obtained however and out of 13 separate experiments the minimum value can only be taken as an indication of the type of behaviour. There is reason to believe that in both groups of experiments the results were vitiated by poisoning, in one group by arsenic which had been added in some previous experiments to the cell solution and in the other group by hydrogen cyanide which was present in the laboratory atmosphere at that period.

In Diag. 39 are plotted the rates of change of concentration with potential against potential for the curves given in Diag. 38.

In Diag. 40 the diffusion coefficient D is plotted against

DIAG. 41. DIFFUSION COEFFICIENT VS. POTENTIAL.

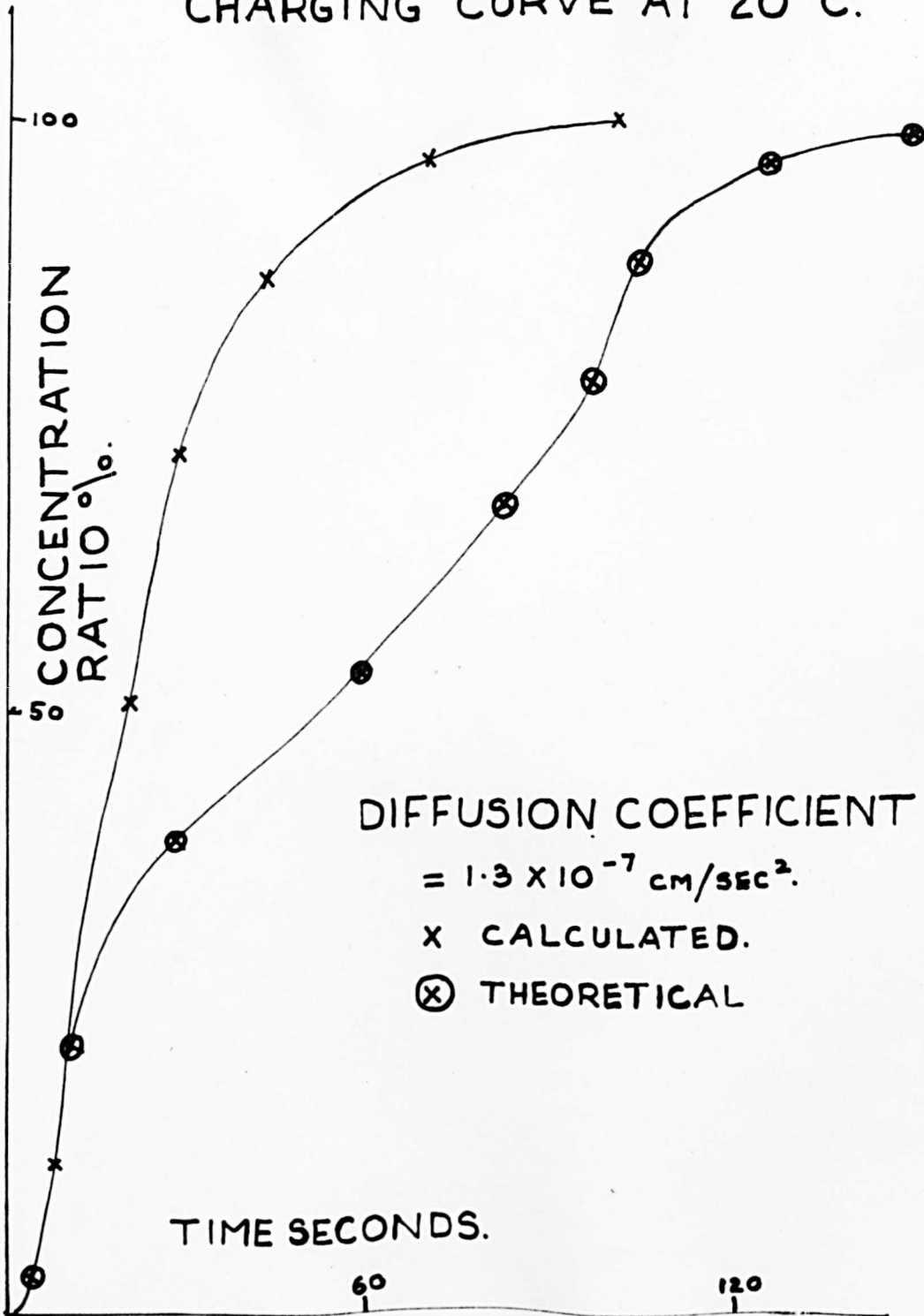


the concentration (C) on the ingoing interface and in Diag. 41 the diffusion coefficient is plotted against the potential of the ingoing interface.

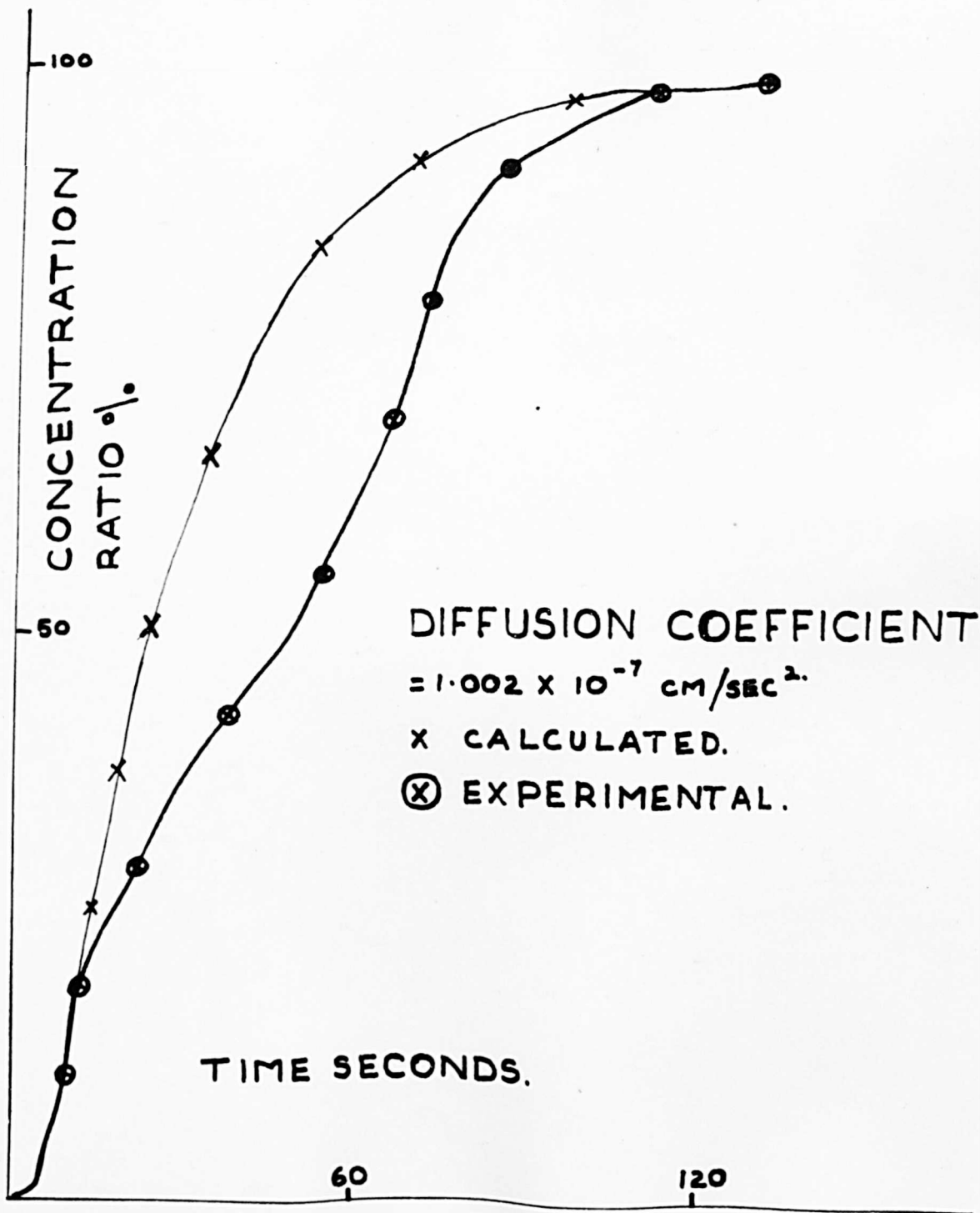
It became apparent during the course of these experiments that the concentration-potential curve had the shape indicated (Diag. 33) by the comparison of cathodic charging curves (Diag. 34) and the theoretical expression (Diag. 35) using the value of the diffusion coefficient. (Results: section 3). Accordingly similar cathodic charging curves, taken during the course of the experiments were compared with concentration-potential curves of the type given in diag. 38.

The electrodes were activated, as in the above experiments, by applying a potential of +100 mv. to both interfaces. They were then discharged to the appropriate potential at each temperature. The diffusion coefficient was then determined as above (according to equation 19) with the ingoing interface at +100 mv., the electrode again discharged, and the cathodic charging curve taken with the ingoing interface at +100 mv. In this way only small cathodic and anodic currents were allowed to flow to the interfaces and by discharging the electrodes through both interfaces the time for the complete experiment, as compared to the time taken in the experiments described in Results: Section 3, was considerably reduced. Possible errors due to poisoning were thereby minimised. The potential of

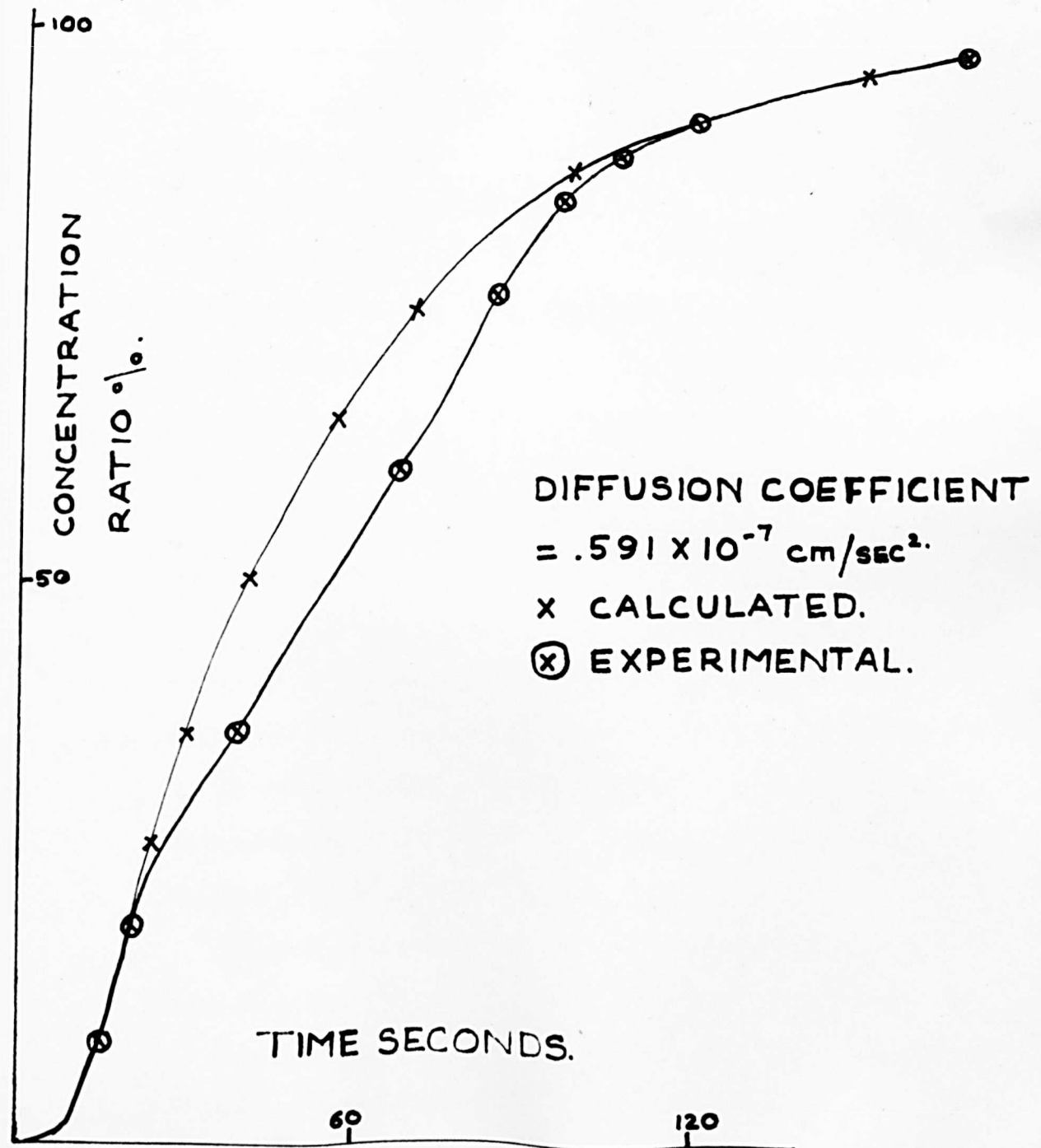
DIAG. 42. INTERPRETATION OF CHARGING CURVE AT 20°C.



DIAG 43. INTERPRETATION OF CHARGING CURVE AT 30°C.



DIAG. 44. INTERPRETATION OF CHARGING CURVE AT 40°C.



+100 mv. was chosen as it became apparent during the course of the above experiments that there was a maximum in the concentration of hydrogen within platinum at this potential and it was thought that part of the deviations from Fick's laws might have been caused by applying cathodic potentials to the ingoing interface.

The concentrations on the outgoing interface were assumed to be the same at each potential as those on the ingoing interface. The concentration, c , at any potential was determined as above and was plotted against the potential. The concentration ratio $c/C\%$, was evaluated at each potential, C being the concentration at the maximum of the concentration-potential curve. This maximum lay somewhat on the positive side of +100 mv. in these experiments.

The experimental values of $c/C\%$ were plotted against the time in Diags. 42, 43 and 44, at 20° , 30° and 40°C (by comparing the potentials with the potential time curves). The experimental values are marked \odot and the theoretical values calculated from equation 12 using the diffusion coefficient at +100 mv. are marked x .

We may anticipate the discussion at this stage and consider the reasons for which a diffusing system appears to disobey the solutions of Fick's laws. In broad outline:

1. The diffusion coefficient may not be constant with concentration.
2. Slow interface processes may be rate-controlling or at least have an influence on the diffusion process.

3. The system may not conform to the boundary conditions of the solution of the diffusion equation chosen.

The division of 2 and 3 is to a certain extent arbitrary. The deviations in 2 are taken to be of the nature of the "radiation boundary condition" in problems of thermal conductivity, whereas 3 covers all other deviations from the usual boundary conditions.

It is to be noted that the deviations from the theoretical behaviour (Diags. 42, 43 and 44) diminish with increasing temperature. Bearing in mind that the equilibrium concentration of hydrogen in platinum is exceedingly low, and that the dissolution proceeds endothermically, it appeared that if depolarisation i.e., 3 was the reason for the deviations, then this might be caused by adsorption at the interface rather than exchange with the solution. The boundary condition chosen for $x=0$ would therefore be in error for this interface and it would be necessary to allow for the capacity of this interface. This was, however, impossible with the present experiments since no idea could be formed as to the capacity of the interface. Various factors pointed against such an interpretation. Firstly, solutions allowing for the capacity of the interface do not yield curves having the shape of the experimental curves. (Diags. 42, 43 and 44). Secondly, the experimental and theoretical curves coincide at high coverage at the higher temperatures indicating

no net depolarisation. Finally, the decreasing deviations with increasing temperature are presumably to be associated (using equation 19 to evaluate the diffusion coefficient) with the decreasing variation of the diffusion coefficient with concentration with increasing temperature. (Diag. 40).

Further tests along the above lines seemed difficult. It appeared that to isolate 2, namely the effect of any slow interface processes, it would be necessary to isolate one interface and to investigate the transfer of material in both directions across this interface. Membrane experiments appeared to be unsuitable for this work since these always involve the consideration of two interfaces and therefore both transfer processes (surface to bulk and bulk to surface) occur simultaneously. To isolate these two transfer processes the experiments described in the next section were devised. In these the charging and discharging of wires was investigated. The experimental points could then be compared with the theoretical expressions in order to discover to what extent the interface was interfering.

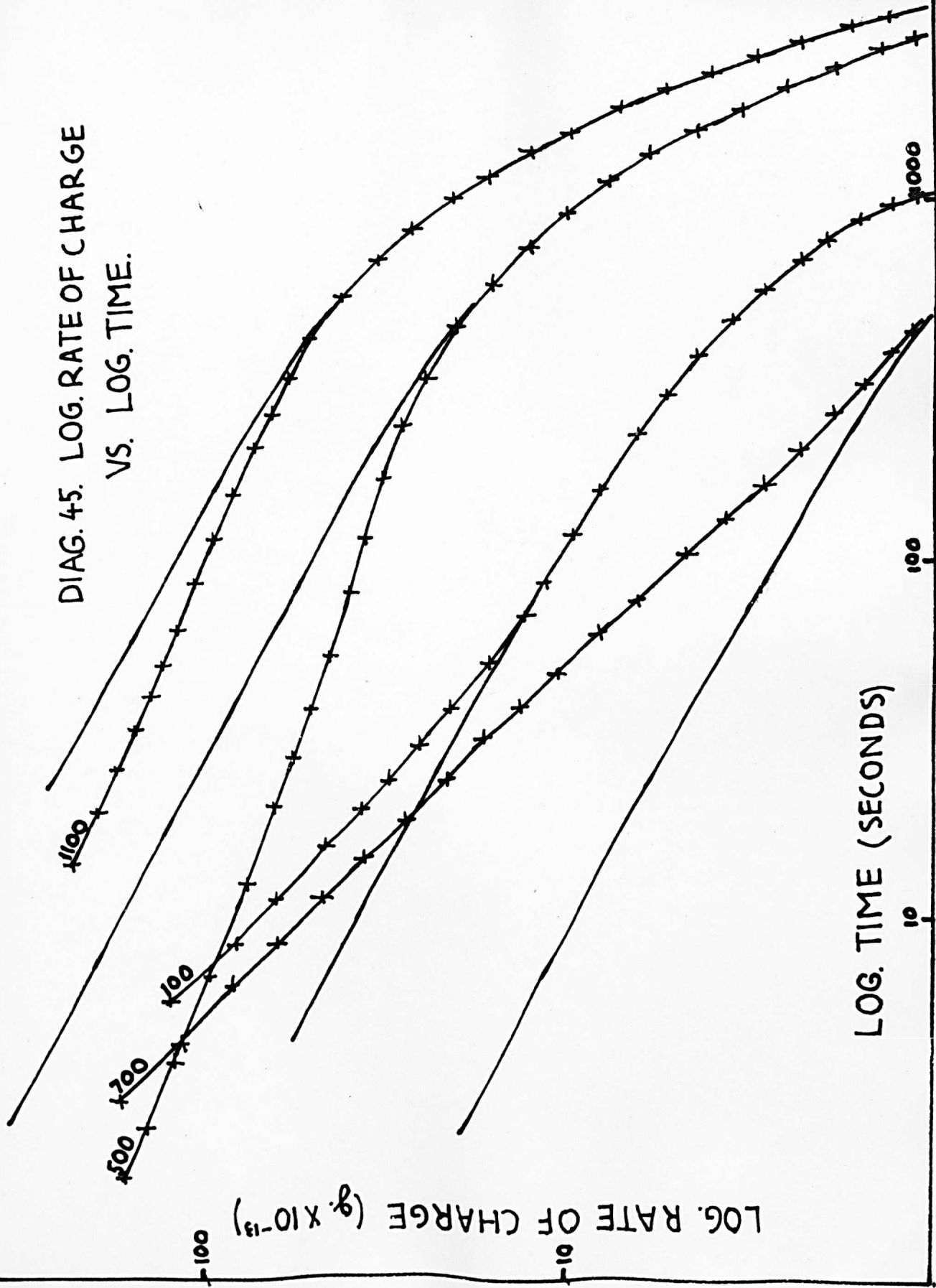
Further discussion of the extent to which Fick's laws are obeyed will be deferred to the discussion.

