69. *The Hydrogen–Calomel Cell. Part I. The Hydrogen Electrode.*

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Some errors to which the hydrogen electrode is susceptible are discussed. A new form of hydrogen electrode is described and some comments are made on the theory of operation of the hydrogen electrode.
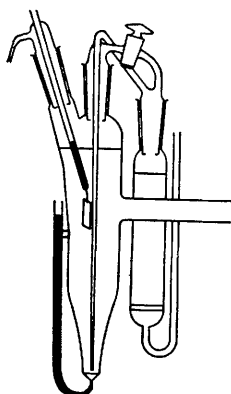
The hydrogen–calomel cell, $H_2, Pt | HCl(aq.) | Hg_2Cl_2 | Hg$, has not hitherto been used for electro-chemical work of high precision, and its standard E.M.F. has not been directly determined.

This is because the calomel electrode has shown intractably erratic behaviour in dilute solutions and has therefore been discarded in favour of the silver/silver chloride electrode, with which nearly all the potentiometric work of general thermodynamic importance has been done. No good reasons have been advanced for the defects of the calomel electrode and it seemed desirable to try to remedy this situation because it was felt that, in fact, this electrode should be superior to its silver analogue. Any electrode in which the metal phase is the reduced form of the redox equilibrium system must vary in potential according to the state of the metal, which, in turn, will depend upon purity and thermal and mechanical history. The difficulties encountered with hard metals are by no means absent in the case of silver, but hardly arise with liquid mercury, which may be easily brought to a reproducible, standard state. Of all metals, therefore, mercury should be the most suitable for forming a truly reversible and reproducible electrode. Evidence will be given in the following papers that, in conformity with this view, the calomel electrode is superior to the silver/silver chloride electrode : means have been found to minimise the defects that have hitherto obscured this position and the hydrogen–calomel cell is suggested as being the most suitable for accurate thermodynamic work. In the course of this study it has been found necessary to devote some attention to the hydrogen electrode, to which all other measured electrode potentials are referred, and this forms the subject matter of Part I.

The Hydrogen Electrode.

It is common practice to use a number of hydrogen electrodes in the same half-cell, and interagreement is accepted as an indication that the true, reversible potential has been attained. Effective use of this criterion requires the individual electrodes to differ in type and preparation to minimise the possibility of common errors.

FIG. 1.

Available hydrogen electrodes, however, vary but little : all in current use consist of catalytically active platinum electrodeposited on a noble-metal substrate, and it was therefore considered whether some wide deviation from the normal type might not be advantageous. The view was taken that the hydrogen electrode resembles oxidation-reduction electrodes (*e.g.*, $Pt|Fe^{2+},Fe^{3+}$) in that both oxidised and reduced forms (hydrogen ions and dissolved molecular hydrogen) are contained in the solution phase but differs in that, in the absence of catalyst, there is no free electron transfer either between the components in the solution or across the metal/solution interface. The one system could be brought closest in line with the other by dispersal of catalyst throughout the solution rather than by confining it to the interface, and this might facilitate general mobility in the redox equilibrium system. The argument is tenuous, but it was found that Biilman and Klit (*Z. physikal. Chem.*, 1927, **130**, 566) had already adopted the idea, and used a bright platinum or gold electrode immersed in a hydrogen-saturated solution to which a small amount of colloidal platinum had been added. The results were satisfactory, but the method does not lend itself to general application. It has been found, however, that a small quantity of dry platinum black may be added in place of the platinum sol and leads to an extremely satisfactory electrode, which will be called " the catalyst electrode." The requirements that (*a*) the heavy platinum black should be continuously dispersed throughout the half-cell solution, (*b*) it should come repeatedly into contact with the bright platinum electrode, and (*c*) it should be unable to collect in recesses undisturbed by circulating solution defined the physical design of the electrode. which is illustrated in Fig. 1. A normal hydrogen electrode included in the same vessel showed agreement in potential with the catalyst electrode to within 10 μv., and the two together furnished a hydrogen-electrode assembly, used in all subsequent measurements, admirably satisfying the criterion of validity previously mentioned. The catalyst electrode has some advantages. The apparatus is robust and can be cleaned and dried by the usual methods without special precautions. In operation, it is less prone to " fatigue " than the normal electrode. It may be significant (cf. Beans and Hammett, *J. Amer. Chem. Soc.*, 1925, **47**, 1215) that the catalyst electrode is free from the disadvantages associated with the electrodeposition of platinum from strongly acid solutions. It does not require special preparations before use, for a large stock of catalyst may be prepared at one time and stored in a dry state, a few mg. being required for each half-cell. The electrode approaches to within 100 μv. of its equilibrium potential in a few minutes after the addition of catalyst and passage of hydrogen, and reaches

its final potential in about an hour. If, during this period, the bubbling of hydrogen is stopped, the potential drifts in a positive sense, but, when the catalyst is completely in equilibrium with hydrogen, this does not occur, and the hydrogen stream may be stopped (in practice, by-passed over the surface of the solution) for measurements to be made. Details of the construction of the electrode are given in the experimental section.

