

Hydrogen Electrode Processes. Part I. Platinum-Hydrogen Electrodes.

By R. H. COUSENS, D. J. G. IVES, and S. SWAROOPA.

[Reprint Order No. 6292.]

The cathodic deposition of hydrogen from dilute acid solutions at bright platinum electrodes in very pure systems has been studied. Results have been obtained consistent with a cathodic component of the current limited by slow discharge, opposed by an anodic component due to ionisation. The behaviour of these electrodes, however, has been found to be critically dependent upon their surface state, for which no adequate means of control has yet been found. Two main kinds of variation in electrode properties have been observed and discussed. The properties of bright platinum electrodes in their resting state, and the behaviour of the cell formed from such an electrode combined with a platinised platinum electrode in a hydrogen-saturated acid solution have been investigated. The results lend support to a theory of the mechanism of the reversible hydrogen electrode previously proposed.

HAMMETT (*J. Amer. Chem. Soc.*, 1924, **46**, 7; *Trans. Faraday Soc.*, 1933, **29**, 770) studied the behaviour of bright platinum electrodes in hydrogen-saturated, aqueous hydrochloric acid. Electrode potentials, E , measured with respect to a reversible hydrogen electrode in the same solution, gave plots against current density, i , which passed through the origin with no change of sign of d^2E/di^2 . With increasing cathodic polarisation, $dE/d\log i$ tended to a value of 0.118 v at 25° c for a number of electrodes of different activity. These characteristics are consistent with the behaviour of an electrode at which the net current is defined by a cathodic component limited by slow discharge and an anodic component due to ionisation. On this basis Hills and Ives (*J.*, 1951, 305) calculated the values of these discharge and ionisation components of the total current at Hammett's electrodes. The results supported the "differentiated site theory" of the hydrogen electrode mechanism developed by these authors from the well-known theory of Butler (*Proc. Roy. Soc.*, 1936, **A**, **157**, 423) on lines suggested by Audubert (*Discuss. Faraday Soc.*, 1947, **1**, 72).

Hammett's measurements, however, were not extended to cathodic potentials high enough to establish the Tafel slope, $b = 0.118$ v, for the discharge process without ambiguity, and potential-current density curves of a different kind have been reported for platinum electrodes in a similar potential range (Volmer and Wick, *Z. physikal. Chem.*, 1935, **A**, **172**, 429; cf., however, Lorich, *Trans. Electrochem. Soc.*, 1936, **70**, 401; Dolin, Ershler, and Frumkin, *Acta Physicochim.*, 1940, **13**, 779). Although linear Tafel plots of slope near to 0.118 v have more recently been obtained with platinum electrodes of low activity (Kheifets and Polyakova, *Zhur. priklad. Khim.*, 1949, **22**, 801), the accepted view is that a slope of 0.029 v is typical of platinum, corresponding with rate limitation by slow recombination (Bockris, "Electrochemistry," Butterworths, 1954, p. 210). Change of mechanism at a given platinum electrode between one current density and another has been reported by Schuldiner (*J. Electrochem. Soc.*, 1952, **99**, 488) but, contrary to this author's statement, no sign of this can be found in Hammett's measurements. In general, it appears that platinum electrodes are capable of the most diverse behaviour under nominally similar conditions (cf. Parsons, *J. Chim. phys.*, 1952, **49**, 82); their great sensitivity to anodic activation and to the presence of impurities is well known. It is clear that the postulation of a single, exclusive mechanism for the hydrogen deposition reaction at platinum cannot be defended, and enquiry is needed into the conditions which promote one reaction mechanism or another. In particular, it seemed desirable to attempt a reproduction of the conditions which, in Hammett's work, led to a clear-cut reaction mechanism, ostensibly rate-limitation by slow discharge. This was the purpose of the present work, which, however, developed on somewhat unexpected lines.