5. Measurements of the charging and discharging of wires.

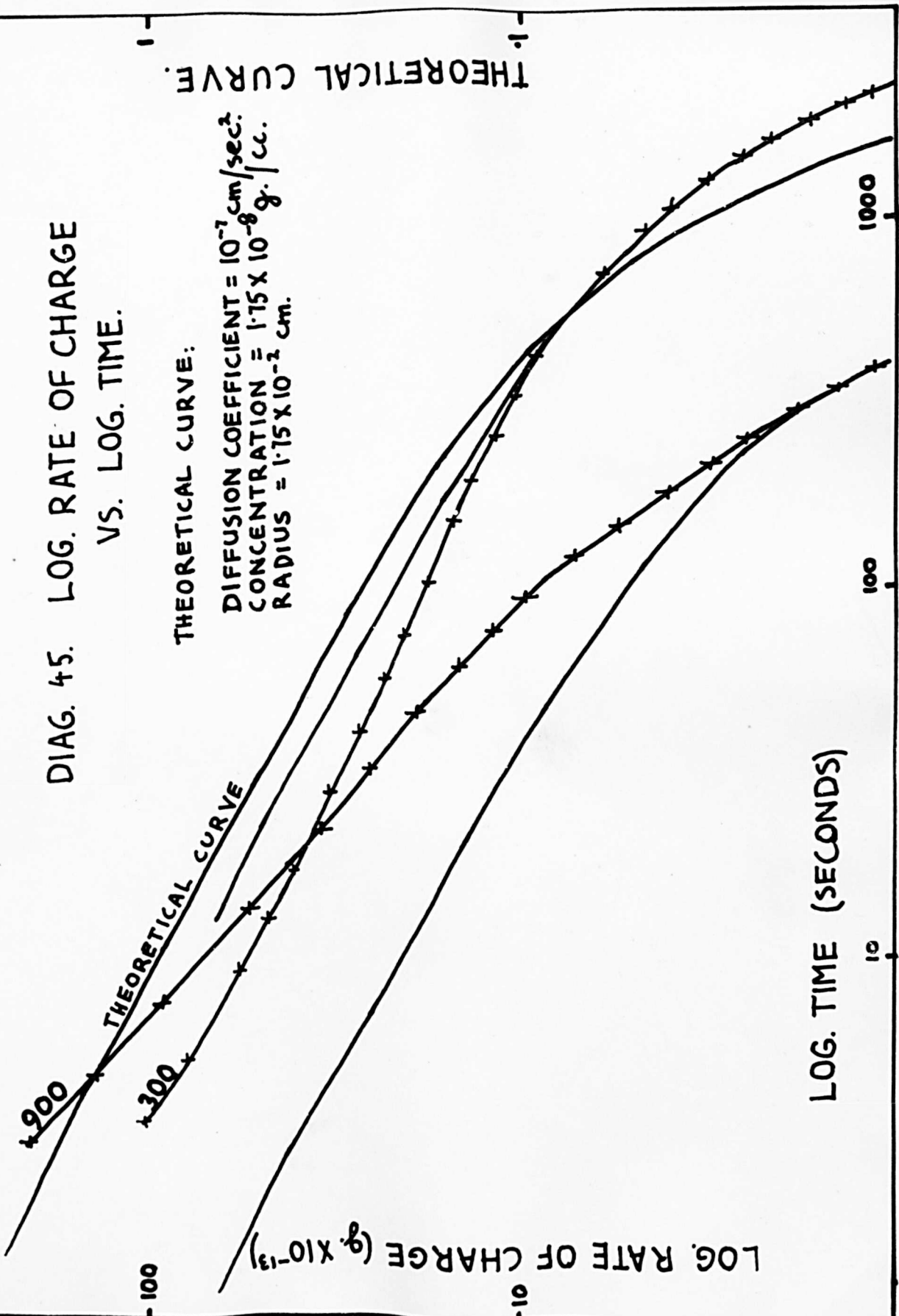
The experiments followed the plan outlined in the Introduction. The surface of the wire was maintained at potentials between +1280 and +100 mv. , the electrical circuit 3 being used in conjunction with a non-polarisable cathode. The apparatus used was that shown in Diag. 21. The cathodic currents flowing into the wire and the anodic currents flowing from the wire were measured at decreasing positive and increasing positive potentials respectively. These currents represented the difference between the dissolution current + depolarisation current and the depolarisation current. The results were evaluated as indicated in the Introduction.

In Diag. 45 are shown the plots of rate of dissolution of hydrogen versus time at potentials +1000 to +100 mv. on double logarithmic graph paper. The calibration curve calculated for a wire 0.0175 cm. radius, $C = 1.75 \times 10^{-8}$ g. hydrogen/cc. and $D = 10^{-7}$ cm./sec.² is also indicated. These experiments were carried out at 40°C. On the graph are also shown the degree of coincidence between the experimental points and the theoretical lines when these have been displaced to fit at the points indicated. The graphs were fitted as far as possible at time values about 1000 secs. after the start of saturation. At such times any irregularity due to depolarisation currents was at a minimum, inaccuracy due to timing errors or slowness in response of the galvanometer was minimised, and at the same time the rate of uptake

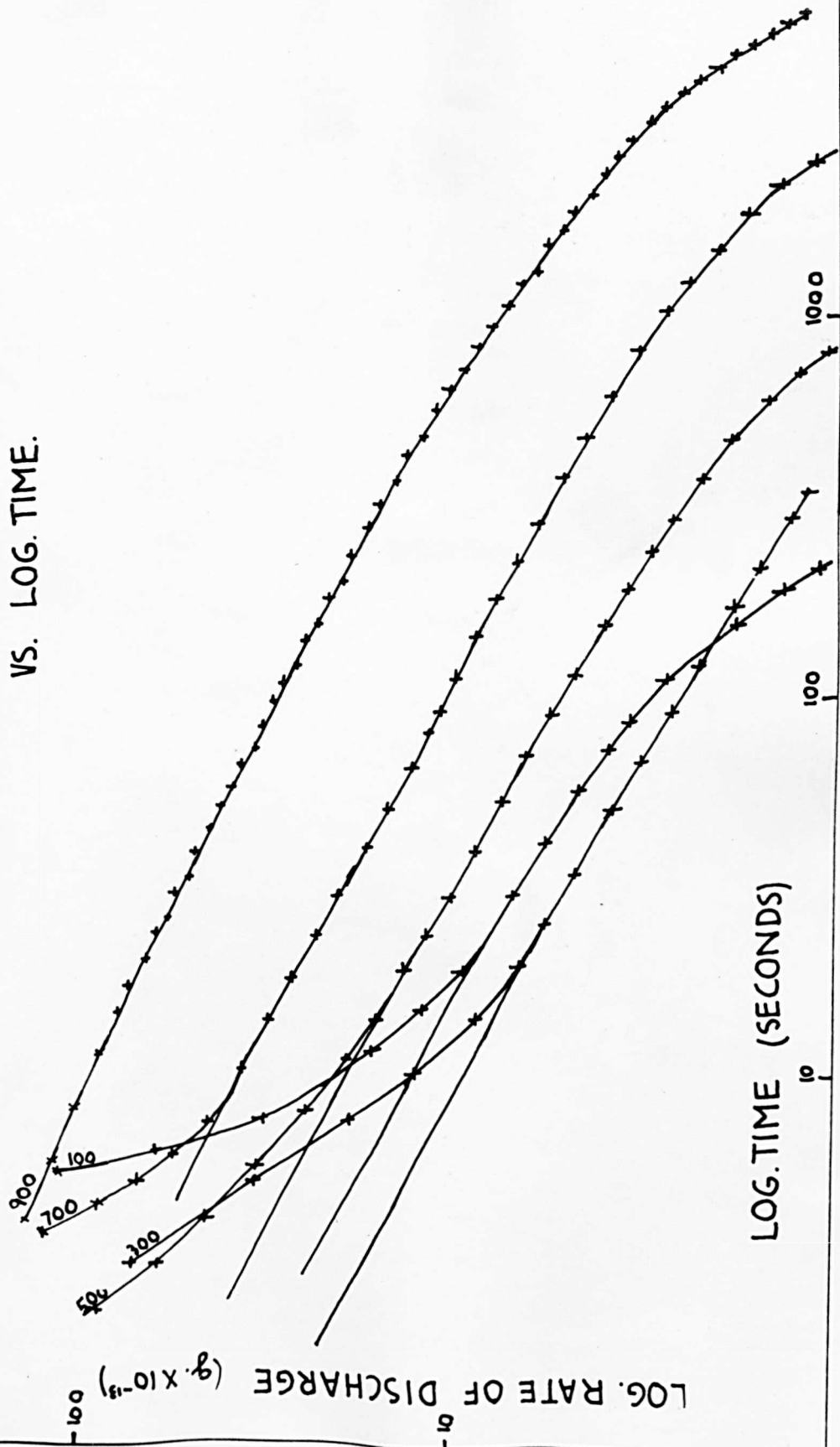
DIAG. 45. LOG. RATE OF CHARGE
VS. LOG. TIME.



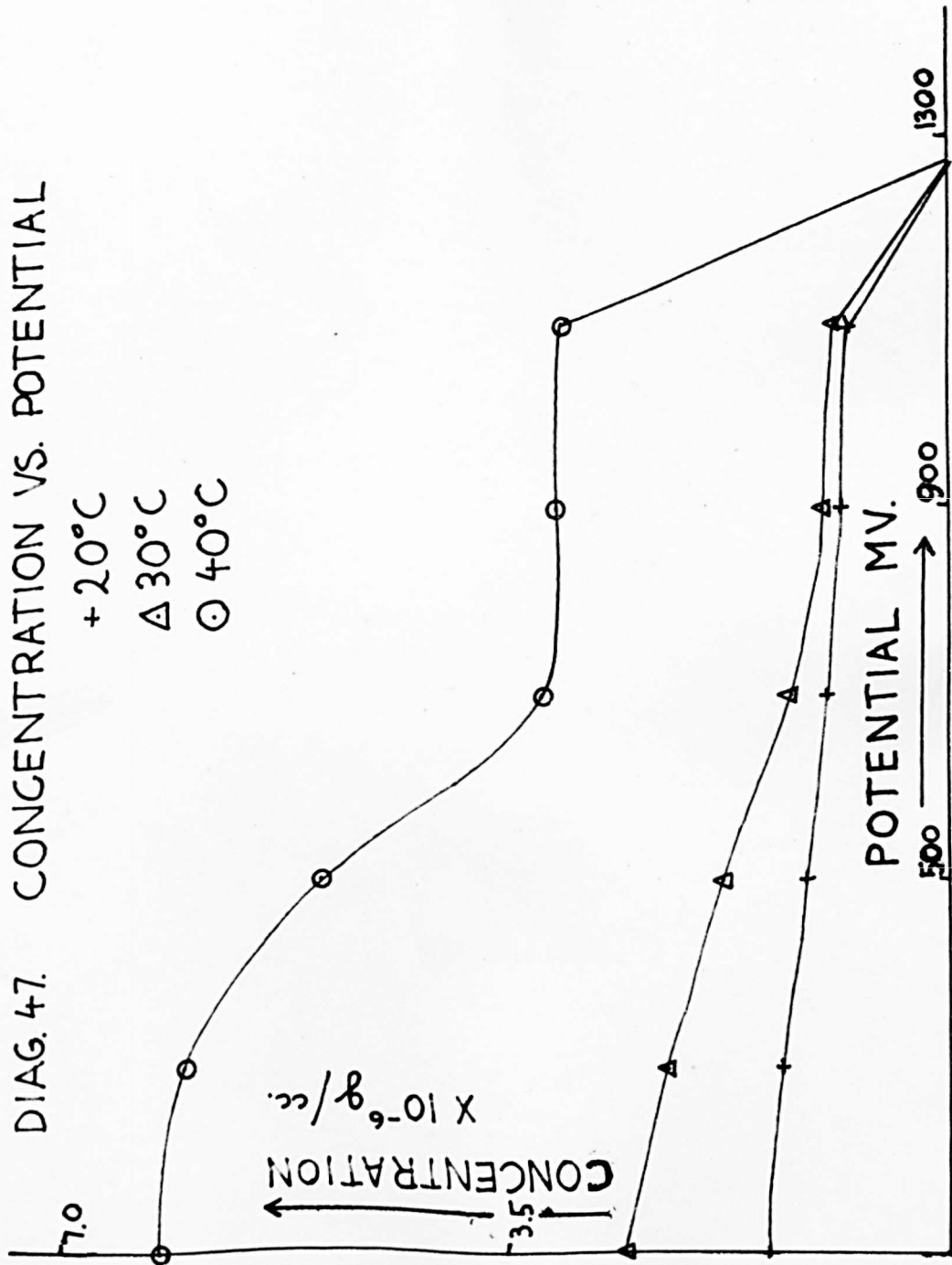
DIAG. 45. LOG. RATE OF CHARGE
VS. LOG. TIME.



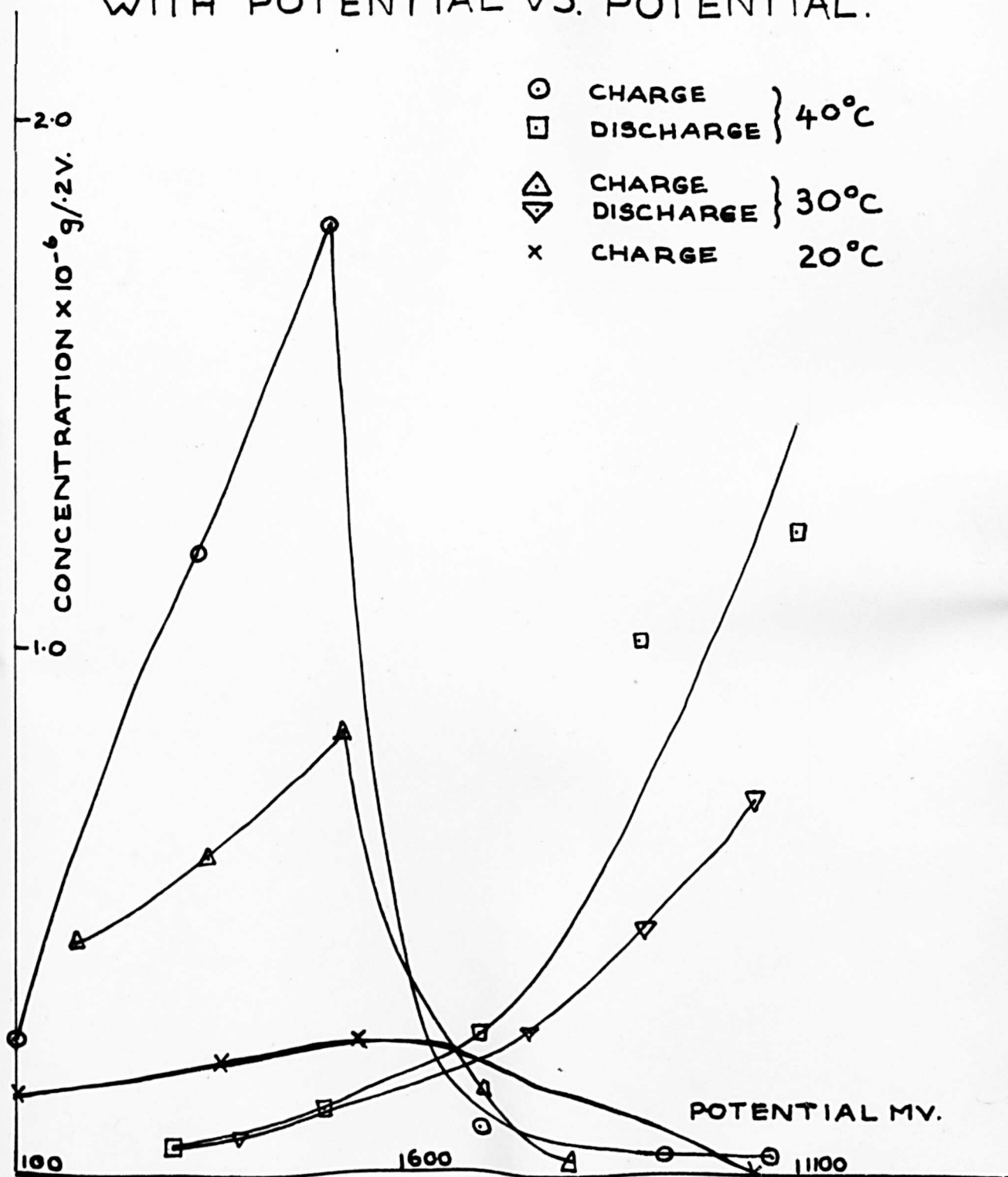
DIAG. 46. LOG. RATE OF DISCHARGE
VS. LOG. TIME.