During the course of the work with hydrogen electrodes, a source of error was identified of which no mention can be found in the literature and on which a preliminary report has been made (Hills and Ives, *Nature*, 1949, **163**, 997). The potential of a normal hydrogen electrode is independent of its depth of immersion below the surface of the solution, since a reasonable bubbling rate of hydrogen ensures sufficient stirring to make the solution homogeneous with respect to dissolved hydrogen. The potential of the electrode, however, is dependent upon the depth at which hydrogen bubbles are delivered in the solution; because of the additional hydrostatic pressure within the gas bubbles, the solution becomes supersaturated with respect to the pressure of gas over the solution. It is therefore necessary to determine the pressure of hydrogen, in excess of atmospheric pressure, with which the solution is effectively in equilibrium, for it is this which is potential-determining and not the measured barometric pressure. It was found to be impracticable to solve this problem except by an empirical study. For this purpose a cell was set up consisting of two well-separated electrode compartments; one of these contained a normal hydrogen electrode supplied with hydrogen from a bubbler of fixed depth, the other also contained a normal hydrogen electrode but could be supplied with hydrogen either from a fixed jet at the bottom of the vessel, or, alternatively, from a jet of variable depth of immersion. The E.M.F. of this cell (ideally zero) varied according to the depth of delivery of hydrogen in the second half-cell; the behaviour was quite systematic, the E.M.F. responding rapidly when the hydrogen was diverted from one jet to the other. The results, for a cell containing N/10-hydrochloric acid, are shown in the table. The first column shows the difference in depth between the fixed and variable jets in the second half-cell; the second column shows the change in E.M.F. on passing from the lower, fixed bubbler to the upper, variable one and is compared in the third column with the change which would be expected if the full hydrostatic head of solution were operative. The last column gives the ratio of these quantities.

Change of bubbler depth, cm.	ΔE (obs.), μv.	ΔE (calc.), μv.	$\dfrac{\Delta E \text{ (obs.)}}{\Delta E \text{ (calc.)}}$
3·3	20	41	0·49
7·8	42	98	0·43
11·0	57	137	0·41
14·0	72	175	0·42
17·5	88	219	0·42

A plot of change of E.M.F. against change in bubbler depth is sensibly linear, and the slope of the best straight line gives a value, for what may be termed " the supersaturation factor," of $0·42 \pm 0·02$. This is the factor by which the depth of immersion of the hydrogen bubbler must be multiplied in order to obtain the effective excess of hydrostatic pressure. It must be applied as a correction to all hydrogen-electrode measurements in the course of adjusting the observed potentials to the standard hydrogen pressure of one atmosphere.

It might be expected that this factor would vary considerably according to the area of the upper free surface of the solution, in direct contact with hydrogen at atmospheric pressure. This appears not to be the case because of the very low rate of transfer of hydrogen across the free-surface interface as compared with the much greater rate of transfer across the interface of a rising bubble. This has been demonstrated in the following ways :

(*a*) A hydrogen half-cell was fitted with a restricted gas outlet and manometer, permitting hydrogen to be bubbled through the solution, or by-passed over its surface, at controlled pressures in excess of atmospheric. In a typical experiment of this kind, hydrogen was bubbled at an excess of pressure of 13·5 cm. of water and the electrode showed an enhanced (negative) potential of 160 μv., in reasonable agreement with the calculated increment (170 μv.). When the hydrogen stream was by-passed over the surface of the solution and the excess of pressure simultaneously released, the increment of potential remained unchanged for at least two hours. A similar experiment in which, on the release of excess of pressure, hydrogen at normal pressure was bubbled through the solution gave an entirely different result, the initial 160-μv. increment in potential falling almost immediately to zero. In a third experiment, an identical excess of pressure applied whilst hydrogen was by-passing over the surface of the solution produced no perceptible effect.