In this work, bright platinum electrodes have been used as cathodes in the electrolysis of aqueous 0.1N-hydrochloric acid under the conditions of high purity now known to be essential for hydrogen overpotential measurements (Azzam, Bockris, Conway, and

Rosenberg, *Trans. Faraday Soc.*, 1950, **46**, 918). The method is fully described in the experimental section, but it may be mentioned that importance was attached to the following points in designing the electrolytic cell: (1) elimination of concentration polarisation and removal from the electrode surface of cathodically-generated hydrogen in the dissolved state by use of vigorous, non-turbulent stirring (Hammett, *loc. cit.*); (2) uniformity of current density over the whole electrode surface (Goodeve, *Discuss. Faraday Soc.*, 1947, **1**, 139); (3) exclusion of glass-to-metal seals in contact with solution (Garrett, Hogge, and Hukes, *Science*, 1940, **92**, 18); (4) provision for pre-treatment of electrodes by heating them in hydrogen and introducing them into the solution without exposure to air.

The first measurements to be reported were made with platinum electrodes which had been subjected to chemical cleaning processes (see Experimental section) but not to heat treatment in hydrogen. The dependence of electrode potential, referred to a hydrogen electrode in the same solution, upon current density was studied by the "rapid method," increments of current being made at fixed time intervals long enough for the potential at each current density to become sensibly constant. The reproducibility of the results was unsatisfactory and it became clear that an important variable defining electrode behaviour was neither properly understood nor controlled. This is believed to be the metallographic state of the bulk phase of the electrode and, in particular, the nature of its surface. In spite of this, results of the kind shown in Fig. 1 were obtained, but could not be depended upon in any given experiment. It is seen that they lead to Tafel plots with slopes varying somewhat on either side of 0.118 v, with deviations in the lower current density range of the kind expected from the effect of increasing ionisation with falling cathodic potential. In experiments in which nitrogen, instead of hydrogen, was passed through the electrolyte, these deviations were decreased, but not eliminated. It is clear that, under these conditions, the hydrogen atoms deposited by discharge of hydrogen ions partly combine to form molecular hydrogen and partly re-ionise. At the higher current densities, overpotentials were insensitive to change of gas, confirming that the back-reaction, or ionisation, was suppressed at sufficiently high cathodic polarisations. This is consistent with the repression of deuterium exchange between gas and solution phases at platinum by cathodic polarisation, whilst the concomitant acceleration of para-hydrogen conversion indicates increased production of hydrogen atoms and maintenance of the atomisation-recombination equilibrium (Calvin, *Trans. Faraday Soc.*, 1936, **32**, 1428).

These results, obtained with electrodes of differing activity, support the view that under suitable, but ill-defined, conditions the hydrogen deposition reaction at platinum follows a Tafel law consistent with rate-limitation by slow discharge, and therefore satisfy, with some reservation, the original objective of the work.

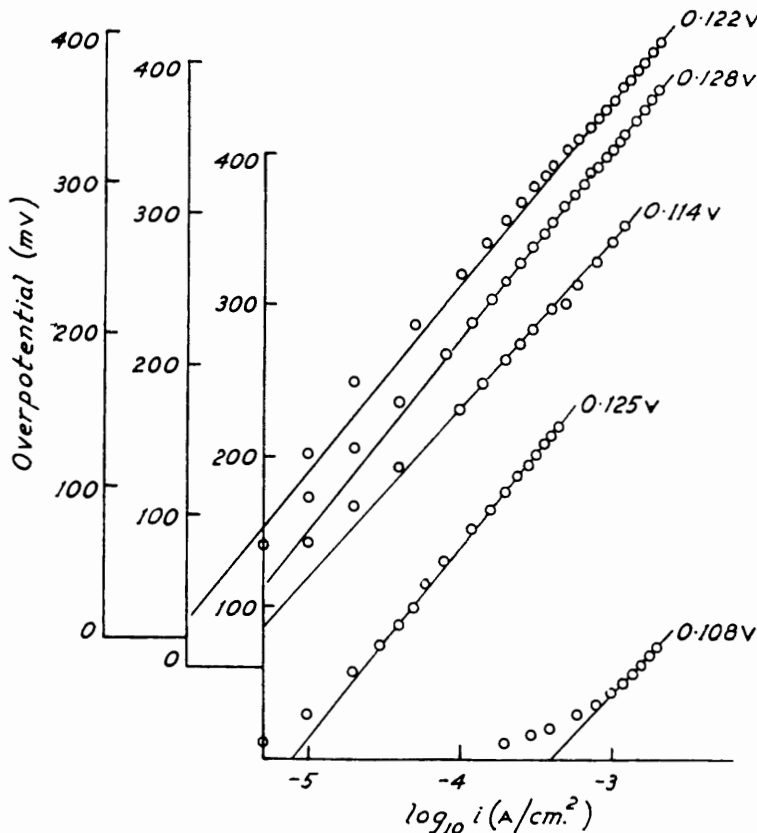
Some of the variations in properties of the platinum electrodes were found to result from progressive changes of two different kinds:

(1) Long-continued cathodic polarisation in hydrogen-saturated solution caused an increase in the initially positive rest-potentials of these bright platinum electrodes. There was also a slow, progressive rise in the cathodic overpotentials at each current density (cf. Butler and Armstrong, *J.*, 1934, 746) and an increase in the slopes of the linear sections of the Tafel plots (cf. Bowden, *Proc. Roy. Soc.*, 1929, *A*, **126**, 107). This kind of behaviour has been attributed to poisoning. It was, however, observed that this change in the electrode system was arrested and reversed by allowing the electrode to rest whilst sweeping out the solution with nitrogen. This suggests that the "poisoning," or deactivation, may have been due to progressive absorption of hydrogen by the electrode, and its reversal to slow desorption from the metal in a system rigorously freed from hydrogen.

(2) The repeated use of an electrode in successively assembled cells, with intervening exposure to air and cleaning agents, caused a fall of positive rest-potential to zero, a decrease of cathodic overpotential at a given current density, and a rapid fall of Tafel slope. Consecutive values of this slope in one sequence of experiments were: 0.120, 0.096, 0.083, and 0.055 v. It is evident that this kind of change is associated with progressive activation of the electrode, no doubt because of its alternate exposure to oxidising and reducing conditions.

Loss of activity on prolonged cathodic polarisation, attributable to "hydrogen poisoning," has been observed before (Baars, *Ber. Ges. Beförd. Naturw. Marburg*, 1928, **63**, 213; Butler and Armstrong, *loc. cit.*; Masing and Laue, *Z. phys. Chem.*, 1936, **178**, A, 1), and it is of interest that Bodenstein (*Annalen*, 1924, **440**, 177) found that saturation with hydrogen reduced the catalytic activity of palladium. It is of particular interest that the Tafel slope decreases with increasing electrode activity. Knorr and Schwartz (*Z. phys. Chem.*, 1936, **176**, A, 161) found this to be the case for palladium, measuring catalytic activity unequivocally in terms of the rate at which a given electrode would take up hydrogen from the gas phase. The situation appears to arise that the more active an electrode in catalysing recombination, the more consistent is its Tafel slope with rate

FIG. 1.



limitation by recombination; special pleading therefore seems to be necessary to maintain the view that recombination is rate-limiting at platinum or palladium. It seems probable that low Tafel slopes more frequently arise in the manner indicated by Kandler, Knorr, and Schwitzer (*ibid.*, 1937, **180**, A, 281).