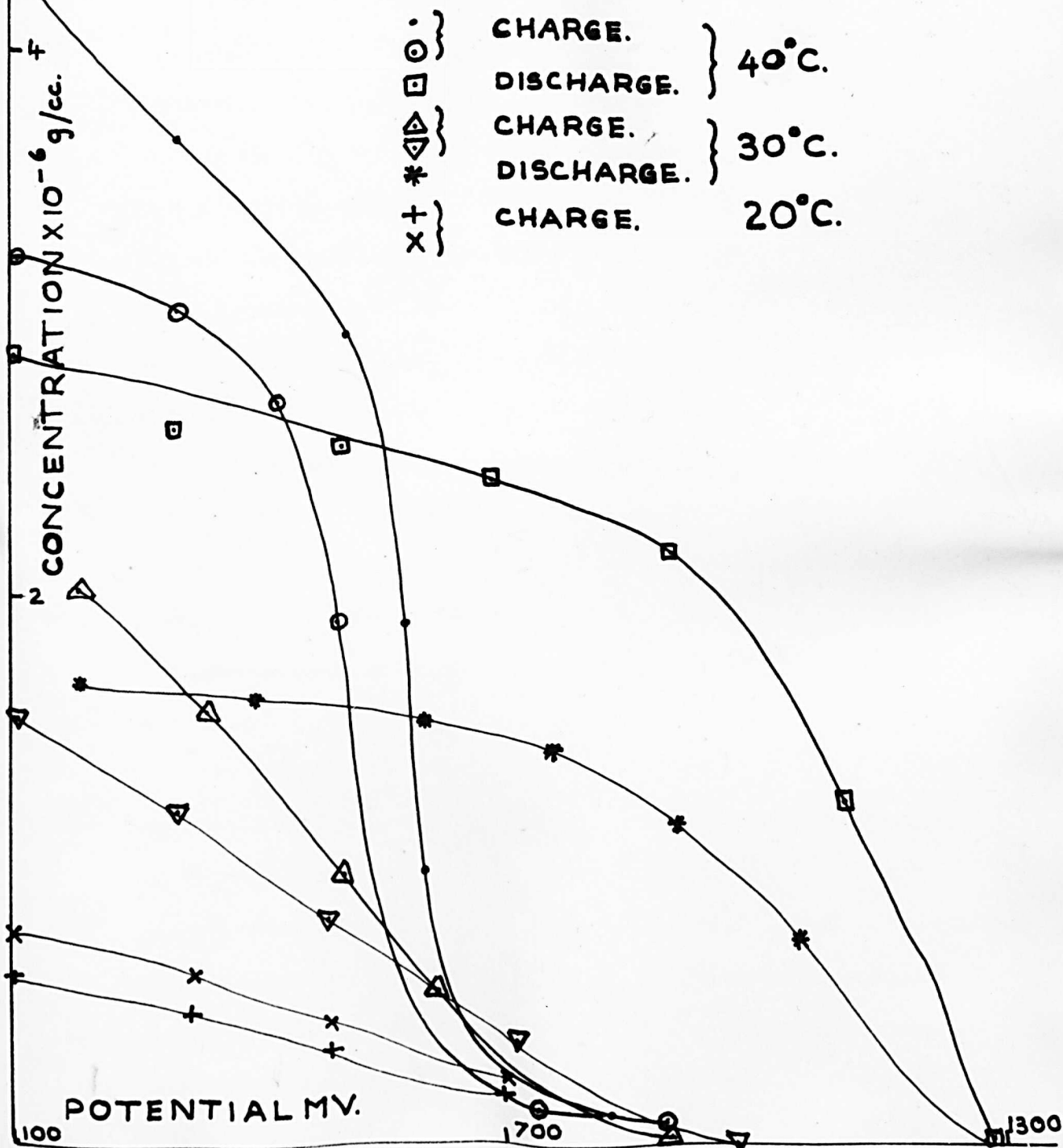
DIAG. 47. CONCENTRATION VS. POTENTIAL



DIAG 48. CHANGE OF CONCENTRATION WITH POTENTIAL VS. POTENTIAL.



DIAG. 49. CONCENTRATION VS. POTENTIAL.



was still sufficiently large to be accurately measurable.

In Diag. 46 a similar comparison is made for the discharge of a wire from potentials +100 to +1280 mv. at 40°C. with the theoretical predictions from Fick's laws.

In Diag. 47 the concentration of hydrogen is plotted against the potential; in Diag. 48 the rate of dissolution is plotted against the potential. Charging curves are given at 20°, 30°, and 40° and discharge curves at 30° and 40°C.

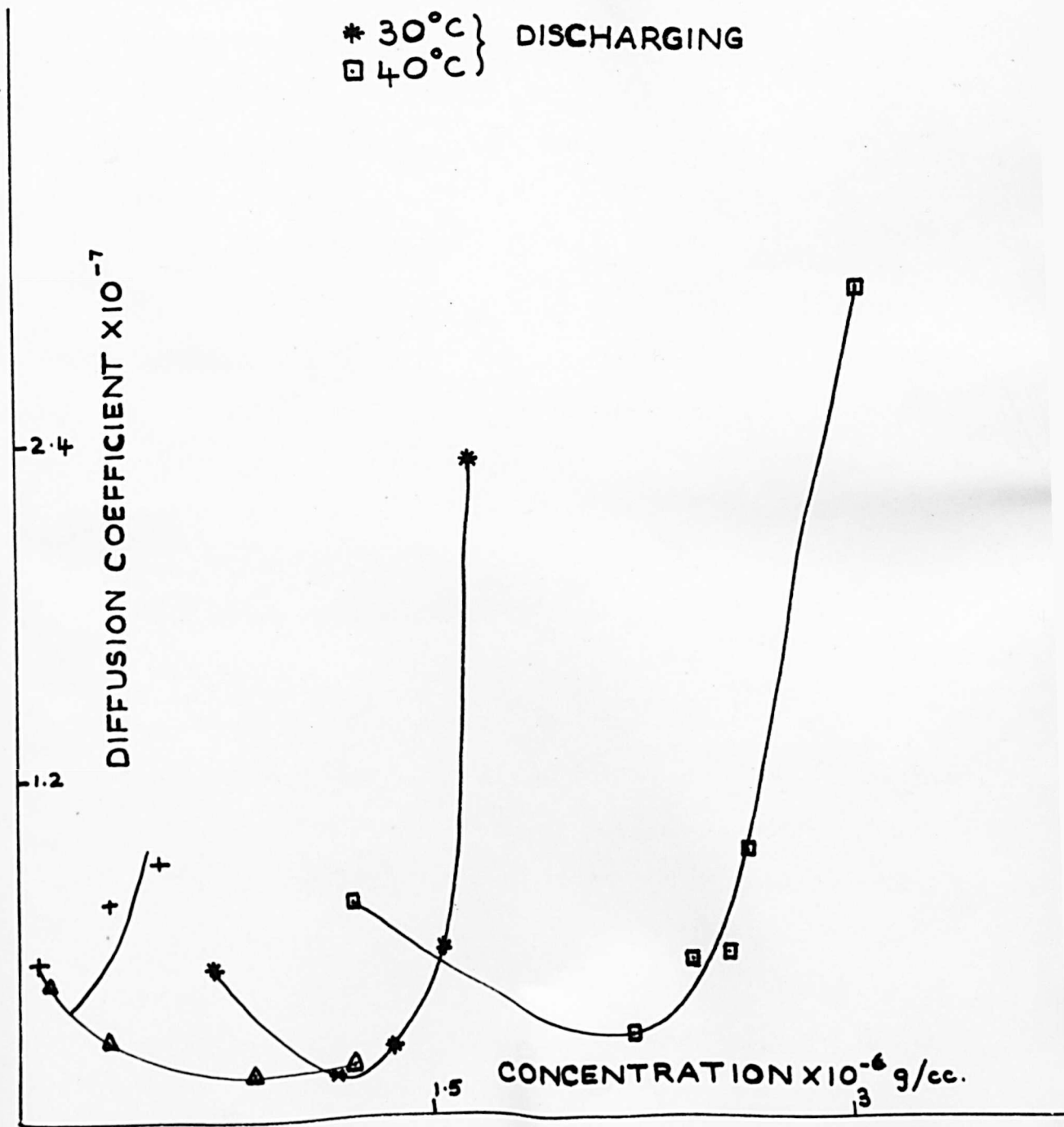
It is apparent from Diags. 47 and 48 that the dissolution between ca +1300 mv. and +1100 mv. is anomalous. According to experiments in the previous section there is only a very small concentration of hydrogen within the platinum surface at +1100 mv. To compare the results of the experiments in this section and Section 4, the dissolution down to +1100 mv. may be neglected. The concentration-potential curves then have the shape shown in Diag. 49.

The results for the concentration of hydrogen were found to be irreproducible both within and between different experiments as in Section 4. The results were selected according to the minimum value which was again found to be the first set of points determined. In the experiments with wires there was not such a general increase in the concentrations at each potential during the successive determinations in each experiment. Subsequent

DIAG. 50. DIFFUSION COEFFICIENT VS. CONCENTRATION FOR WIRES.

Δ 30°C } CHARGING
 + 20°C }

* 30°C } DISCHARGING
 □ 40°C }



values were higher than the first determination but the third value was sometimes lower than second. It does not seem possible to attach so much significance to the variation with time in the experiments with wires as with those with membranes since these experiments took a much longer time and the chance for contamination of the electrode surface was therefore much greater.

In Diag. 50 is shown the plot of diffusion coefficient against concentration for the above curves both for charging and discharging.

DISCUSSION.

In discussing the results obtained by the methods described above the kinetics of the processes must in the first instance be carefully considered. Many previous investigations of diffusion systems have been marred by a disregard of the importance of the diffusion kinetics (by this the approach to the steady state is implied) and interference by factors outside the simple diffusion steps. It is necessary, therefore, to consider in what way, if any, the system deviates from the ideal behaviour postulated in the solutions of the diffusion equations used.

The reasons for possible deviations may be divided into two main categories:

1. The diffusion coefficient may be a function of the concentration.
2. The system may deviate from the boundary conditions $c = C$ (constant), at $x = 1, t > 0$; $c = 0$ or $dc/dx = 0$ at $x = 0, t > 0$, used in the solutions of the diffusion equation given.

Two categories of deviations may be considered:

- a. Slow processes occur at the interfaces of the kind postulated in problems dealing with the "radiation boundary condition" in heat conduction.
- b. All other deviations from the above boundary conditions e.g., depolarisation, arbitrary variation of the interface concentration, not covered by a.

The process a. has been assumed (51) in order to explain the proportionality of the permeation rate to the square root of the pressure up to very high pressures for the diffusion occurring at high temperatures and also to explain the effect of the activity of the ingoing interface on the electrodiffusion at room temperature (54).

The interface $x = 1$ may be considered. In all the systems investigated in the experiments described above the concentration at $x = 1$ has been maintained "constant". It was assumed that the boundary condition was given by $c = C$ where c is the concentration and C is a constant. The boundary condition could thus be written $dc/dx = 0$. If a slow process takes place at this interface a concentration discontinuity will arise and the concentration will no longer be given by $c = C$. In many problems of heat conduction it has been assumed that the flux across the interface will be proportional to the temperature difference from one medium to the other at this interface. The concept has been applied to diffusion problems where slow transfer processes at the interfaces take the place of radiation. If the concentration at the face $x = 1$ of the medium $0 < x < 1$ is c and the concentration at $x > 1$ is C (a constant) for $t > 0$ then the flux across the interface will be given by: $H(C - c)$ where H is termed the external conductivity. The boundary condition at this interface may therefore be written as: $D \cdot dc/dx = H(C - c)$ or $dc/dx + hc = hC$ where $h = H/D$, a constant.

In the notation of the Laplace transformation this becomes:

$d\bar{c}/dx + h\bar{c} = (hC)/p$, and the diffusion equation must be solved with this boundary condition. The alterations from the usual form of the solutions of Fick's laws of diffusion caused by the substitution of the radiation boundary condition may be considered separately, since great importance has been attached to processes of this kind, and the majority of the solutions have been worked out in connection with problems in heat conduction.

The deviations covered by 2b. are more complex and give rise to a wide variety of boundary conditions. The boundary conditions assumed in the interpretation of the experimental results may not be correct owing to either depolarisation at the interfaces or interference at the interfaces by processes not related to the diffusion kinetics. Depolarisation may arise, for example in the charging curves described in Results: Sections 3 and 4 if the interface $x = 0$ has a capacity for adsorbing hydrogen comparable to the solubility of hydrogen in the metal, or else if there is exchange of hydrogen with the electrolyte. The problem may be compared to problems in the conduction of heat in which the interfaces are in contact with a mass of well stirred liquid, i.e., a "thermal capacity" is assigned to the interfaces. Solutions which involve the consideration of processes at the interfaces not related to the diffusion kinetics may be compared to problems in

heat conduction where an arbitrary variation in the surface temperatures is assumed.

If depolarisation at the interface $x = 0$ is assumed to take place so that a quantity Q of hydrogen raises the concentration at the interface from 0 to Q/M the boundary condition becomes:

$$\frac{\partial Q}{\partial t} = D \frac{\partial c}{\partial x} = -M \frac{\partial c}{\partial t} \quad (32)$$

instead of $dc/dx = 0$.

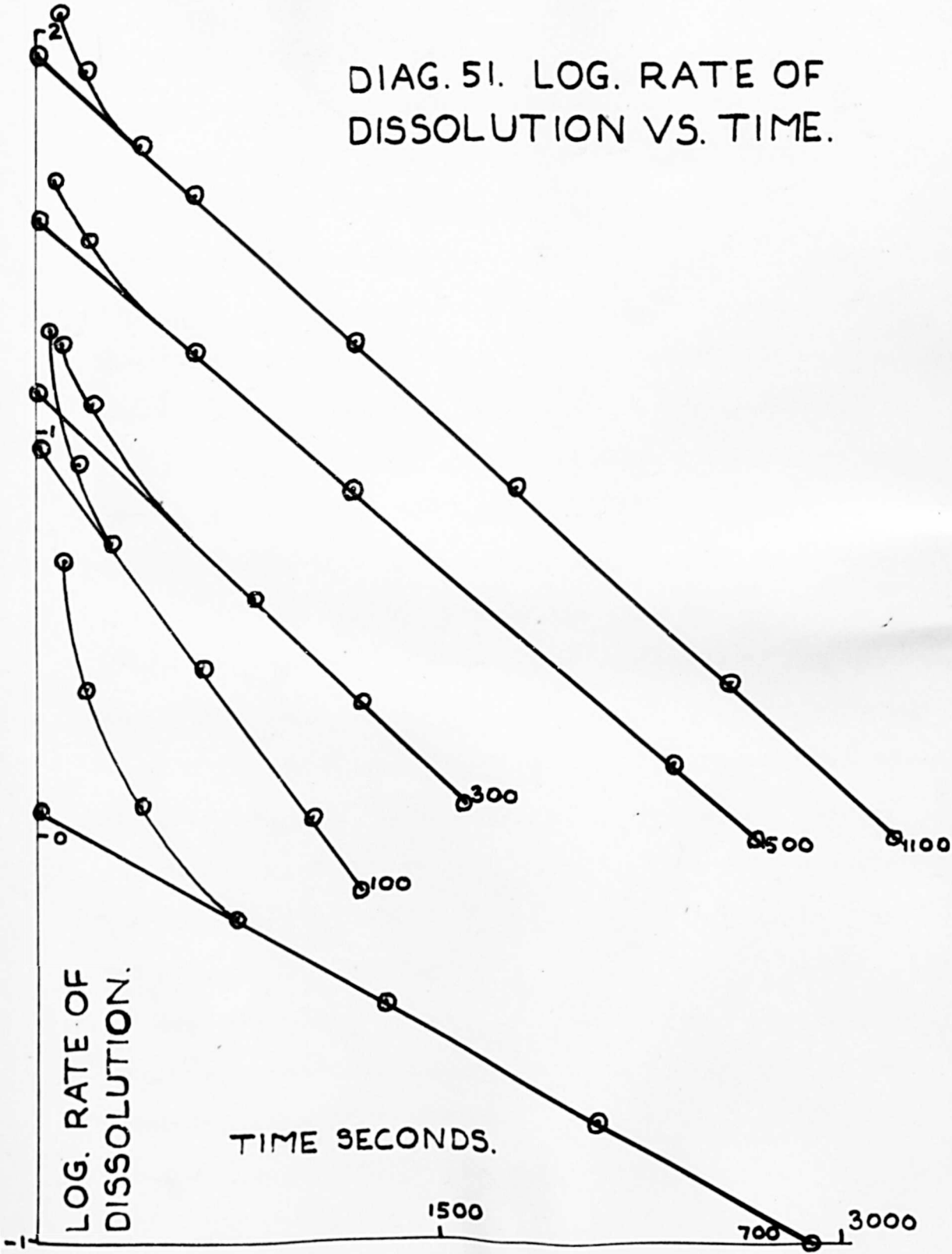
The application of solutions based on boundary conditions of this kind to the experimental results is difficult. Furthermore the "thermal capacity" of the interfaces could not readily be obtained so that systems were chosen in which the measurements could be made independently of any depolarisation at the interfaces.

A large variety of boundary conditions may arise if the concentration at the interface $x = 1$ is assumed to be an arbitrary function of the time. A large number of solutions therefore has to be considered if such deviations appear possible and the evaluation of the diffusion coefficient becomes very difficult. The only boundary condition of this type which will be further considered below corresponds to an exponential rise of the concentration c to the final value C i.e., $c = C (1 - e^{-\beta t})$ or in the notation of the Laplace transformation:

$$(p+\beta) \bar{c} = \frac{\beta C}{p} \quad (33)$$

In order to isolate the ingoing and outgoing interfaces the experiments with wires described in Results: Section 5 were carried out. Experiments with membranes always involve the simultaneous transition of atoms from the surface to the bulk and from the bulk to the surface. Under these conditions it is very difficult to isolate the diffusion kinetics from any slow processes occurring at both interfaces although this is theoretically possible. A system with a single surface such as the rod can, however, be charged and discharged and the kinetics of either the transition surface to bulk or bulk to surface can be investigated. From the comparison of the experimental plot of the amount dissolving vs. the time with the theoretical expression in diags. 45 and 46 it became apparent that the kinetics of the discharging process followed Fick's laws over nearly the whole range of the time that could be investigated. It is evident therefore that there is no slow stage during the transition of atoms from the bulk of the metal to the interface. Furthermore these curves show (diag. 46) that there is no appreciable depolarisation of the interface at potentials more positive than + 300 mv. or else that any depolarisation is so fast that it is virtually complete by the time measurements of the current can be made. Appreciable deviations from Fick's laws of diffusion are apparent, however, from the investigation of the charging process. (diag. 45). It is evident that the ingoing interface is

DIAG. 51. LOG. RATE OF DISSOLUTION VS. TIME.