(b) A normal hydrogen half-cell was set up, with hydrogen bubbling through the solution. When a very rapid stream of pure nitrogen was passed directly over the free surface of the solution so as to render the partial pressure of hydrogen at the surface almost negligible, the electrode showed a positive increment of potential of only 2·7 mv. A very rough calculation on this basis indicated that the " hydrogen transfer efficiency " of the free surface is of the order of 4% of that of the rising bubble surface.

(c) In very many experiments it has been found that hydrogen-electrode potential is sensibly independent of the rate of bubbling; it is therefore also independent of the ratio of bubble surface area to free surface area, which can only be the case if the free surface is virtually ineffective in controlling the concentration of hydrogen in solution.

These experiments leave no doubt that it is the concentration of dissolved hydrogen which is potential-determining, and this concentration must therefore be controlled, in electrochemical work of high precision, with as great care as that of any other solute.

Errors can also readily arise by failure to attain or maintain the maximum concentration of dissolved hydrogen. This is likely to occur in ill-designed half-cells which contain stagnant regions of solution not swept out by bubbles of hydrogen, or when connection is opened between the hydrogen-electrode vessel and another half-cell. It has been found advisable, in this connection, to interpose a buffer compartment, containing a guard hydrogen electrode, between the two halves of, for example, the hydrogen–calomel cell.

EXPERIMENTAL.

Normal Hydrogen Electrodes.—Pieces of platinum or gold foil were welded to 28-S.W.G. platinum wires, which were sealed into soft-glass tubes mounted on *B*19 soft-glass cones. The electrodes were annealed in an alcohol flame and used as cathodes in the electrolysis of 2% platinic chloride solution in 2N-hydrochloric acid for 10—20 minutes (2 v.; 10—20 ma./cm.²). The resulting, lightly platinised electrodes were dark grey with the original metal sheen clearly visible. They were washed well with water and kept in water when not in use. The use of lead acetate in the plating solution, and the alternating cathodic and anodic electrolyses both in the platinising solution and afterwards in dilute sulphuric acid (Popoff, Kunz, and Snow, *J. Physical Chem.*, 1928, **32**, 1056) were not found to be beneficial and were discarded.

The Catalyst Electrode.—The conditions necessary for the proper operation of this electrode could only be met by arranging a conical electrode of bright platinum foil at the base of the electrode vessel, the hydrogen stream being delivered close to the apex of the cone so as to lift the catalyst continually into suspension. Since it was necessary to make the electrode vessel of Pyrex glass and to avoid any crevices in the construction where catalyst might collect and be occluded, latitude in design was small. Constructions involving seals of platinum wire through Pyrex were unsatisfactory; apart from tendencies to leak or crack, the potentials recorded at such electrodes were very erratic. It has been pointed out that such misbehaviour may arise from strain effects at metal/glass/solution junctions (Garrett, Hogge, and Huikes, *Science*, 1940, **92**, 18), and it is believed that this is the case. The difficulty was obviated by using very thin, light, glass construction and extremely thin platinum foil (0·0004″), a narrow strip of which may be " pinch-sealed " into Pyrex glass to give a vacuum-tight seal (Campbell, *J. Amer. Chem. Soc.*, 1929, **51**, 2419). A disc, 8 mm. in diameter, was punched from the platinum foil and a segment was cut out so as to allow of the formation of a cone. A narrow contact strip was cut along one of the edges left by removal of the segment and was bent down so as to be coaxial with the cone, which was shaped by hand. The resulting electrode was slipped into the thin-walled, conical base of the electrode vessel, the contact strip protruding into a small contact tube provided. The pinch seal was then made and the platinum cone sweated to its glass substrate, forming an assembly free from strain, leaks, and crevices.

Catalyst. A 2% solution of platinic chloride, containing 5% of sodium acetate, was shaken in an atmosphere of hydrogen until reduction was complete. The platinum black was filtered off, washed, repeatedly soaked in water, and finally dried in a vacuum.

Hydrogen. Cylinder hydrogen was purified by passage over platinised asbestos and reduced copper, heated in silica tubes at *ca.* 700°. Connections between the cylinder and the furnace tubes were made with polyvinyl chloride tubing, rubber being excluded. After purification, the gas passed through all-glass connections to presaturators mounted adjacent to the electrode vessels in the thermostat, which was maintained at 25° in all the experiments.