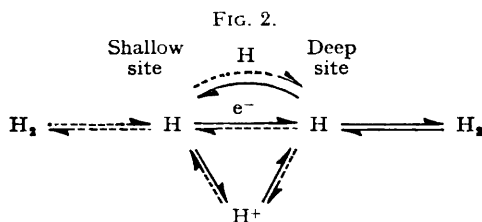
An attempt was made to obviate these uncontrolled variations in electrode properties by heat-treatment of an electrode in hydrogen. This was done by withdrawing the electrode from the solution into a silica furnace tube which formed an integral part of the electrolytic cell, in which the electrode was heated in hydrogen, cooled, and restored to the same solution. Treatment of this kind was ineffective in bringing the electrode to a standard state; on the contrary, the behaviour afterwards was characterised by curved Tafel plots reaching very high slopes at the higher current densities. This has been ascribed to a highly inhomogeneous electrode surface which changes rapidly in properties as a function of current density (Busing and Kauzmann, *J. Chem. Phys.*, 1952, **20**, 1129).

Further work designed to control electrode state and to trace its effect on electrochemical behaviour was carried out with gold, under the supposition that this metal might show less extreme variations of properties than platinum, and is described in the following paper. One aspect of this problem, however, may be discussed immediately.

The persistent positive rest-potentials often shown by bright platinum electrodes in hydrogen-saturated, acid solutions have long been known (Plzák, *Z. anorg. Chem.*, 1902, **32**, 385) and have been attributed to poisons in solution, removable by prolonged contact with platinised platinum (Aten and Zieren, *Rec. Trav. chim.*, 1929, **48**, 944). It is difficult to explain the persistence of a potential difference for months between bright and platinised platinum, in hydrogen-saturated hydrochloric acid, in a closed system in this way, for such a system should be "self-cleaning" (Beans and Hammett, *J. Amer. Chem. Soc.*, 1925, **47**, 1215). In any case, the phenomenon is of interest and possible value in the elucidation of the hydrogen electrode mechanism, and some new experiments bearing upon it have been made.

Two platinised platinum, one bright platinum, and one gold electrode were enclosed, together with 0.1N-hydrochloric acid and hydrogen, in a totally-sealed, vacuum-tight cell, every effort being made to secure high purity. The platinised platinum electrodes were used as reference electrodes. The initial rest-potentials of the bright platinum and gold electrodes were +340 and +420 mv and were persistently recorded after the disturbing effects of interconnection of the electrodes, gentle cathodisation or anodisation, or heating to 90° had died away. Connection of either of these electrodes to one of the platinised electrodes showed, on a microammeter, an initial current flow of about 10 μ A, falling rapidly to a steady value of about 0.5 μ A which persisted indefinitely, but was greatly increased by shaking the cell. With rise of temperature, the potential of the bright platinum electrode fell to zero at 70°; that of the gold electrode decreased steadily by about 2 mv per degree, both these changes being reversible. After three weeks on open circuit, *both* rest-potentials had fallen by 80 mv, and after two months by about 330 mv. The identical decline in the apparent positive potentials of the dissimilar electrodes indicated that the change had really taken place in the reference electrodes by a process of slow deactivation.

These results may be discussed in relation with the "differentiated site theory" of the hydrogen electrode (Hills and Ives, *loc. cit.*). According to this theory a satisfactory, reversible hydrogen electrode must have surface sites of widely varying adsorption energy, for only in this way can an exchange current of adequate magnitude be attained. Discharge of hydrogen ions occurs preferentially at the "deeper" adsorption sites; ionisation of hydrogen atoms occurs more easily from "shallower" sites, sufficiently free migration of adsorbed atoms over the surface providing the necessary redistribution. This reaction scheme is represented formally in Fig. 2, where, for simplicity, only two kinds of site are shown.



Heavy arrows show the predominant directions of the various partial processes. It will be noted that the deep sites are cathodic and the shallow sites anodic, and that electrons flow within the metal phase from one to the other in a manner precisely analogous to the flow of current between local elements discussed in corrosion theory. If the two kinds of site are close together, the whole reaction scheme is mobile and the exchange current considerable; if they are far apart, the migration of adsorbed hydrogen atoms will be hindered. If, in the limit, the two kinds of site are situated on separate pieces of platinum, the migration of hydrogen atoms from one to the other becomes impossible and the general equilibrium scheme of Fig. 2 must be disturbed. The cell formed from bright and platinised

platinum electrodes acts as a model in which the main kinds of site are completely separated. Its behaviour may be discussed on the assumption that the general equilibrium scheme will always be established as far as conditions permit.