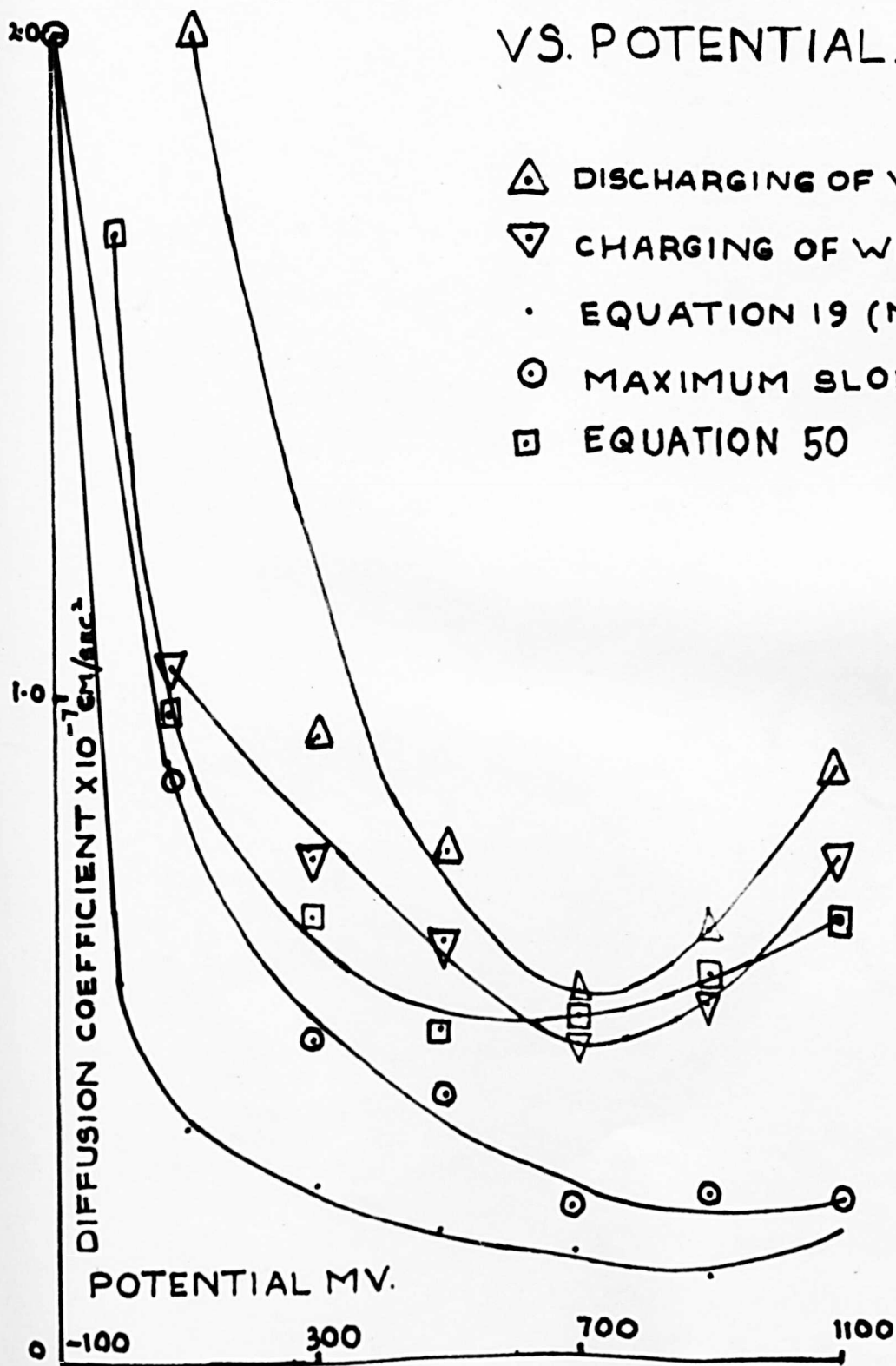


interfering with the diffusion process. The deviations pass through a maximum at about + 700 mv. and cannot be correlated with any increase or decrease in the apparent diffusion coefficient, i.e., a decreasing value of the diffusion coefficient does not necessarily give rise to negative deviations from Fick's laws of diffusion.

The use of double logarithmic axes to present the results, although convenient from the point of view of evaluation, is deceptive as it tends to emphasise the deviations. For the major part of the curves the amount dissolving varies exponentially with the time as can be seen by plotting the logarithm of the amount dissolving against the time. diag. 51. As can be seen from equation 29 the slope of the straight line at high values of time tends to $D\alpha_1^2$, where α_1 is the first root of $J_0(a\alpha) = 0$, if the system is obeying Fick's laws of diffusion. It may be noted that this means of evaluating the diffusion coefficient was rejected by Eyringer (53) since the rate of dissolution could not be accurately measured at high values of the time. The current passing can however be followed accurately and it is therefore feasible to measure the slopes of the lines.

The two means of evaluating the results give identical values for D . Furthermore the values of the diffusion coefficient obtained for the charging and the discharging process are almost identical, the values for the charging process being slightly smaller. If a slow transfer is assumed at the interface $x = a$ the boundary condition

DIAG. 52. DIFFUSION COEFFICIENT VS. POTENTIAL.



becomes

$$\frac{d\bar{c}}{dr} + h\bar{c} = \frac{hC}{r} \quad (34)$$

and the solution (60).

$$\bar{c} = \frac{hC I_0(qr)}{r[qI_1(qa) + hI_0(qa)]} \quad (35)$$

i.e.

$$\frac{c}{C} = 1 - \sum_{n=1}^{\infty} e^{-D\alpha_n^2 t} \frac{2hJ_0(r\alpha_n)}{a(h^2 + \alpha_n^2)J_0(a\alpha_n)} \quad (36)$$

where

$$\alpha J_1(a\alpha) = hJ_0(a\alpha)$$

The slope of the straight lines in diag. 51 at high values of the time therefore becomes $D\alpha_1^2$. It is evident that the interface is only interfering to a small extent in the diffusion process at high values of the time and it appears that the large deviations occurring at small values of the time cannot be explained by a process such as slow transfer at the ingoing interface which affects the results uniformly at all values of the time. It can be readily shown that the intercept of the lines in diag. 52 on the y-axis is

$$\frac{2DC h\alpha_1 J_1(a\alpha_1)}{a(h^2 + \alpha_1^2)J_0(a\alpha_1)} = \frac{2DC h^2}{a(h^2 + \alpha_1^2)} \quad (37)$$

The value of the concentration cannot be readily obtained however, since graphical integration of the current with respect to the time is difficult. Furthermore the solution applicable to small values of the time (which can be obtained by using asymptotic expansions of the Bessel functions in the Laplace transform equation (35)) gives an expression containing several terms of comparable magnitude at all values of the time. Further interpretation of the results is therefore difficult. It may be concluded, however, that if slow processes in the nature of the "radiation boundary condition" take place, then these will only occur at the ingoing interface, i.e., in the transition of atoms from the surface to the bulk of the metal.

With this limitation the possible effect of a slow transfer process on the determination of the concentration and the diffusion coefficient in the experiments with membranes, may now be considered. As has been shown above at the ingoing interface the boundary condition is

$$\frac{d\bar{c}}{dx} + h\bar{c} = \frac{hC}{\rho}$$

while at $x = 0$, $\bar{c} = 0$ at $t > 0$ as in the consideration of equation

13. This Laplace transform now becomes

$$\bar{c} = \frac{hC \sinh qx}{\rho [h \sinh q\ell + q \cosh q\ell]} \quad (37)$$

while the Laplace transform for the total amount of hydrogen that has diffused through the membrane (equation 15) becomes

$$\bar{Q} = \frac{hDCq}{\rho^2 [h \sinh q\ell + q \cosh q\ell]} \quad (38)$$

and therefore using the inversion theorem

$$c = \frac{hCx}{1+lh} - 2hC \sum_{n=1}^{\infty} \frac{e^{-D\beta_n^2 t} \sin\beta_n x}{[h+l(\beta_n^2+h^2)] \sin\beta_n l} \quad (39)$$

and

$$Q_{x=c} = \frac{DhC}{1+lh} \left[t - \frac{2(1+lh)}{D} \sum_{n=1}^{\infty} \frac{(1-e^{-D\beta_n^2 t})}{[h+l(\beta_n^2+h^2)] \beta_n \sin\beta_n l} \right] \quad (40)$$

where β_n are the roots of the equation

$$\beta_n \cot\beta_n l + h = 0$$

Furthermore the rate of steady permeation is

$$P_{\infty} = \frac{DhC}{1+lh}$$

Instead of equation 19 the time lag is given by

$$Q = \frac{DhC}{1+lh} \left[t - \frac{2(1+lh)}{D} \sum_{n=1}^{\infty} \frac{1}{[h+l(\beta_n^2+h^2)] \beta_n \sin\beta_n l} \right] \quad (41)$$

The diffusion coefficient cannot therefore be evaluated from a measurement of the time intercept alone. The limiting effect as the diffusion coefficient becomes large compared to the rate of transfer of material across the ingoing interface may however be considered. Under these conditions $h \rightarrow 0$ and $\beta_n l \rightarrow \pi/2$.

The time lag is therefore given by

$$Q = \frac{DhC}{1+lh} \left[t - \frac{l^2}{2D} \right] \quad (42)$$

It is evident that for a diffusion process almost completely controlled by the ingoing interface the values evaluated by the assumption of equation 19 i.e., a pure diffusion process are $1/3$ of the correct values. Furthermore instead of the value

$$c = \frac{hCl}{1+lh}$$

for the limiting concentration at the ingoing interface the value

$$\frac{P_{\infty} 6t \ell}{\ell^2} = \frac{\ell^2}{2t} \frac{hC}{1+lh} \frac{6t \ell}{\ell^2} = \frac{3hCl}{1+lh}$$

is obtained. The concentration evaluated as in Results: section 4 would therefore be three times too large if the diffusion were almost completely controlled by a slow transfer process at the ingoing interface. For intermediate values of h the diffusion coefficient and concentration will be in error to a smaller extent, the above values giving the maximum deviations.

The values of the diffusion coefficient as a function of the concentration, obtained in the experiments with membranes, may now be considered. (diag. 40). The results of two experiments at 20°C . and two experiments at 40°C . are indicated for foils 0.001 inch thick, and of one experiment at 30°C . on foil 0.003 inch thick. The reproducibility, subject to the limitations stated in Results: section 4 was satisfactory. It is a matter of extreme difficulty to explain the shape of the diffusion coefficient - concentration plot.

It is evident, if the thin membranes only are considered, that the diffusion coefficient shows a region of positive and a region of negative temperature coefficients. The values of the diffusion coefficient are smaller than those obtained in the experiments with wire electrodes, diag. 52. It is not strictly valid to compare the diffusion coefficient as a function of the potential as in diag. 52. The potential has been chosen rather than the concentration since there is a marked difference between the equilibrium concentrations at any potential observed in the experiments with wires and membranes. Diags. 38 and 49. It is nevertheless apparent that the variation of the diffusion coefficient with the concentration as well as the actual magnitude of the diffusion coefficient is smaller in the experiments with membranes than in those with wires. Moreover the diffusion coefficient does not appear to be a single valued function of the concentration. The most probable explanation of this behaviour is that the diffusion is in fact a composite process, and that the kinetics are dependent on the potential of the ingoing interface. At any one concentration, the lower part of the plot of diffusion coefficient against concentration in diag. 40 corresponds to more positive potentials than the upper part, and it is evident that the deviations therefore increase with increasing positive potential of the ingoing interface. Two explanations may be considered: firstly that two diffusion

processes, e.g., lattice and grain boundary diffusion, are present to a varying extent in the different potential regions, or secondly, that some interface reaction increasingly takes control as the potential becomes more positive. The regular nature of the deviations of the approach to the steady state of permeation at all potentials from that predicted on the basis of Fick's laws of diffusion (see below diag. 53) suggests that the first alternative is not applicable. It is evident that as the potential becomes more positive the discharge of protons on to the surface must become increasingly hindered and it was considered at the time of carrying out these experiments that an explanation along these lines was most probable.

The divergence of the values of the diffusion coefficient at any concentration may again be considered on the basis of the "radiation boundary condition". As has been seen above the apparent value of the diffusion coefficient evaluated according to equation 19 is lower than the actual value, and the deviation increases as the diffusion becomes increasingly controlled by the ingoing interface, until, for a process almost completely controlled by a slow transfer process, the diffusion coefficient is $1/3$ of its correct value. The general shape of the plot of diffusion coefficient against concentration is therefore correct on the basis of this interpretation, i.e., as the potential becomes more positive the deviations increase. It is clear however, that this explanation is not adequate for

explaining the fact that diffusion is not a single valued function of the concentration. If the values of the diffusion coefficient in the lower part of the diagram are multiplied by 3, the maximum error on the basis of this explanation, the values at the more positive potential at any one concentration, for the experiments at 40°C., still fall below the values at the less positive potentials. The deviations are larger than is suggested by this procedure, since any increase in the diffusion coefficient automatically displaces the point to a lower concentration. Although the explanation would be adequate for explaining the results obtained at 20°C. and at 30°C it seems unlikely that a different explanation would hold at lower temperatures than at higher temperatures. It may be concluded that if slow transfer processes occur at the ingoing interface then these processes cannot alone explain the shape of the diffusion coefficient-concentration diagram.

Although the actual shape of the plot of the diffusion coefficient against the concentration can suggest details of the diffusion mechanism it cannot give precise information about any deviation from the simple diffusion kinetics. Further information can, however, be obtained by studying the kinetics as a function of the thickness of the membrane.

The results of the measurements with membranes 0.003 inch thick at 30°C may be compared to the measurements with the thinner membranes.

As has been stated above (Results: section 4) satisfactory measurements could not be made with membranes 0.001 inch thick at 30°C. The results obtained with the thicker membranes can however be compared with those on the thinner membranes at 20°C. and at 40°C. since the position only of the curves will be considered. It is evident from diag. 40 that the values of the diffusion coefficient lie uniformly too high, i.e., both at the less positive, and at the more positive potential at any one concentration, the diffusion coefficient is larger than would be expected from the measurements carried out with the thinner membranes. The variation of the time lag with thickness (equation 19) is therefore less rapid than indicated by the term and it may be concluded that the diffusion process is not completely controlled by the transition through the bulk of the metal. The consideration of the variation of the time lag with thickness again points against the presence of a slow transition at the ingoing interface since for this case also the time lag varies as the square of the thickness. Further information cannot, however, be obtained from a consideration of diag. 40.

It was considered that an analysis of the potential-time curves (Results: section 4) could give information as to the nature of the deviations from the simple diffusion step through the bulk of the metal. As has been shown above the diffusion coefficient can be assumed to be correct to a factor smaller than 3. (Equations 19, 42). Furthermore if the deviations are independent of the potential (or

nearly so) then the effect of any uncertainty in the diffusion coefficient on the concentration-potential curves will largely be eliminated by considering a concentration ratio (as in diags. 42, 43 and 44). In order to ensure that only the behaviour in the more positive potential regions would be considered (corresponding to the lower part of the diffusion coefficient-concentration curves) the ingoing interface was maintained at a potential of +100mv. during the determination of the charging curves.

As has been noted in Results: section 4 the deviations are consistently negative. The deviations decrease with increasing temperature and pass through a maximum at a point corresponding to a potential of about +700 mv. on the charging curves. Since the experimental and theoretical curves at 30°C and at 40°C coincide at high values of the time it appears to be improbable that the deviations are caused by depolarisation at the outgoing interface of the kind covered by equation (32), i.e., from the boundary condition $dc/dx = 0$ at $x = 0$ for $t > 0$. Such deviations are not however ruled out at 20°C as can be seen from diag. 42. It appears probable, however, that the deviations cannot be explained by any alteration in the boundary condition at the outgoing interface. The variation of the diffusion coefficient with the concentration must also be considered in an examination of the deviations. The experiments with wire electrodes (diag. 52) suggest that the deviations should increase and then again decrease as is actually

found to be the case. Diag. 40 shows that the variation of the diffusion coefficient with the concentration decreases with the temperature and therefore the extent of the deviations should decrease with the temperature. Comparison of these experiments to the diffusion coefficients obtained in the experiments with the wire electrodes is not strictly valid however, since the concentrations at any one potential in the two experiments do not agree. Although the value of the diffusion coefficient used in the interpretation of the charging curves is probably not greatly in error (since it already lies in the upper part of diag. 40) further deductions from the values of the diffusion coefficient at positive potentials (diag. 40) are not valid since these values presumably do not correspond to a true diffusion step. It is probable, however, that the diffusion coefficient decreases down to about +200 mv. so that the deviations of the experimental from the theoretical lines in Diags. 42, 43, and 44 should increase with the time to higher values of the time than actually observed. It appears unlikely therefore, that the deviations can be explained on the basis of the variation of the diffusion coefficient with the concentration. It may be noted that the deviations, as in the charging of the wire electrodes, pass through a maximum at a point corresponding to a potential of about +700 mv. so that the deviations are presumably again associated with a slow process at the ingoing interface.

Further interpretation of the charging curves on the basis of a slow process at the ingoing interface is difficult. The Laplace transform of the solution assuming the "radiation boundary condition" is

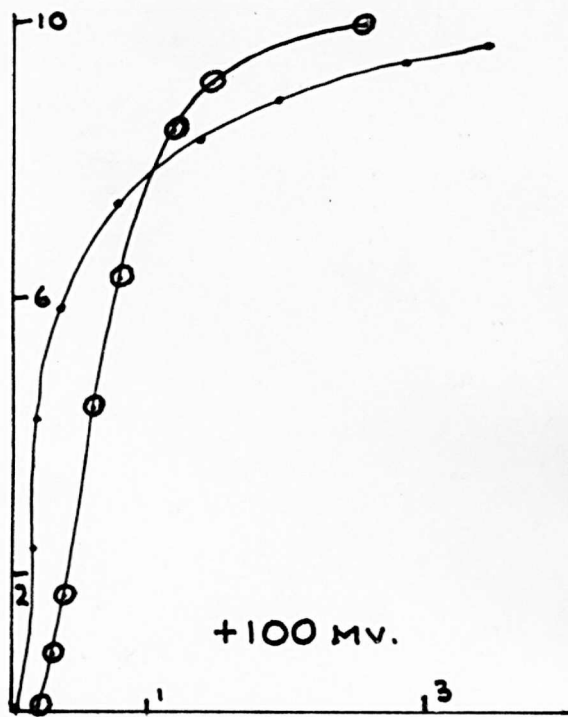
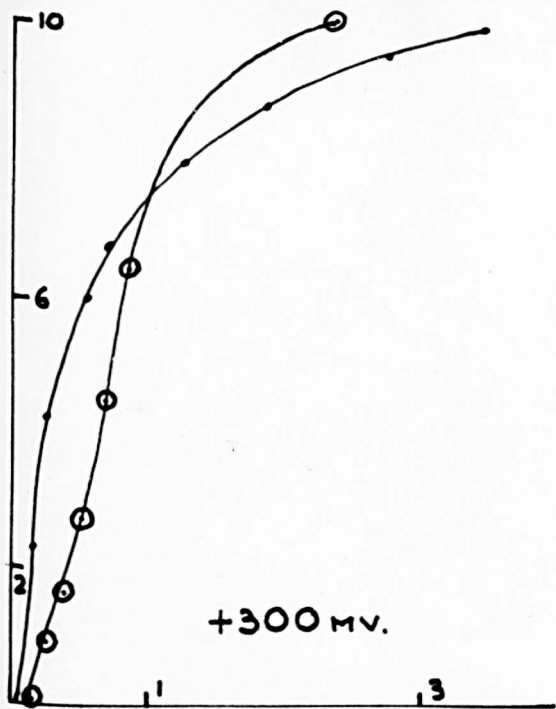
$$\bar{c} = \frac{hC \cosh qx}{\rho [q \sinh q\ell + h \cosh q\ell]} \quad (43)$$

giving

$$c = 2hC \sum_{n=1}^{\infty} \frac{e^{-D\alpha_n^2 t} \cos \alpha_n x}{[\ell(\alpha_n^2 + h^2) + h] \cos \alpha_n \ell}, \quad \alpha_n \tan \alpha \ell = h \quad (44)$$

The use of this equation is difficult. The exponential terms in the series obtained by using the expansions for the hyperbolic functions in equation (43), in an analogous manner to equation 11, have coefficients which are complicated functions of q . Although the first few terms can be readily evaluated the expression obtained, for the probable values of h and D is not as useful as equation 12. Consideration of the probable value of α_1 does not give any indication as to the possible value of h at the ingoing interface since a comparatively small alteration in D can cause a very large change in h .