Hydrochloric acid. Hydrogen chloride, generated from " AnalaR " ammonium chloride, was dissolved in conductivity water, and the solution chlorinated and boiled to remove traces of other halogens. The acid was then fractionally distilled, and a constant-boiling fraction collected and stored in a quartz flask. This stock acid was diluted with conductivity water as necessary.

Potentiometric measurements. The apparatus and technique are fully described in Part III (*J.,* 1950, 318).

DISCUSSION.

There is some difficulty in understanding the mechanism of the reversible hydrogen electrode. Whereas the discharge of hydrogen ions from solution normally requires an overpotential, it

occurs freely at a platinised-platinum surface without appreciable activation energy, and this is attributed to the heat of adsorption of hydrogen atoms on the catalytically active surface. But this very property of platinised platinum which facilitates discharge would appear to hinder the reverse process; yet the transition must be unhindered in either direction if the electrode is to operate reversibly. According to Butler (*Proc. Roy. Soc.*, *A*, 1936, **157**, 423), a hydrogen atom (or ion) may occupy alternatively two potential-energy minima, one on each side of the transition process of charge or discharge. On the one hand, as a hydrogen ion, it may occupy the lowest vibrational level in a water molecule close to the metal surface; on the other hand, as an atom, it may occupy a position of minimum energy at an adsorption site on the platinum surface. The equilibrium potential is that at which these alternative minima are at approximately the same level on the energy scale and are separated from each other by a small barrier which allows the charge and discharge processes to occur at equal and appreciable rates.

There can be little doubt that this theory is substantially correct, but a difficulty remains in that the potential of the reversible hydrogen electrode must be uniquely defined by the thermodynamic relationship $2\mu_{H^+} - \mu_{H_2} - 2EF = 0$, which does not allow of self-adjustment of potential to fit a possibly variable adsorption energy. This further difficulty may be obviated by the suggestion (Audubert, *Faraday Soc. Discussions*, 1947, **1**, 72) that charge and discharge do not necessarily occur at the same sites and are not necessarily strictly the reverse of each other. Any metal surface is inhomogeneous, containing sites for atoms, some occupied and some not, covering a range of energies. This must also be the case for adsorption sites on a metal surface, for which there will be a range of adsorption energies (indicated by decreasing differential heat of adsorption); only certain of the corresponding energy levels for adsorbed hydrogen atoms will be suitable for the charge and discharge processes of the hydrogen electrode. All those metals for which differential adsorption energies fall within the required range will operate as reversible hydrogen electrodes, showing potentials defined only by the thermodynamic equilibrium between hydrogen gas and solution ions, the function of the metal being solely to decapitate the barrier separating these two extreme states. Even within the limited range of suitable levels, it is likely that discharge occurs preferentially at sites of lower level, and charge at sites of higher level, a cyclic equilibrium being maintained by the ready redistribution of adsorbed hydrogen atoms which must occur. The Butler theory may then be modified by replacing a single potential-energy curve for a hydrogen atom under the influence of the surface by a band, spread over the relevant energy range : each process can then occur at the site best suited to it and no non-thermodynamic restriction is imposed on the potential of the electrode.

Differentiation between charge and discharge sites is indicated in studies of working hydrogen electrodes. Hammett (*J. Amer. Chem. Soc.*, 1924, **46**, 7) has made a careful study of " the velocity of the hydrogen electrode reaction " at various platinum electrodes under small anodic and somewhat larger cathodic polarisations. For a series of electrodes of varying catalytic activity, current, plotted against polarising potential, gave smooth curves passing through the origin without inflexion (cf. Dolin, Ershler, and Frumkin, *Acta physicochim. U.R.S.S.*, 1940, **13**, 779) which were shown (Hammett, *Trans. Faraday Soc.*, 1933, **29**, 770) to be accurately interpreted by the equations

$$I = -k_1 e^{-FV/2RT} + k_2[H]e^{FV/2RT} \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\frac{d[H]}{dt} = 0 = k_1 e^{-FV/2RT} - k_2[H]e^{FV/2RT} + k_3[H_2] - k_4[H]^2 \quad . \quad . \quad . \quad (2)$$

where I is the net current flowing at a polarisation V with respect to the reversible hydrogen electrode (cathodic current and potential being given negative sign), [H] is the particular surface activity of adsorbed hydrogen atoms on the electrode when the steady current appropriate to each polarisation is established, and the other symbols have their usual significance.