Although the bright electrode carries mainly shallow adsorption sites, hydrogen-ion discharge can occur at this electrode with some facility, if less readily than at the platinised electrode. This has been strikingly shown by examination of the behaviour of a bright platinum electrode in an electrolyte of constant-boiling hydrochloric acid vigorously swept out with nitrogen. The following table records cathodic current densities and corresponding potentials measured with respect to a platinised platinum electrode in equilibrium with the same solution and with hydrogen gas at 1 atm. pressure.

E (mv)	10	20	50	100	200	500	565
i ($\mu\text{A}/\text{cm}^2$)	36	22	2.8	1.2	0.8	0.3	0

Ionisation of hydrogen atoms, on the other hand, is believed to take place more easily at a bright platinum surface than at a platinised one. But in the "model" cell under discussion, the supply of hydrogen atoms to the bright electrode is restricted, for the bright platinum is not a very active catalyst for the atomisation of molecular hydrogen (Butler and Armstrong, *J.*, 1934, 734). The electrode thus acquires little atomic hydrogen from this source and none by any migration process. In these circumstances the main source of hydrogen atoms at the bright electrode is the discharge process. Thus, although intrinsically easier, ionisation at this electrode must wait upon discharge, and the electrode will assume such a positive potential as to bring the rates of these opposing processes to equality. This is considered to be the source of the positive rest-potential of the bright platinum electrode, which therefore carries a surface concentration of hydrogen atoms not in equilibrium with the gas phase (cf. Butler and Armstrong, *J.*, 1934, 732). This is known to be the case (Slygin and Frumkin, *Acta Physicochim.*, 1935, 3, 791; Ershler, *ibid.*, 1937, 7, 327; Pearson and Butler, *Trans. Faraday Soc.*, 1938, 34, 1163; Hickling, *ibid.*, 1945, 41, 333; Wicke and Weblus, *Z. Elektrochem.*, 1952, 56, 169). The effect of increasing temperature is consistent with this view, for as the hindered atomisation process occurs with increasing facility, the electrode eventually becomes reversible and its rest-potential falls to zero. Insofar as poisons promote these positive rest-potentials, it may be suggested that their poisoning action is exerted principally upon the atomisation process (cf. Aten and Zieren; Volmer and Wick; *loc. cit.*).

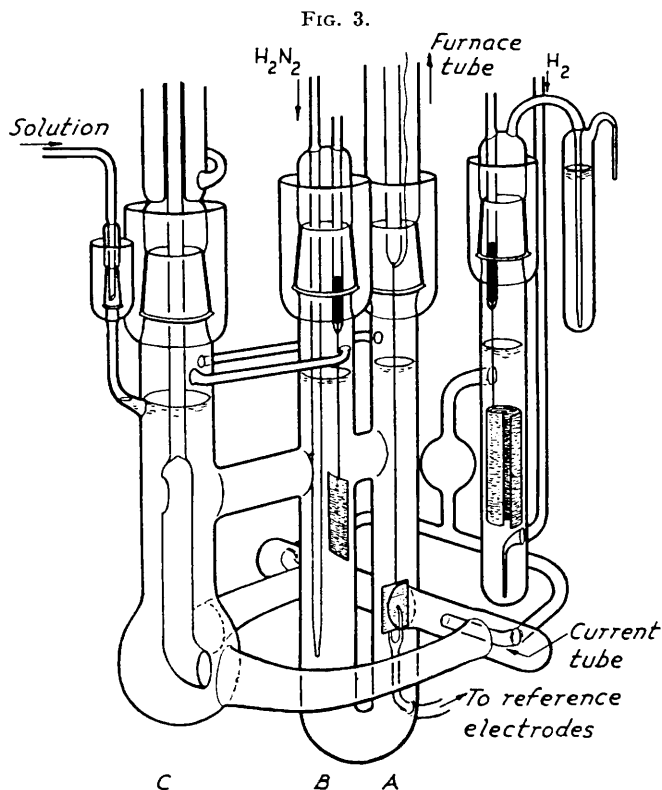
This interpretation carries implications which will not be discussed at present, but it must be further examined in relation to the behaviour of the "model" cell. When the external circuit is closed, electrons flow from the platinised electrode to the bright electrode, increasing the rates of discharge and of ionisation, respectively, at these electrodes. The two, connected directly together, operate as a reversible hydrogen electrode at the proper equilibrium potential (Beans and Hammett, *loc. cit.*). This multiple hydrogen electrode offers an extreme example of "site differentiation," in which the normally unobserved local currents become demonstrable; it also clarifies the operation of the "catalyst electrode" of Hills and Ives (*loc. cit.*).