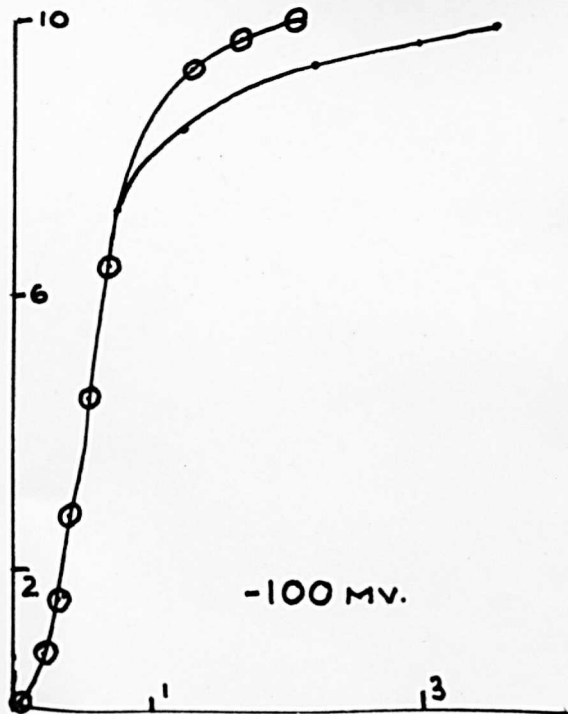
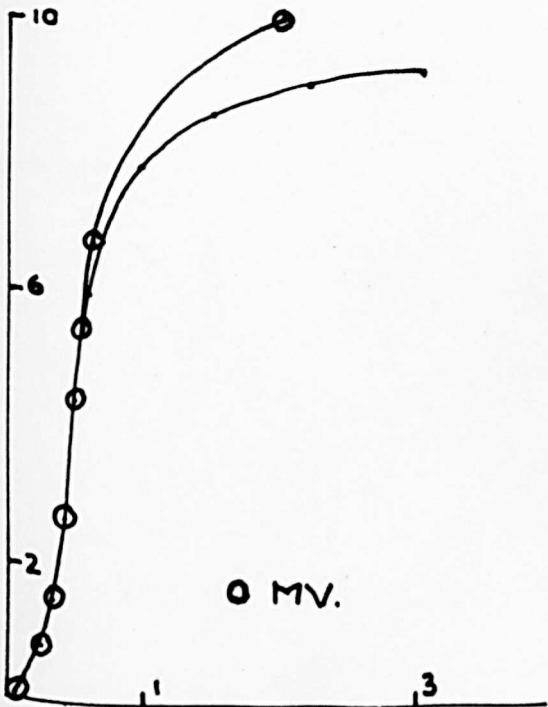
The kinetics cannot therefore readily be elucidated by studying a system of this kind and a relatively simple system must be chosen if the effect of the ingoing interface is to be investigated. The approach to the steady state of diffusion actually used in the evaluation of the diffusion coefficient, according to equation 19,

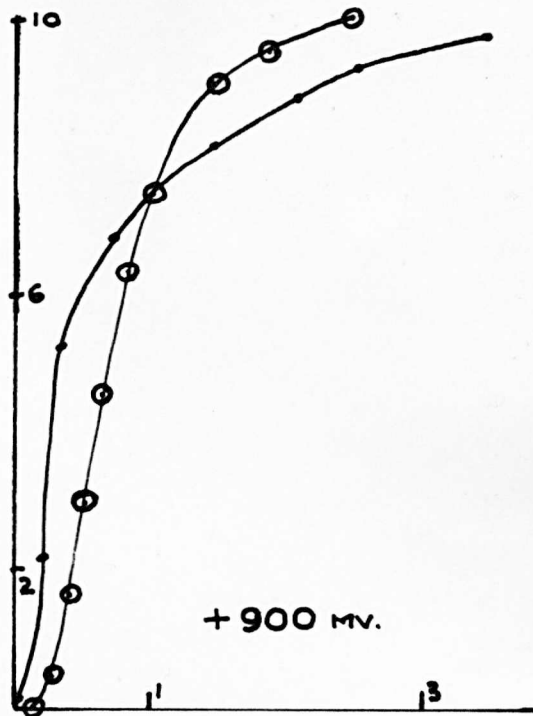
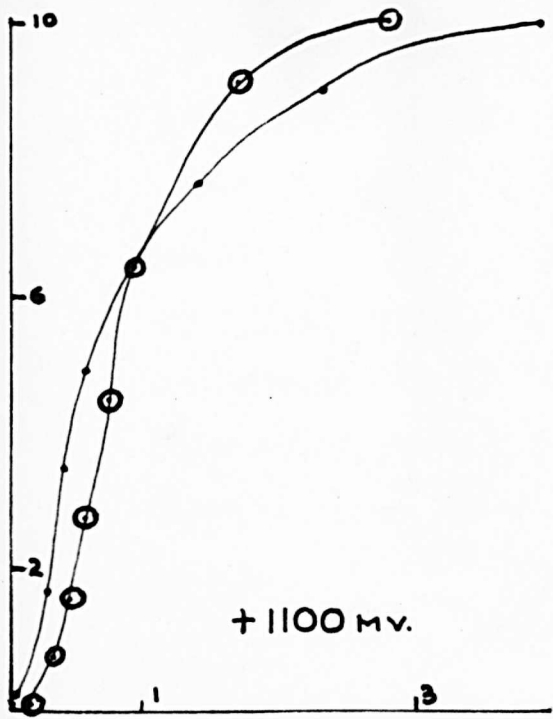


P/P₀

DIAG. 53.

TIME

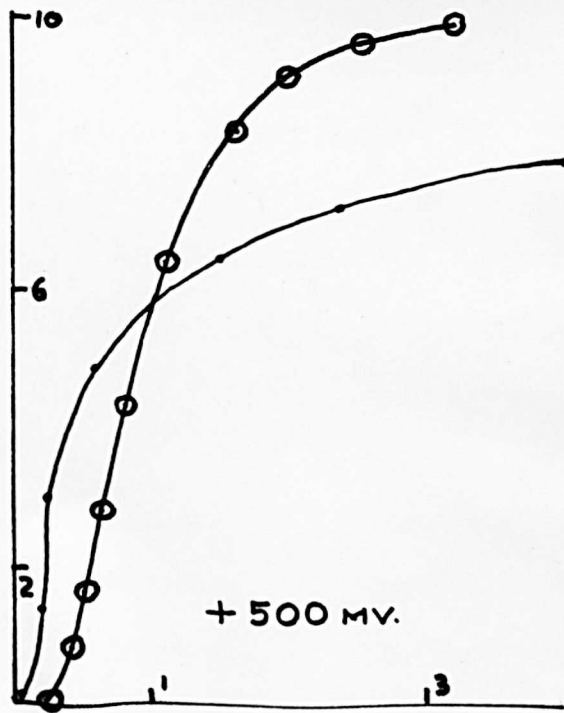
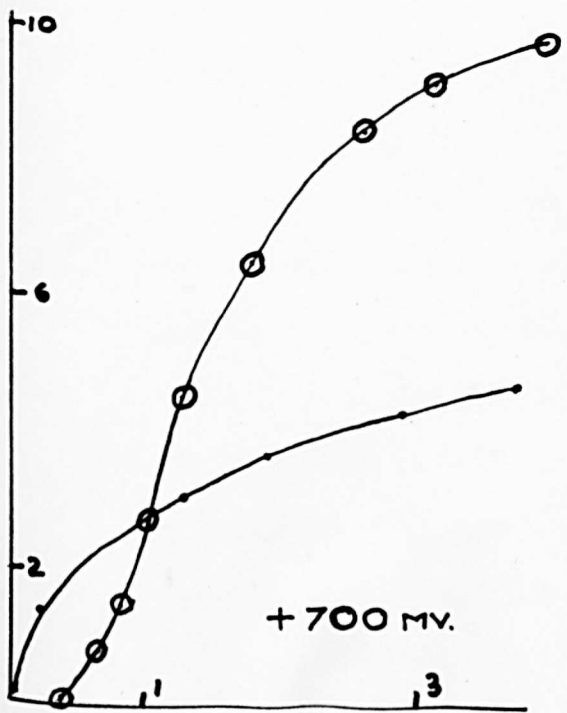




TIME →

↑ P/P₀

DIAG. 53.

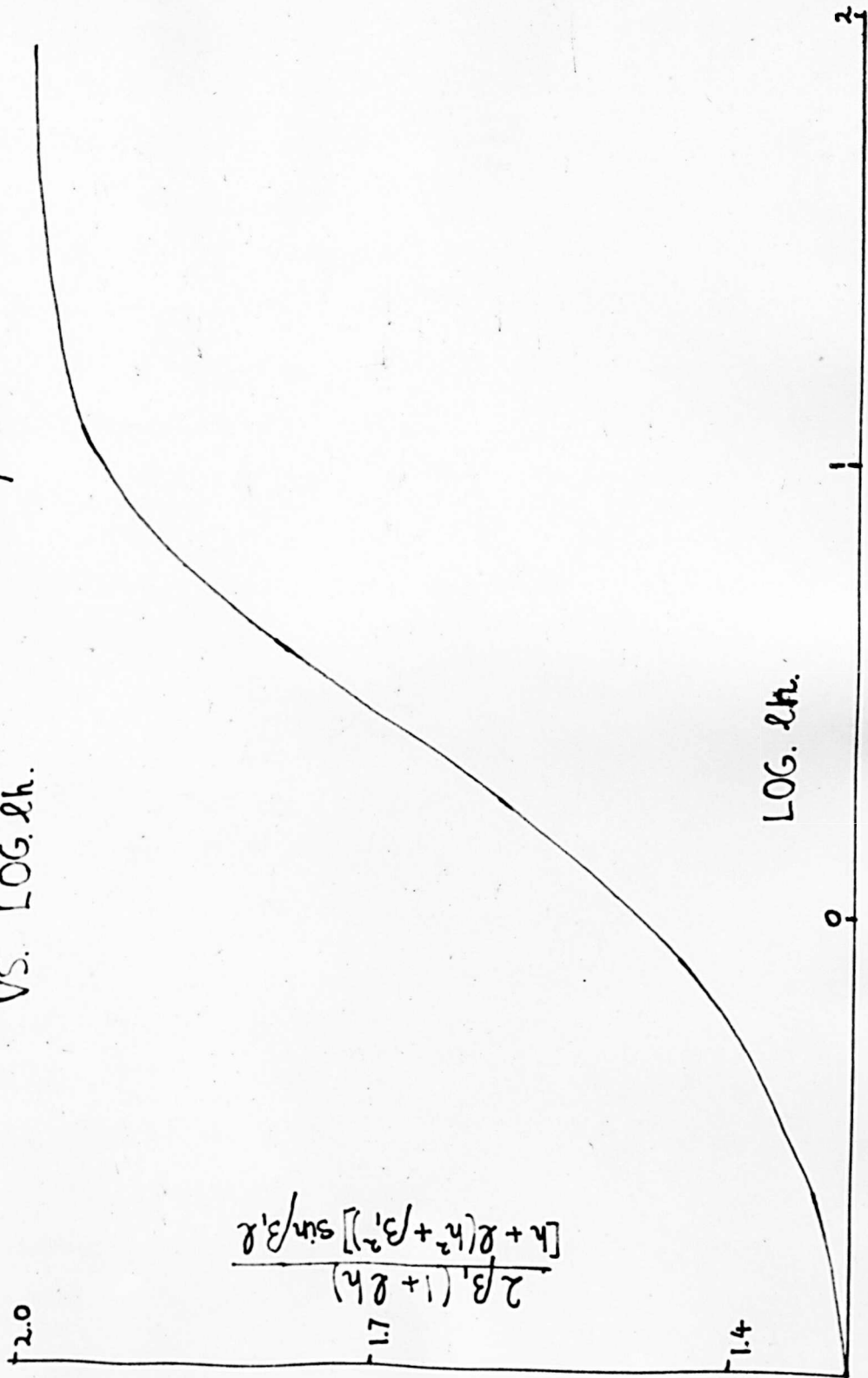


appeared to be suitable. The permeation rate could be instantaneously measured as a function of the time with the methods evolved in the experiments described above. Accordingly the experimental results can be readily compared to the theoretical expressions both at small, and at large values of the time. The use of a single determination avoids unnecessary ambiguity and any arbitrary variations of the concentration at the ingoing interface (suggested by the shape of the experimental results in diags. 42, 43, and 44) can be more readily detected.

The comparison of the approach to the steady state experimentally observed to that predicted theoretically is shown in diag. 53, for an experiment at 40°C . The theoretical values (marked \odot) were calculated according to equation 21 using the value of the diffusion coefficient evaluated according to equation 19. In order to obtain a comparison between the determinations at different potentials the permeation rates are expressed as a ratio of the final permeation rate and the values of the time are expressed as a ratio of the time at which the experimental and theoretical curves cross. This procedure is arbitrary and tends to minimise the apparent extent of the deviations. It is evident that the experimental values at positive potentials show positive deviations from the theoretical curves at small values of the time and then show negative deviations. At the reversible potential and at negative potentials the experimental curves only show negative deviations at large values of the time. The extent of the

deviations increases with decreasing positive potential and passes through a maximum when the ingoing interface is at + 700 mv. (in agreement with the measurements with wire electrodes, see above.) At very positive and at negative potentials the deviations are comparatively small and the system appears to follow the predictions based on a simple diffusion step relatively well. Furthermore the experimental curves at small values of the time indicate a diffusion process with a higher diffusion coefficient than that given by equation (19) and this suggests that the positive and the negative deviations are caused by a decreasing value of the diffusion coefficient with increasing concentration. As has been noted above the charging and discharging of the wire electrodes (Results: section 5) indicate that the diffusion coefficient at first falls and then increases with the concentration (diag. 52). A comparison of the diffusion coefficient as a function of the potential for the experiments in Results: sections 4 and 5 is not strictly valid (see above) since the diffusion coefficient as a function of the concentration should be considered. The method of measurement of the diffusion coefficient in the experiments with wire electrodes ensured that it was being determined at practically constant concentration so that any effect of a variation of the diffusion coefficient with the time was at a minimum. In addition the concentration interval was smaller than that in the determinations in the experiments with membranes. It appeared probable (from a consideration of diag. 52) that at small

DIAG. 54. VALUES OF $\frac{2\beta_1(1+2h)}{[h+2(\beta_1^2+h^2)]\sin\beta_1}$
 VS. LOG. $2h$.



positive potentials and at the reversible and negative potentials, the permeation rate at large values of the time (where any concentration variation was again reduced) should vary exponentially with the time at a larger rate than that indicated by the mean value of the diffusion coefficient.

It can be readily shown from equation 37 or 39 that for the general case of a diffusion process coupled with a slow transition at the ingoing interface

$$P_{x=0} = \frac{hDC}{1+lh} - 2hDC \sum_{n=1}^{\infty} \frac{\beta_n e^{-D\beta_n^2 t}}{[h + l(\beta_n^2 + h^2)] \sin \beta_n l}$$

and hence

$$\frac{P_{\infty} - P}{P_{\infty}} = 2(1+lh) \sum_{n=1}^{\infty} \frac{\beta_n e^{-D\beta_n^2 t}}{[h + l(\beta_n^2 + h^2)] \sin \beta_n l} \quad (45)$$

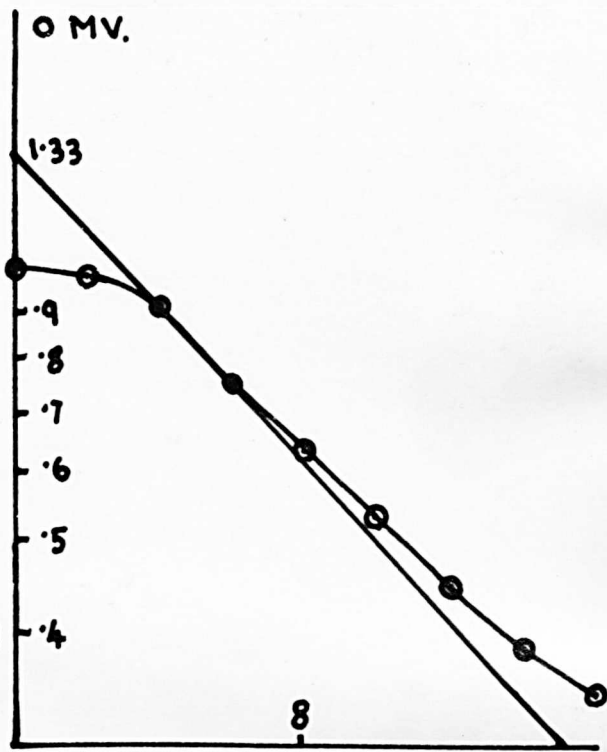
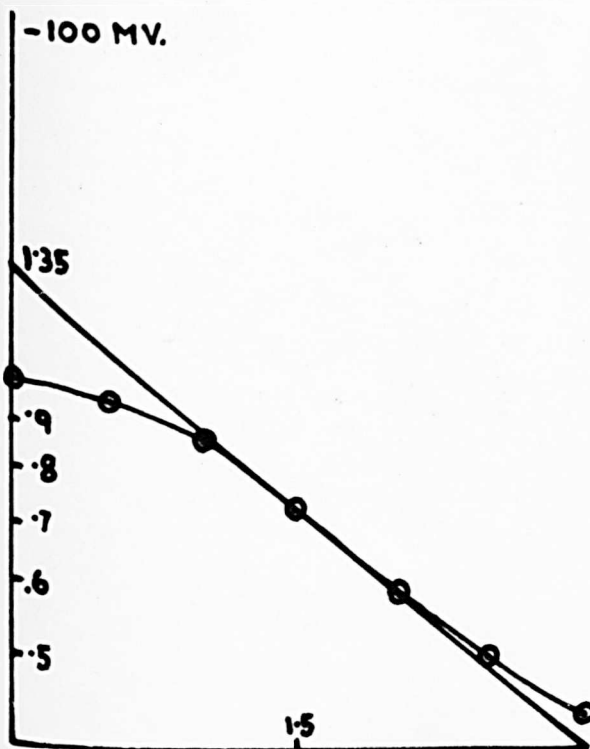
If the logarithm of the left hand side of equation (45) is plotted against the time then in the limit at high values of the time a line of slope $D\beta_1^2$ is obtained with an intercept

$$I = \frac{2(1+lh)\beta_1}{[h + l(\beta_1^2 + h^2)] \sin \beta_1 l} \quad (46)$$

on the $\log \frac{P_{\infty} - P}{P_{\infty}}$ axis. The value of this intercept as a function of h is shown in diag. 54. The variation is from 2 for a pure diffusion process to 1.3 for a process almost completely controlled by a slow transition across the ingoing interface.