These results have been re-examined by using equation (1) modified to include the characteristic activation energies of discharge and charge processes (ω and ω', respectively) and the relevant energy-transfer factors, α and β, not necessarily equal to 0·5. For example, the gross discharge current is expressed by
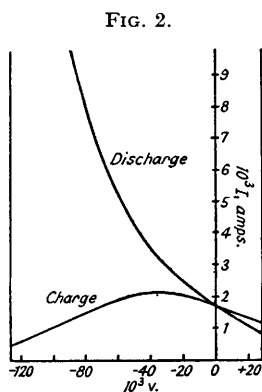
$$I_{discharge} = -ke^{(\omega + \alpha FV)/RT} \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Plots of $\log_{10} (-I)$ against $(-V)$ for each of the four electrodes considered gave a series of curves asymptotic in the direction of increasing cathodic polarisation to parallel straight lines, the common slope of which gave a value of 0·50 for α and a Tafel " b value " of 0·118, consistent with well-established overvoltage results at unpoisoned platinum electrodes. On the assump-

tion that no change in mechanism of discharge occurred over the whole polarisation range (—0·1 to 0·02 v.), these straight lines were used to calculate the value of the gross discharge current for each polarisation, and, by subtraction from the known net current, the value of the gross charge current. A typical result is shown in Fig. 2, the main features of which require comment.

At the highest cathodic polarisation the charge current is surprisingly high, much greater than the discharge current under correspondingly unfavourable (anodic) polarisation. As the negative polarisation is reduced, discharge current of course decreases in the manner dictated by the initial assumption and, at first, charge current increases in the manner to be expected if the main rate-limiting step were $H \longrightarrow H^+ + e^-$. With further decrease in negative polarisation, however, the charge current passes through a flat maximum and there-after decreases steadily, even when anodic polarisation supervenes. This can only be because the rate of provision of hydrogen atoms is becoming rate-limiting : as the charge process increases in facility, a major supply of hydrogen atoms, the discharge process, dwindles until eventually charging can only occur at the rate defined by the atomisation of molecular hydrogen. Intermediately, charging will take place with a velocity proportional to $[H]e^{-(\omega' - \beta FV)/RT}$, where [H] is defined by the resultant effect of the four processes indicated in equation (2).

At the equilibrium potential, $V = 0$, the exchange current, even with these comparatively inactive electrodes, is considerable. The discharge current, it is credibly assumed, is controlled solely by the step $H^+ + e^- \longrightarrow H$, but the equal and opposite charge current flows at a rate largely restricted by the supply of hydrogen atoms, as indicated by the slopes of the " charge curve " previously discussed, and is effectively unhindered by any barrier in the step $H \longrightarrow H^+ + e^-$. It follows that the activation energy for charge is smaller than that for discharge. Further, for all these differing electrodes which operate as reversible hydrogen electrodes, it is clear that the adsorbed hydrogen atoms must be in equilibrium with molecular hydrogen, so that the activity of hydrogen atoms on the electrode must be defined by the hydrogen gas pressure alone. This is also clear from the necessary equality, at equilibrium, of the third and fourth terms on the right-hand side of equation (2). The question then arises whether it is charge or discharge which is decisive in controlling the magnitude of the exchange current. It is unlikely that discharge is, over the small polarisation range involved, in any way dependent upon the population of hydrogen atoms on the electrode and may be assumed to occur at a rate defined, at $V = 0$, solely by the properties of a given electrode and of the

FIG. 2.

solution with which it is in equilibrium. There will be variation from electrode to electrode, but for *all* electrodes that operate reversibly, the charge current must in each case come to the same value as the discharge current. There must therefore be some self-adjusting kinetic factor in the charge process and the non-exponential factors are excluded from this rôle by thermodynamic considerations. The evidence strongly favours the view that it is the activation energy of charging which is self-adjusting. The migration of hydrogen atoms to adsorption sites covering a range of higher energy levels seems to be the only way in which this could be so. The fact that in a number of cases, and perhaps in most, the activation energy for charge is less than that for discharge lends support to this view.

If it is accepted that the reversible hydrogen electrode operates by a cyclic process of the type envisaged, it is probable that at the catalyst electrode discharge of hydrogen ions occurs predominantly on the suspended platinum black, and charge of hydrogen atoms mainly at the platinum cone. The rapid circulation of catalyst, and its frequent and repeated contact with the cone, redistributes the hydrogen and brings the cone to the true equilibrium hydrogen electrode potential.