The cell reaction of the "model" cell is, on this basis, the transfer of hydrogen gas from one electrode to the other, and this is consistent with the ready polarisation which occurs when current is allowed to pass and with the relief of polarisation by shaking. This, however, is the example used by Ostwald ("Lehrbuch der allgemeine Chemie," 1903, II, 896) of a cell reaction forbidden by the second law of thermodynamics, so that some other change must be involved. This is found by consideration of the platinum electrodes. It is known that hydrogen electrodes are subject to fatigue and become inactive with increasing age at a rate which increases with the removal of the last traces of oxygen from the solution. Hammett and Lorch (*J. Amer. Chem. Soc.*, 1933, 55, 70) have found that platinum black slowly loses activity when it is kept in hydrogen, and attribute this to the sintering of active points at which the highly exothermic recombination of hydrogen atoms continually occurs. There can be no doubt that electrolytically deposited platinum black is higher in energy content than the same weight of massive platinum, and that the dissipation of this excess of energy is a natural process attended by a decrease in free energy. Since, in

the cell under discussion, this cannot occur by processes of anodic dissolution and cathodic re-deposition of the metal itself, an alternative mechanism operates in which the hydrogen acts as the intermediary. Calculations in orders of magnitude of the probable energy terms involved show this explanation to be feasible. The total cell reaction does not therefore infringe the second law, and the discussion based upon the behaviour of this cell stands.

EXPERIMENTAL

Electrolytic Cell.—The electrolytic cell is illustrated in Fig. 3. The rectangular test electrode of "thermopure" platinum foil, 0.05 mm. thick and 5.2 cm.² in apparent surface area, was welded to a suspension wire of the same metal. It was accurately located in the cathode compartment, *A*, by internal glass seatings so arranged as to obscure the working surfaces of the electrode as little as possible. An all-glass centrifugal stirrer, driven by glass shafting running



in unlubricated, precision-ground, water-cooled glass bearings, provided a rapid flow of solution, normal to each electrode face, the solution returning to the stirring chamber, *C*, via alternative upper and lower paths. Rate of stirring, uncritical above a certain limit, was standardised by means of a Weston tachometer. Symmetrical design of the cell ensured the even distribution of current over both electrode faces; two "current tubes," equally spaced from the electrode on either side, communicated with an ancillary electrode vessel containing a very large working hydrogen electrode, at which the anodic reaction was hydrogen ionisation. Luggin capillaries approached the two sides of the electrode and communicated with a separate compartment containing duplicate reference hydrogen electrodes. A fifth electrode was situated in the "solution return" compartment, *B*, and consisted in the present experiments of a large platinised platinum electrode for purposes of final de-oxygenation and purification of the solution (Aten and Zieren, *loc. cit.*).

A "Vitreosil" furnace tube was fitted above compartment *A*. The test electrode could be raised into, or lowered from, this tube by means of a long, cylindrical ground joint, the inner

member of which carried the supporting wire for the electrode. Connection to the electrode was made by means of a coil of fine platinum wire, welded to the upper end of the supporting wire and issuing from the apparatus through a gas outlet bubbler at the top of the furnace tube. All the head fittings to the cell were attached by solution-sealed ground joints. A pressure of hydrogen, or nitrogen, in excess of atmospheric pressure was always maintained in the cell and could be sustained without passing gas for a prolonged period. Purified gases were supplied to the main cell by a bubbler entering compartment B.