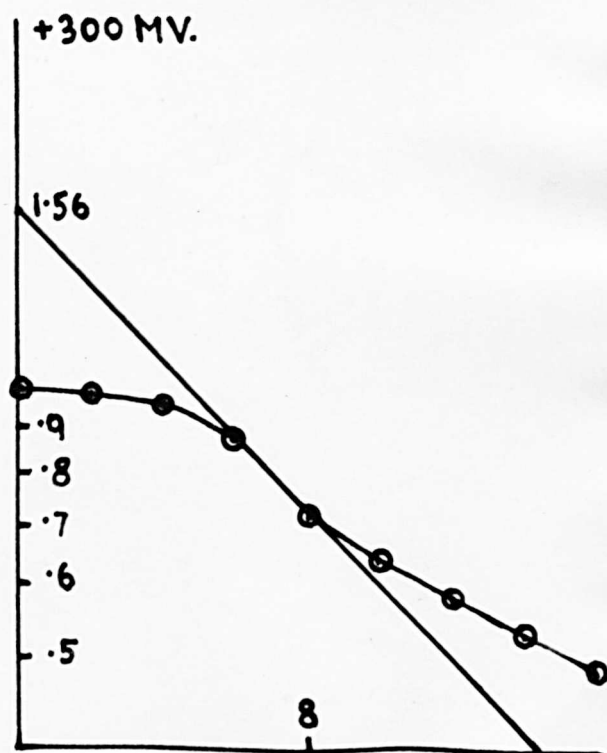
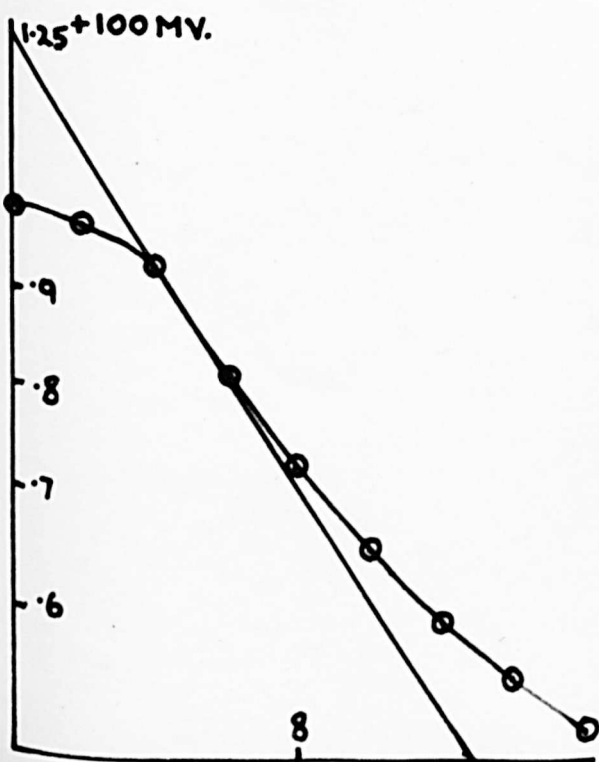
Values of $\log \frac{P_{\infty} - P}{P_{\infty}}$ for the experimental data were plotted against the time. The shape of the experimental curves did not agree

DIAG. 55 LOG. $\frac{P_{\infty} - P}{P_{\infty}}$ VS. TIME

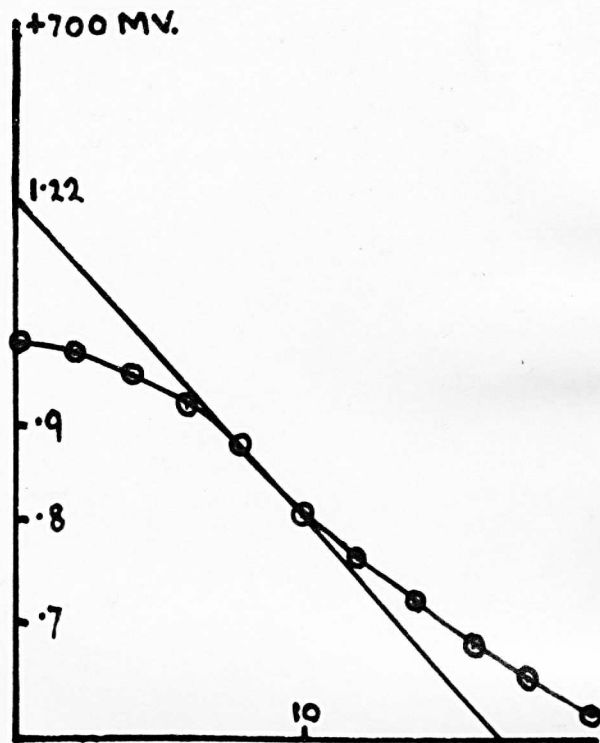
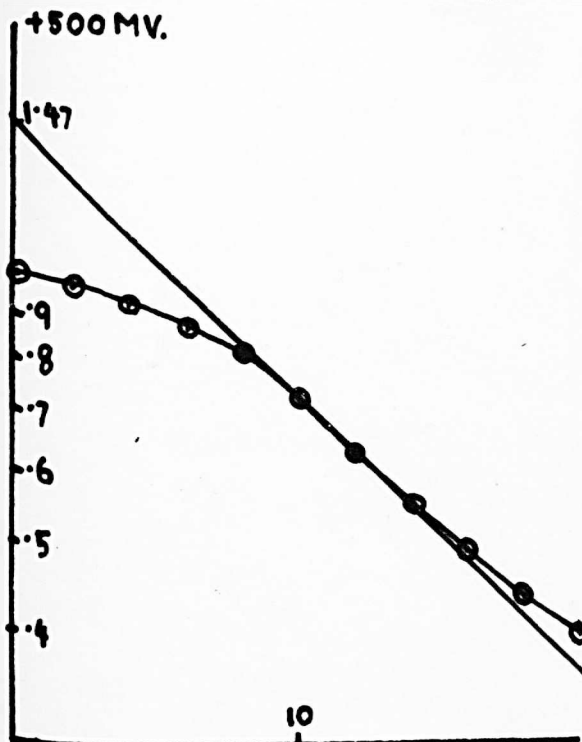


$\frac{P_{\infty} - P}{P_{\infty}}$

TIME (SECONDS)

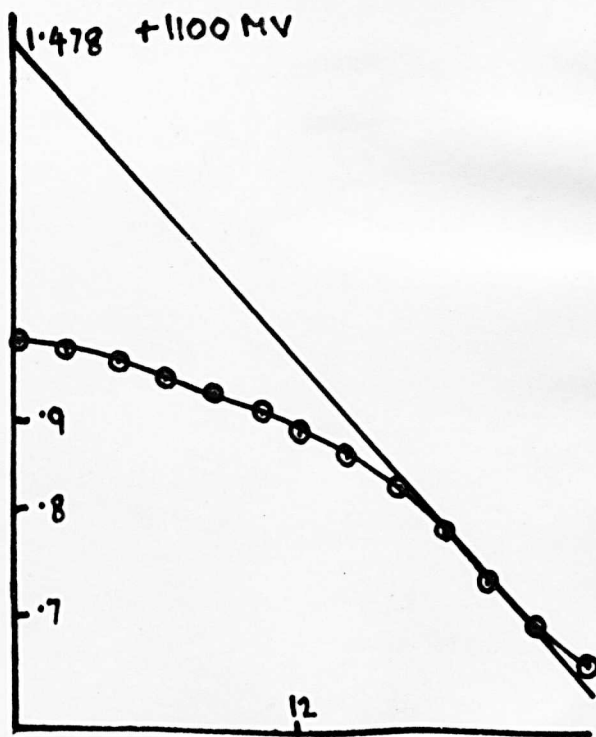
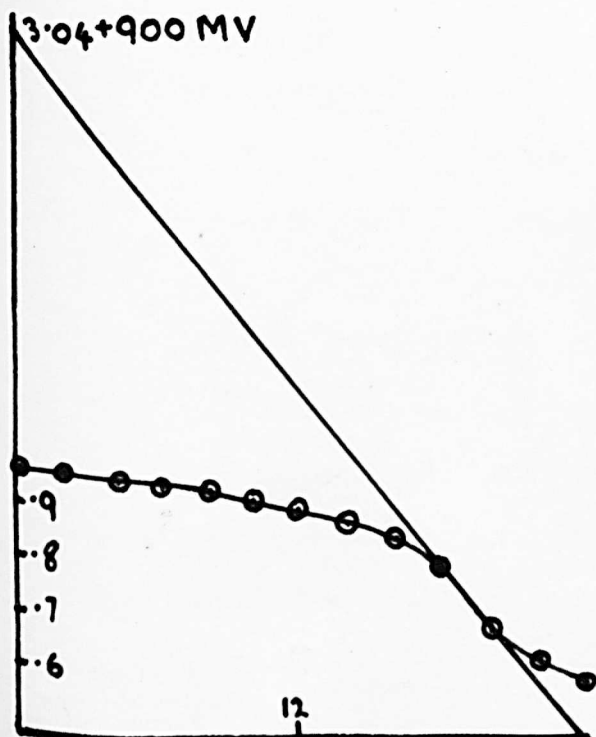


DIAG. 55 LOG. $\frac{P_0 - P}{P_0}$ VS. TIME



$\frac{P_0 - P}{P_0}$

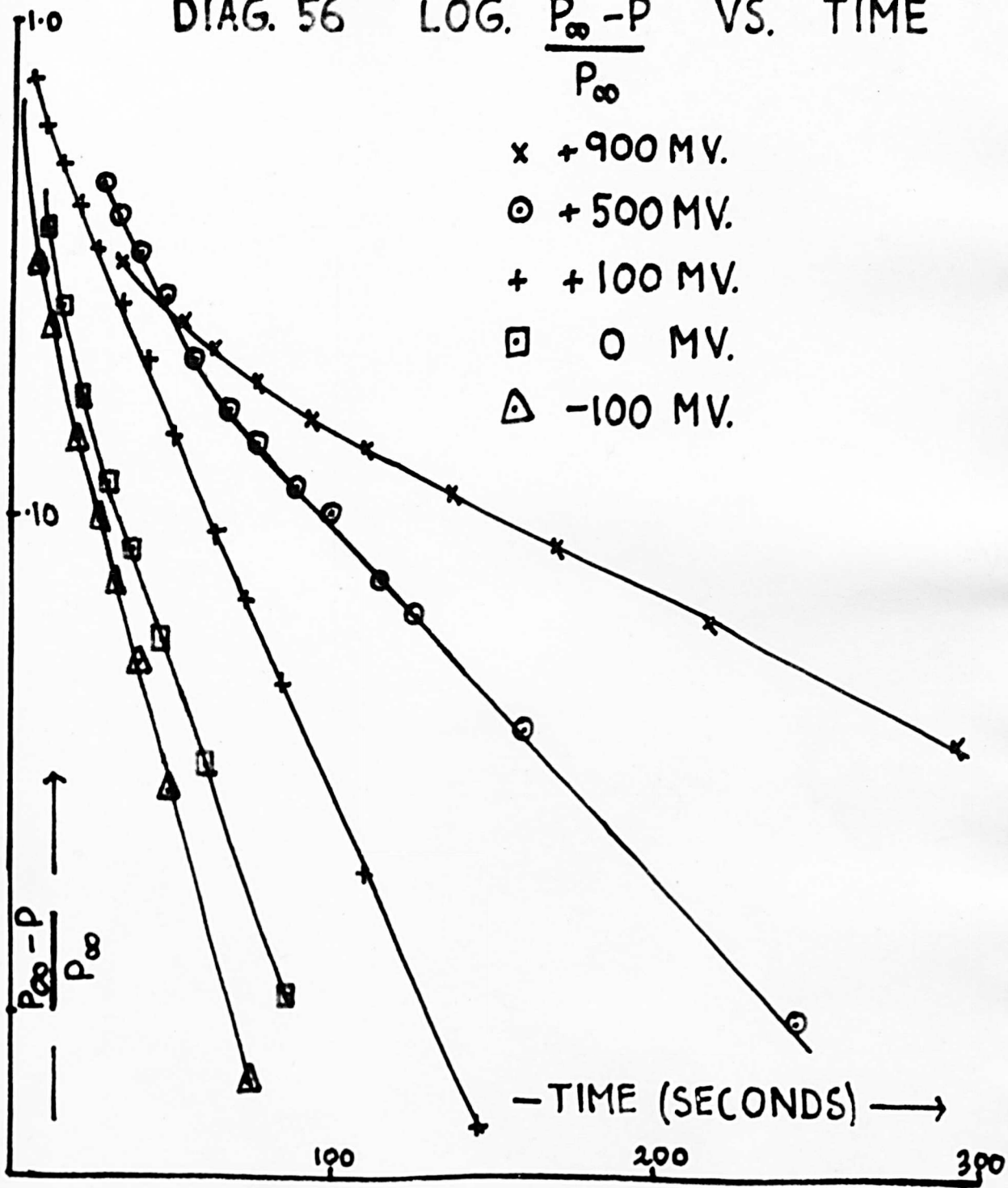
TIME (SECONDS)



with that predicted from equation 45. At small values of the time a sigmoidal curve was obtained as is shown in diag. 55 for an experiment of 40°C. The extent of the initial (slowly varying) part of the sigmoid decreased with decreasing temperature until at 20°C it was hardly apparent. The results nevertheless indicate that at small values of the time the values of $\log \frac{P_{\infty} - P}{P_{\infty}}$ fall away from the line drawn through the maximum slope of the curve indicating that a series is operative. According to the magnitude of the diffusion coefficient the first term only of the series (equation 45) should be operative at the values of the time at which an inflexion is apparent. A line drawn asymptotically to the curves at this point should therefore have an intercept on the $\log \frac{P_{\infty} - P}{P_{\infty}}$ axis given by equation 46. The value of the intercept at 40°C is of the order 1.5 at 30°C of the order 1.1 and at 20°C of the order 1.0. It is evident therefore that the experimental data do not fit the predictions based on equation 45. If the slope of the curves at the inflexion is assumed to be $\frac{D\pi^2}{l^2}$ then the values of the diffusion coefficient obtained are more nearly in agreement with the values obtained with wire electrodes than are those given by equation 19. (diag. 52.)

The lower part of the sigmoid, i.e., the positive deviations from the straight line could be caused by a decreasing value of the diffusion coefficient. As has been stated above the final value of the slope of the $\log \frac{P_{\infty} - P}{P_{\infty}}$ vs time curve should for small positive and for

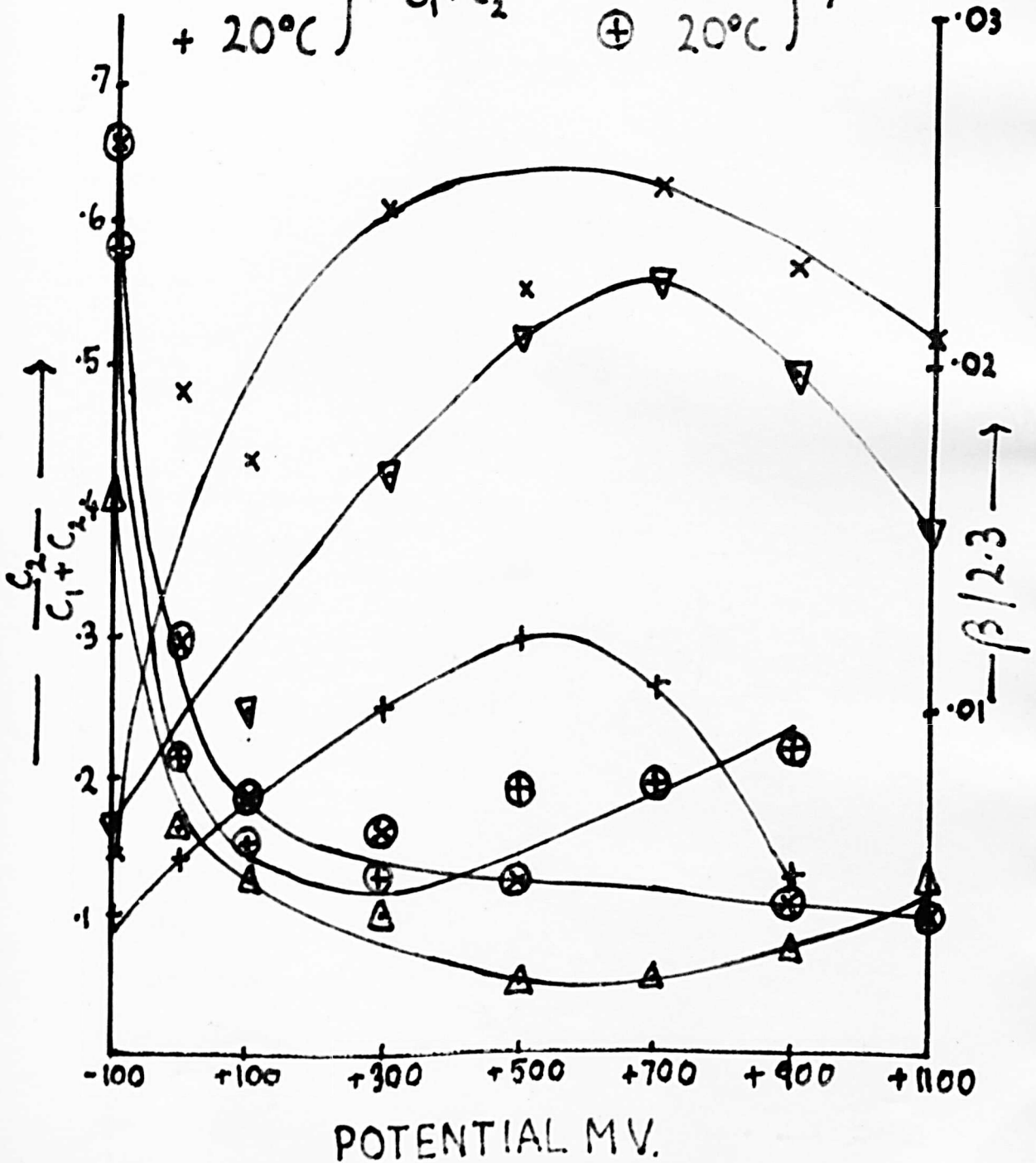
DIAG. 56 LOG. $\frac{P_{\infty} - P}{P_{\infty}}$ VS. TIME



DIAG. 57 $\frac{C_2}{C_1+C_2}$ VS. POTENTIAL

β VS. POTENTIAL

\times 40°C } $\frac{C_2}{C_1+C_2}$ \otimes 40°C } β
 ∇ 30°C } Δ 30°C }
 $+$ 20°C } \oplus 20°C }



negative potentials and at large values of the time be larger than that indicated by the value of the diffusion coefficient. At all potentials the slope should be of the order of the slope expected from the diffusion coefficient. In diag. 56 the values of $\log \frac{P_{\infty} - P}{P_{\infty}}$ are plotted against the time at high values of the time for an experiment at 40°C. As can be seen good straight line plots are obtained indicating an exponential process. The value of the intercepts on the $\log \frac{P_{\infty} - P}{P_{\infty}}$ axis in this and in all the other experiments lies in the vicinity of 0.5 which is in complete disagreement with the theoretical predictions (equation 46). Moreover, the values of the slopes of the lines are not in agreement with the predictions from the diffusion coefficient. For the lines in diag. 56 the "diffusion coefficient" is of the order 3×10^{-9} whereas the mean value for the charging and discharging of the wire electrodes is of the order 7×10^{-7} . It is evident that the exponential process observed at high values of the time is not related to the diffusion process. The fact is brought out clearly when the values for the 0.003 inch thick membranes are compared to those for the 0.001 inch thick membranes, diag. 57. The accuracy of the experiments is not sufficiently high in order to carry out any definite interpretation, but it is evident that the exponential process at large values of the time is not related to the thickness of the membrane, i.e., not related to the diffusion process. This process is therefore to be associated with the ingoing interface. It is evident that the rate of the process increases with decreasing positive potential and shows a rapid increase at negative potentials.

Presumably the process is to be associated with the slow establishment of the equilibrium concentration on the ingoing interface.

It is to be noted that there is an exponential process, slow compared to the diffusion, even at negative potentials so that there is a time lag in the establishment of the final steady concentration at cathodic potentials.

The interpretation is in essential agreement with the measurements on the wire electrodes. As has been noted above the deviations occurring during the charging of the wires, in comparison to the discharging, cannot be explained on the basis of a slow transition at the ingoing interface. The marked deviations occur at small values of the time and are substantially complete after ca. 400 seconds after the beginning of a determination (diag. 51). It is evident that this is in agreement with the measurements on the membrane electrodes (diag. 56), and that the deviations are again due to the slow establishment of the equilibrium surface concentration. It may be noted that the charging of the wire electrodes (diag. 45), the interpretation of the charging curves (diags. 42, 43, and 45), and the approach to the steady state of permeation (diag. 53) all show that the deviations from Fick's laws of diffusion are at a maximum when the ingoing interface is at about +700 mv. and that the deviations are due to a slow process at the ingoing interface which is not related to the diffusion step through the bulk of the metal. The analysis of the approach to the steady state of permeation shows that this process is due to an exponential approach to the equilibrium surface concentration at the ingoing interface.

In order to carry the interpretation of diags. 55 and 56 further the theoretical expression must be considered. The surface concentration on the ingoing interface approaches the equilibrium value exponentially and therefore the boundary condition at $x = 1$ may be written

$$c = C(1 - e^{-\beta t})$$

where β is the slope of the lines in diag. 56, the boundary condition at $x = 0$ being $c = 0$ for $t > 0$. Similar problems have been solved in the literature by the use of Duhamel's theorem, the solution for the surface concentration $\varphi_1(t)$, $\varphi_2(t)$ being derived from that for the surface concentrations c_1 and c_2 . For the above problem the use of Duhamel's theorem gives an expression containing a divergent series before the term $e^{-\beta t}$ and this expression cannot therefore be summed by the use of the calculus of residues.

The problem can, however, again be solved by the use of the Laplace transformation. The transform of the boundary condition at $x = 1$ is

$$(\rho + \beta)\bar{c} = \frac{\beta C}{\rho}$$

and the transform of the solution

$$\bar{c} = \frac{\beta C \sinh \rho x}{\rho(\rho + \beta) \sinh \rho l} \quad \bar{P} = \frac{D\beta C q}{\rho(\rho + \beta) \sinh \rho l} \quad (47)$$

The solution is therefore

$$P = \frac{-DC\beta}{2\pi i} \int_{\gamma - i\infty}^{\gamma + i\infty} \frac{e^{\rho t} q d\rho}{\rho(\rho + \beta) \sinh \rho l}$$

The residue at the point $p = 0$ is $1/l\beta$. At the point $p = -\beta$ the residue is $\frac{e^{-\beta t}}{-l\beta}$ and at the pole $q = \frac{n\pi i}{l}$ the residue is

$$\frac{-2(-1)^n e^{-\frac{n^2 \pi^2 D t}{l^2}}}{\left[\beta - \frac{n^2 \pi^2 D}{l^2}\right] l}$$

The complete solution is therefore

$$P_{x=0} = DC\beta \left[\frac{1}{l\beta} - \frac{e^{-\beta t}}{l\beta} - 2 \sum_{n=1}^{\infty} \frac{e^{-\frac{n^2 \pi^2 D t}{l^2}} (-1)^n}{\left[\beta - \frac{n^2 \pi^2 D}{l^2}\right] l} \right]$$

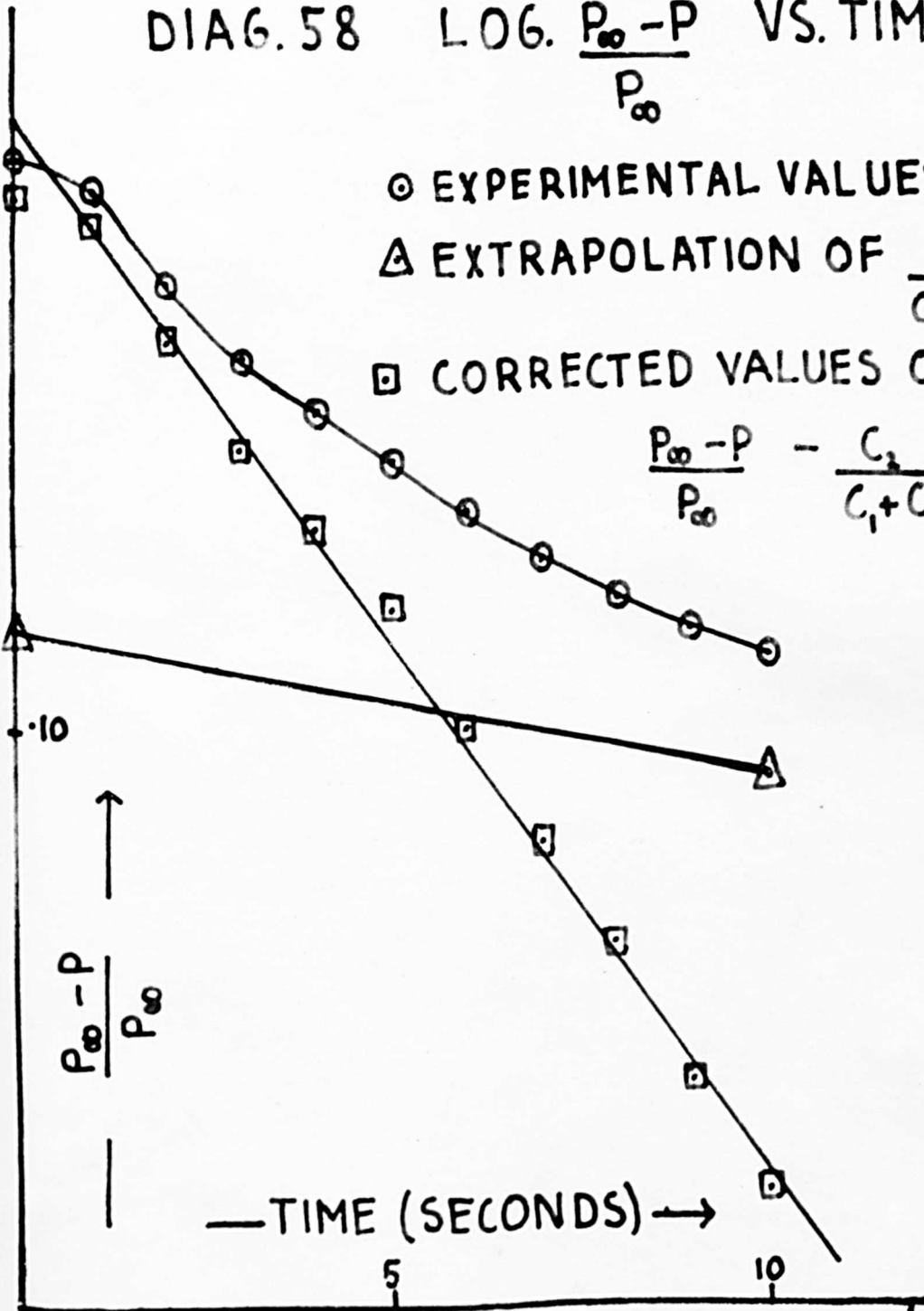
or in the form of equation (45)

$$\frac{P_{\infty} - P}{P_{\infty}} = e^{-\beta t} + 2 \sum_{n=1}^{\infty} \frac{(-1)^n \beta e^{-\frac{n^2 \pi^2 D t}{l^2}}}{\beta - \frac{n^2 \pi^2 D}{l^2}} \quad (48)$$

The coefficient of the term $e^{-\beta t}$ is unity and hence the intercept of the plot of $\log \frac{P_{\infty} - P}{P_{\infty}}$ vs. time in diag. 56 on the $\log \frac{P_{\infty} - P}{P_{\infty}}$ axis should be unity. Since the actual value is of the order 0.5 it may be concluded that the establishment of the final constant surface concentration C may be represented by an initial rapid change C_1 followed by a slow variation $C_2 (1 - e^{-\beta t})$ where $C = C_1 + C_2$.

The approach to the steady state of permeation therefore contains a term due to the initial rapid change C_1 , as well as the term (equation 48) due to the slowly varying concentration C_2 . The

DIAG. 58 LOG. $\frac{P_{\infty} - P}{P_{\infty}}$ VS. TIME



contribution due to C_1 may be deduced from equation 13. The transform is

$$P = \frac{DC_1 q \cosh qx}{n \sinh ql}$$

and therefore

$$P_{x=0} = \frac{DC_1}{l} + \frac{2DC_1}{l} \sum_{n=1}^{\infty} (-1)^n e^{-\frac{n^2 \pi^2 Dt}{l^2}} \quad (49)$$

The combined permeation rate due to the concentrations C_1 and C_2 is therefore given by

$$P_{x=0} = \frac{D[C_1 + C_2]}{l} - \frac{DC_2 e^{-\beta t}}{l} - \frac{2D}{l} \sum_{n=1}^{\infty} \left[\frac{\beta C_2}{\beta - \frac{n^2 \pi^2 D}{l^2}} - C_1 \right] (-1)^n e^{-\frac{n^2 \pi^2 Dt}{l^2}}$$

or in the form of equation 48

$$\frac{P_{\infty} - P}{P_{\infty}} = \frac{C_2 e^{-\beta t}}{C_1 + C_2} + 2 \sum_{n=1}^{\infty} \left[\frac{\beta C_2}{[C_1 + C_2] \left[\beta - \frac{n^2 \pi^2 D}{l^2} \right]} - \frac{C_1}{C_1 + C_2} \right] (-1)^n e^{-\frac{n^2 \pi^2 Dt}{l^2}} \quad (50)$$

If the term due to the exponential approach to the steady concentration C_2 is subtracted from the permeation rate then

$$\frac{P_{\infty} - P}{P_{\infty}} - \frac{C_2 e^{-\beta t}}{C_1 + C_2} = 2 \sum_{n=1}^{\infty} \left[\frac{\beta C_2}{[C_1 + C_2] \left[\beta - \frac{n^2 \pi^2 D}{l^2} \right]} - \frac{C_1}{C_1 + C_2} \right] (-1)^n e^{-\frac{n^2 \pi^2 Dt}{l^2}}$$

If the logarithm of $\frac{P_{\infty} - P}{P_{\infty}} - \frac{C_2 e^{-\beta t}}{C_1 + C_2}$ is plotted against the time a line of slope $\frac{D \pi^2}{l^2}$ should be obtained at high values of the time and the diffusion coefficient may be evaluated. At small positive and at cathodic potentials this is found to be the case. In diag. 58 the effect of correcting the values of $\frac{P_{\infty} - P}{P_{\infty}}$ for the variation in surface

concentration is shown for an experiment at 40°C and at a potential of -100mv. It is evident that except at very small values of the time the approach to the steady state of permeation observed at the outgoing interface may be represented by the addition of two processes varying exponentially with the time as is indicated by equation (50). At small values of the time negative deviations from a process varying exponentially with the time occur indicating that series due to the diffusion process is operative. At high values of the time the method of correction is bound to be inaccurate since the correction term represents a large part of $\frac{P_{\infty} - P}{P_{\infty}}$, and the variation of the difference of two comparable large quantities is therefore observed. The degree of agreement with the theoretical predictions may therefore be considered satisfactory.

At potentials more positive than +300 mv. the corrected values of $\frac{P_{\infty} - P}{P_{\infty}}$ show a decreasing slope with increasing values of the time and the behaviour is similar to that indicated in diag. 55, the extent of the deviations being reduced. This behaviour is probably to be attributed to the variation of the diffusion coefficient with the concentration since at +900 mv. and +1100 mv., in those cases in which the correction can be carried out the behaviour is similar to that shown in diag. 57. The correction is not easily applied at the most positive potentials since the permeation rate is too small for the variation at high values of the time to be accurately measurable. At intermediate values of the potential the extent of the variation of the diffusion coefficient is sufficiently great for the approach to the steady state of permeation to be affected

while at negative potentials, the reversible potential and at small and high positive potentials the diffusion coefficient has an apparently constant, mean value. It may be noted that the slope of the plot of the corrected values of $\log \frac{P_0 - P}{P_0}$ vs. time is in approximate agreement with the maximum slope of the plot of the uncorrected values. The values of the diffusion coefficient obtained by correcting for the variation in surface concentration are in fair agreement with the values observed during the charging and discharging of the wire electrodes. (diag. 52). The true diffusion coefficient may therefore, in the presence of a slow interface process of this kind, be obtained from the slope of the corrected values of $\log \frac{P_0 - P}{P_0}$ as a function of the time in the manner indicated above. The thickness of the membrane electrode must be chosen so that at high values of the time the kinetics of the process are only controlled by the interface and so that a sharp separation of the surface and bulk controlled processes is possible at small values of the time. It may be noted that the diffusion process could not readily be separated from the kinetics of the interface process using 0.003 inch thick membranes in the experiments described above.

The values of the intercepts on the $\log \frac{P_0 - P}{P_0}$ axis of the plots of the corrected values of $\log \frac{P_0 - P}{P_0}$ vs time are not in agreement with those predicted from equation 50. It is difficult to obtain an accurate value for this intercept since a small displacement of the $\log \frac{P_0 - P}{P_0}$ axis, corresponding to a small error in the initial timing can cause a very large change in the value of the intercept. In consequence of this the values of the intercept show a

considerable scatter at any potential between different experiments and it is not possible to observe any relation between the intercept and the potential. If the intercept is expressed as a ratio of that observed experimentally to that predicted by the substitution of the experimental values of C_1 , C_2 , D , l , and β into equation 50 and a mean value of this ratio is taken from the most positive to the most negative potential in any one series of determinations, then the value of .77 is obtained at 40°C and the value .56 is obtained at 20°C, the theoretical value for the diffusion process being 1.0. It appears to be probable therefore that there is some barrier to the passage of atoms from the surface into the bulk of the metal at the ingoing interface. The accuracy of the experiments is not sufficient to show whether this is of the nature of the "radiation boundary condition". It is evident however that the deviations decrease with increasing temperature and that the transition across the ingoing interface is therefore facilitated at higher temperatures.