Measuring Instruments.—Current, stabilised by variable series resistances (10^3 to 5×10^6 ohms), was measured by means of a multi-range microammeter, calibrated in terms of the iR drop across Sullivan standard resistors. E.M.F. measurements were made with a Tinsley 4025 potentiometer in the usual way. Attention was paid to screening and to insulation; Polythene and Silicone products were used where appropriate.

Materials.—Hydrogen. Commercial "oxygen-free" hydrogen used in some of the experiments was later replaced by hydrogen purified by active carbon at a pressure of 100–140 atm. and -196° . This gas was supplied by the British Oxygen Co., Ltd., and was stated to be of 99.998% purity. In either case the gas was passed through a purification train containing in its final form the following components: Baker Platinum "De-oxo" cartridge, non-absorbent cotton-wool filter, potash pellets, reduced "Specpure" copper at $500-550^\circ$, trap at -80° , platinised asbestos at 300° , traps packed with glass fragments and long glass spirals at -183° . Distribution of hydrogen to the various cell components was effected by tap systems, grease-lubricated, separated from the cell by the traps and spirals at liquid-oxygen temperature. No effect was observed attributable to change in source of hydrogen supplied to this purification train.

Nitrogen. Commercial "oxygen-free" nitrogen was passed through a similar purification train, suitably modified.

Water. Conductance water was prepared in a still of the Stuart and Wormwell type (*J.*, 1930, 85), in which steam from alkaline potassium permanganate solution was scrubbed with dilute phosphoric acid, admixed with a rapid stream of purified, oxygen-free nitrogen, and condensed in a Vitreosil condenser. The distillate was run to waste until its conductance fell to less than 0.08×10^{-6} ohm $^{-1}$; it was then collected in a 5-l. flask in which an atmosphere of pure nitrogen was always maintained.

Hydrochloric acid. "AnalaR" potassium chloride was freed from traces of other halogens by the method of Pinching and Bates (*J. Res. Nat. Bur. Stand.*, 1946, 37, 311), and twice crystallised from conductance water with rejection of head and tail fractions. The product was dried at 150° and used to generate, by action of "AnalaR" sulphuric acid, hydrogen chloride gas, which, after passing through traps at -80° , was absorbed in conductance water. The concentrated solution so obtained was distilled as constant-boiling mixture and stored in a silica vessel under an atmosphere of pure nitrogen.

Procedure.—Glass apparatus was cleaned for 12 hr. in freshly prepared chromic-sulphuric acid, washed thoroughly, and soaked for several hours in conductance water. Further washing with conductance water was followed by steaming from conductance water and drying at 100° . The cell was mounted in the thermostat bath ($25^\circ \pm 0.01^\circ$) and attached to the gas supply lines by glass-blowing operations, the apparatus being protected from contamination by means of a liquid-oxygen trap. Electrodes were cleaned first in warm, moderately concentrated hydrochloric acid, washed in water and suspended in the vapour of boiling nitric acid (d 1.50). They were then washed again, steamed from conductance water, and dried at 150° before being mounted in the cell. Working, reference, and deoxygenating electrodes were platinised by the method of Hills and Ives (*loc. cit.*) from a solution containing no lead.

After completion of the cell assembly, nitrogen was passed through the various cell compartments for 24 hr., followed by similar passage of hydrogen for at least 24 hr. The solution, prepared from constant-boiling hydrochloric acid and conductance water, without exposure to air at any stage, and through which hydrogen had been passed for 48 hr., was then introduced into the cell by pressure of hydrogen. The solution delivery tube was then sealed. Hydrogen was passed through the solution in the cell, circulated by the stirrer, for some hours before the start of electrical measurements.