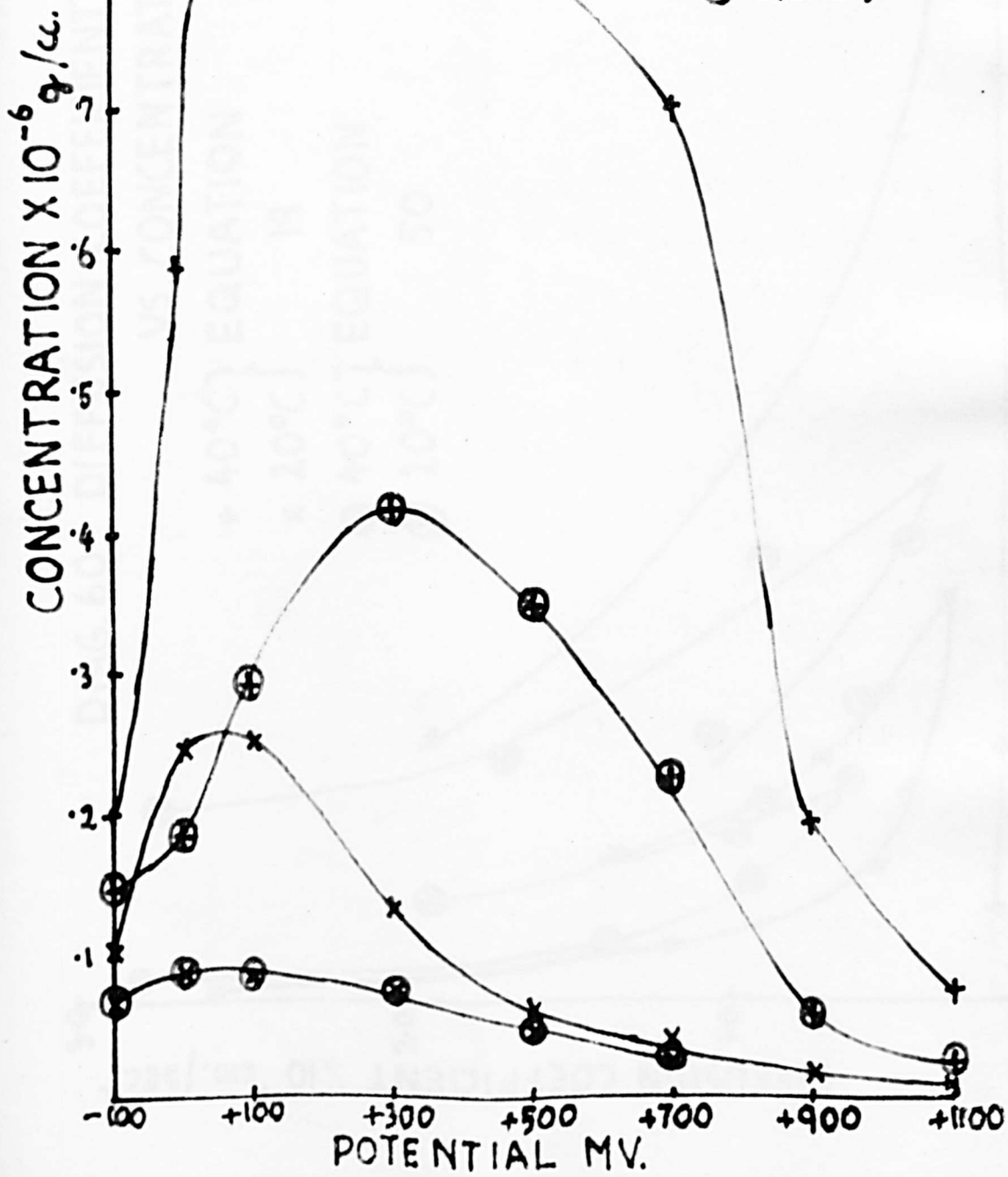
It is evident from diag. 57 that the extent of the slowly varying part of the concentration at the ingoing interface increases with increasing temperature. The accuracy and reproducibility of the experiments is not sufficient, however, to enable a detailed interpretation of the slow exponential process at the ingoing interface to be carried out. The slow process at the ingoing interface may be most readily explained in terms of a rate of deposition on to the interface proportional to the free area available for the deposition process coupled with a rate of removal proportional to the amount of deposited hydrogen, giving rise to

the boundary condition equation 33. This boundary condition differs from the "radiation boundary condition", in that the process of removal is not related to the diffusion process. It is possible that the process of removal is due to the conversion of adsorbed hydrogen atoms into solvated protons. The increasing extent of the slowly varying part of the concentration at the ingoing interface with increasing temperature suggests that the process of deposition occurs with a higher energy of activation than the process of removal, and this indicates that the process of deposition on to the positively charged interface is taking place from a positively charged particle in the solution. The term β represents the sum of the rate constants of the deposition and removal processes. This term is relatively independent of the potential at positive potentials (Diag. 57), and it is difficult to see how this could be explained in terms of deposition and removal processes involving charged particles. The shape of the plot of $\frac{c_2}{c_1 + c_2}$ as a function of potential is also difficult to explain in terms of a single deposition and removal process involving charged particles. Furthermore, at cathodic potentials, the rate of attainment of the equilibrium concentration is slow compared to the known rate of deposition. It would appear to be possible that the slow process at the ingoing interface represents a process not related to the deposition and removal of charged particles, but rather a process such as the migration of atoms over the interface to sites from which the diffusion is preferentially occurring, or the slow removal of an adsorbed layer of oxygen from part of the interface. The processes cannot however be adequately characterised by measurements of the permeation alone, and the

DIAG. 59 CONCENTRATION VS. POTENTIAL

+ 40°C } EQUATION
 x 20°C } 19

⊕ 40°C } EQUATION
 ⊗ 20°C } 50



measurements themselves are not sufficiently accurate to enable a detailed analysis of the possible processes to be carried out.

The effect of evaluating the diffusion coefficient according to equation 50, on the concentration within the ingoing interface at 20°C and at 40°C is shown in Diag. 59. The concentrations obtained by using this method of evaluation are lower at all potentials than the concentrations obtained by using the diffusion coefficient evaluated according to equation 19. The effect on the diffusion coefficient as a function of the concentration of using equation 50 instead of equation 19, is shown in Diag. 60 for experiments at 20°C and at 40°C. It is evident that by correcting the approach to the steady state of diffusion for slow establishment of the equilibrium concentration at the ingoing interface, the negative temperature coefficient of the diffusion coefficient, found at positive potentials according to equation 19, is no longer observed. This negative temperature coefficient is therefore to be associated with the increasing extent, with increasing temperature, of the slowly varying part of the concentration at the ingoing interface. The "diffusion coefficient" evaluated according to equation 19 is in fact determined largely by the slow process at the ingoing interface at the higher temperature.

The diffusion coefficients obtained according to equation 50 are not solely determined by the concentration. At any one concentration the value obtained at the more positive potentials is lower than the value obtained at low positive potentials, the reversible potential or at negative potentials. The variation of the diffusion coefficient obtained

is lower than the maximum possible variation if a slow transition is assumed at the ingoing interface. A slow transition at the ingoing interface is in fact suggested if the concentrations at the ingoing interface of the membranes (diag. 59) are compared with the equilibrium concentrations determined in the experiments with wire electrodes (diag. 49). The concentrations derived from the rate of permeation of the membranes in the steady state are about one tenth of the equilibrium concentrations. A concentration discontinuity therefore exists at the ingoing interface and this may be due to a slow transition at the ingoing interface. It has been noted above that the intercepts of the corrected values of $\log \frac{P_0 - P}{P_0}$ on the $\log \frac{P_0 - P}{P_0}$ axis also indicate that there is a slow transition of atoms at the ingoing interface.

It may be concluded that the diffusion kinetics observed during the establishment of the steady state of diffusion in the experiments with membranes are partly, and at the higher temperatures largely, controlled by the slow establishment in the equilibrium concentration at the ingoing interface. Furthermore that there is a small concentration discontinuity at the ingoing interface which is probably due to a slow transition process at this interface. There is no evidence for any slow processes at the outgoing interface. The slow process at the ingoing interface cannot be sufficiently characterised by measurements of the diffusion alone but the form of the results suggests that this process is not related to the deposition and removal of charged particles.

The values of the diffusion coefficient as a function of the concentration indicate that the energy of activation of the diffusion

process does not exceed 10 kilo calories. The accuracy and reproducibility of the measurements is not sufficient to enable a precise evaluation of the temperature coefficient, or to show whether there is any variation of the energy of activation with the concentration. The above maximum value of the energy of activation of the diffusion coefficient is not in agreement with the energy of activation of the permeation rate determined at higher temperatures for the diffusion from the gas phase. The values 19.6, 18.0, and 19.8 kilo calories have been obtained at the higher temperatures. (65), (66), and (67). If the permeabilities observed at high temperatures are extrapolated to room temperature and expressed as a current flowing through a membrane 0.001 inch thick with the ingoing interface at a pressure of 1 atmosphere the values 1.6×10^{-14} , 2.1×10^{-13} , and 2.3×10^{-13} amperes/cm² are obtained. The experimental values observed with the ingoing interface at the reversible potential are of the order of 10^{-6} amperes/cm². If the diffusion process is taken to be the same at the high and the low temperatures it is necessary to assume that the dissolution observed with the interface in contact with hydrogen at 1 atmosphere pressure in the presence of normal hydrochloric acid is equivalent to a dissolution corresponding to a pressure of 10^7 atmospheres in contact with the gas phase. It has been shown that cathodic currents are equivalent to very high pressures (see above) but the pressure equivalent in the case of platinum would appear to be without any physical significance. Furthermore, no simple relation would be found between the permeation rate and the cathodic current since the diffusion process will take place with the ingoing interface at the

reversible, and at anodic potentials. The positive potentials would also be found to be equivalent to a high pressure of gas on the ingoing interface. It would appear that either the energy of activation of the permeation rate, observed at the higher temperatures, does not correspond to the diffusion process or else that the diffusion process observed at the lower temperatures differs from that observed at the higher temperatures. It may be noted that lower temperatures would favour the observation of grain boundary diffusion processes.

The concentration of hydrogen within the ingoing interface, as a function of the potential, using equation 50 to evaluate the diffusion coefficient, shows a maximum at small positive potentials. The qualitative nature of the results is therefore not affected by using equation 50 rather than equation 19 to evaluate the results although the numerical values are reduced. The data on the charging of the wire electrodes (diag. 48) also indicate that there is a maximum in the concentration within the platinum at small positive potentials. The reduction in the concentration at small positive potentials cannot however be observed with the wire electrodes since at small positive potentials the dissolution in the metal is masked by the dissolution in the solution surrounding the wire. The results at +100 mv. are open to doubt and represent a maximum value in the increase in concentration within the platinum. The results on the wire electrodes therefore show that the concentration is becoming limited and probably reduced at small positive potentials. If the concentration within the platinum is assumed to be related to the concentration on the interface, then the results indicate that the

electrocapillary maximum lies on the positive side of the reversible potential in the vicinity of +100 mv. and that the hydrogen atoms are being adsorbed as unionised particles. Measurements of adsorption at platinum surfaces and of the angle of contact of gas bubbles with platinum also indicate that the electrocapillary maximum lies on the positive side, and in the vicinity of, the reversible potential. (68).

The results on the discharging of the wire electrodes are not in agreement with the results of the charging of the wire electrodes, or with the experiments with membranes. As can be seen from diag. 48 the results do not indicate a maximum in the concentration as a function of the potential but rather an approach to a limiting value as the potential of the interface is made less positive with respect to the solution. The results also show that there is a hysteresis in the dissolution process the hydrogen being more strongly bound to the platinum at any potential for the discharging than for the charging process. A hysteresis in the potential - time curves has been observed in the slow charging of platinum wires (69) and this, and the hysteresis in the dissolution for the charging and discharging process, may be related to a difference in the strength of binding of hydrogen atoms to the surface of the platinum for the deposition and removal processes. It may be noted that potential shifts in the cathodic direction, observed by Ershler during the slow charging when the anodic current was interrupted (69), may be ascribed to the slow removal of hydrogen from the bulk of the metal. The potential shifts were actually attributed by Ershler to the presence of very strongly bound hydrogen atoms on the

surface of the platinum.

The presence of appreciable quantities of hydrogen within the platinum at high positive potentials is not in agreement with the interpretation of the anodic charging of platinum surfaces (47). (69), (70). It has been supposed that hydrogen is removed from the interface at low positive potentials (up to about +300 mv.) and that subsequently the charging of the double layer is observed (up to about +850 mv.) followed by the deposition of an oxygen layer on the interface (up to about +1400 mv.). As can be seen from both the experiments with the membranes and the wire electrodes, appreciable quantities of hydrogen are present in the metal over nearly the whole of this potential range. The charging of the double layer and the deposition of an oxygen layer may occur at the potentials stated but cannot be detected by measurements of the diffusion. It is evident however from the charging curves with membrane electrodes (diags. 28, 29, and 30), that whatever secondary processes are occurring at these potentials, they may be made to take place in either a forward or backward direction, by the addition or removal of hydrogen from the bulk of the metal. Since the concentration of hydrogen in the platinum is very small the effect of any dissolution in the positive potential regions may well be masked by the charging of the double layer or the deposition of oxygen for the case of the slow charging of platinised platinum or the rapid charging of smooth platinum. The presence of hydrogen within the platinum in these potential regions suggests that there is hydrogen on the interface at these potentials. It is not possible to conclude from

the measurements of the diffusion alone that the hydrogen on the interface is present in the presence of an oxide layer. It may be noted that only a very small quantity of hydrogen is necessary to change the potential of the outgoing interface from +1300mv to +800 mv. during the determination of the charging curves (diags. 28 and 29). It is not strictly valid to compare the charging of the interface by diffusion to the direct charging through the solution since in the first system the charging of the bulk of the metal is being considered. In the comparison of the shape of the potential - time curves to the diffusion coefficient by means of the experimental concentration - potential relationships (diags. 42, 43, and 44) it has been assumed that the charging of the bulk only is being observed. The absence of any deviations between the experimental and the theoretically predicted curves at small values of the time, corresponding to the charging in the high positive potential regions, indicates that only a very small part of the hydrogen (equivalent to a current passing through the solution) is used to reduce any oxide layer on the electrode. The results may indicate that only a very slight oxide layer is formed during the charging of the metal. It has in fact been found by Hickling and by Ershler (70), (71) that the presence of chloride ions inhibits the formation of oxide layers, so that in the presence of normal hydrochloric acid only a very slight oxide formation may be observed.

The presence of hydrogen on the positively charged interface is not surprising since the positive potential is only equivalent to about 20 kilo calories and the heat of adsorption may well be of this order.

The mechanism of the deposition reaction is not easy to understand, however. The rate of deposition of protons on to the interface must be greatly reduced and the rate of removal from the interface greatly increased as the potential of the interface becomes more positive.

If the equilibrium concentration of the absorbed and therefore adsorbed hydrogen atoms is assumed to be determined by the balance of the rate of deposition with the rate of removal, it is evident that the concentration should decrease much more rapidly to zero with increasing positive potential than is experimentally observed. It is therefore necessary to assume that only a very small part of the electrode - solution potential is effective in removing adsorbed hydrogen atoms as protons, so that the maximum of the "energy barrier" in this process must lie very near to the electrode surface, and furthermore, that some other process may be effective in the deposition of hydrogen from the solution on to the electrode interface at the positive potentials.

This is in fact also indicated by the independence of β (equation 50) from the potential at positive potentials. It is not possible to calculate the rates of deposition of different ions on to the electrode, however, since various quantities needed in the calculation are unknown, e.g., the free area on the electrode available to the deposition of hydrogen and the concentration of cations in the double layer (determined by the specific anion adsorption). It is possible to conclude, however, that the processes effective in the charging of the electrode interface may be made to take place by the addition

and removal of hydrogen from the bulk of the electrode.

CONCLUSION.

The electrodiffusion of hydrogen through platinum has been investigated using a variety of boundary conditions. It has been found that the rate of electrodiffusion is too small in order to produce a negative potential on the outgoing interface of a membrane when the ingoing interface is polarized cathodically. By removing hydrogen from the ingoing interface, by anodic polarization, the potential of the outgoing interface may be displaced in the positive direction until the electrode is free from hydrogen. Cathodic polarization of the ingoing interface of an electrode free from hydrogen causes the potential of the outgoing interface to shift towards the reversible hydrogen potential. Reproducible charging curves corresponding to the boundary conditions $C = 0, 0 < x < 1, t = 0; C = C_1, x = 1, t > 0; \frac{dc}{dx} = 0, x = 0, t > 0;$ may be taken. It may be concluded that the processes observed during the charging of platinum surfaces between 0 and +1300mv. may be made to take place by the addition and removal of hydrogen atoms.

An attempt has been made to evaluate the diffusion kinetics in terms of a constant current flowing into the outgoing interface for the systems $C = 0$ or $C = C_1, 0 < x < 1, t = 0; C = C_1, x = 1, t > 0;$

$\frac{dc}{dx} = Q, x = 0, t > 0$; for $Q > P_{max}$. and $Q < P_{max}$. The systems have been found to be unsatisfactory and to deviate from Fick's laws of diffusion.

The approach to the steady state of diffusion in the system $C = 0, 0 < x < 1, t = 0$; $C = C_1, x = 1, t > 0$; $C = 0, x = 0, t > 0$ has been found to be most satisfactory for evaluating the diffusion kinetics in experiments with membranes. The results show that the diffusion kinetics are not solely controlled by a transition through the bulk of the metal. Using the observed values of the diffusion coefficient and the concentration as a function of the potential the charging curves (system $C = 0, 0 < x < 1, t = 0$; $C = C_1, x = 1, t > 0$; $\frac{dc}{dx} = 0, x = 0, t > 0$) may be interpreted. The experimental results show deviations from Fick's laws of diffusion which decrease with increasing temperature and are at a maximum at ca. +700mv. The results indicate a stepwise increase with time of the concentration of hydrogen at the ingoing interface and that only a very small capacity can be attributed to the charging of the platinum interface between +800mv. and +1300mv.

Experiments on the charging and discharging of wire electrodes i.e. the systems $C = C_1, 0 < r < a, t = 0$; $C = C_2, r = a, t > 0$ for both $C_1 > C_2$ and $C_1 < C_2$, have shown that the discharge process follows Fick's laws of diffusion but that deviations from these laws occur at small values of the time for the charging process. The deviations are at a maximum when the interface is at ca. +700mv. It may therefore be assumed that deviations from Fick's laws of diffusion only occur at the ingoing interface in the experiments with membranes.

The deviations from Fick's laws of diffusion observed in the experiments with membranes have been examined with this limitation in a variety of ways. The deviations are at a maximum when the ingoing interface is at ca. +700mv. and the analysis shows that the approach to the steady state of permeation may be simulated by the superposition of a slow and fast process. The fast process may be attributed to the diffusion while the slow process is not related to the diffusion process. The form of the results suggests that the slow process is not related to the deposition and removal of charged particles but rather the migration of atoms over the interface or the removal of an adsorbed layer. If the slow process is allowed for in the evaluation of the diffusion coefficient, the negative temperature coefficient, previously observed at positive potentials, is converted into a positive temperature coefficient. The results show that the diffusion kinetics are partly, and at the higher temperatures largely, controlled by the slow process at the ingoing interface and that, in addition to this process there is a small concentration discontinuity at this interface so that there is a barrier to the transfer of hydrogen atoms from the surface to the bulk of the metal.

The results show that the dissolution in platinum proceeds endothermically in agreement with the observations at high temperatures. The temperature coefficient of the diffusion coefficient is not in agreement, however, with the observations at high temperatures. The experiments on the charging of wire and membrane electrodes indicate that there is a maximum in the hydrogen concentration within platinum when the interface is at ca. +100mv. and this potential may correspond to the electrocapillary

maximum on platinum. The experiments on the discharging of wire electrodes are not in agreement with this observation, and indicate a hysteresis in the adsorption and desorption of hydrogen. The form of the relation between the equilibrium concentration and the potential suggests that there is more than one process responsible for the deposition of hydrogen at the platinum interface and that only a small part of the potential drop from the interface to the solution is effective in removing hydrogen from the interface.

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