Hydrogen Electrode Processes. Part II. Gold–Hydrogen Electrodes.*

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The electrodeposition of hydrogen from dilute acid solutions at gold electrodes has been studied, with results which show similarities with, and some differences from, this reaction occurring at platinum. The nature of the gold electrode, however, has been found to be radically changed by thermal pretreatment in hydrogen, the behaviour then corresponding with that of a " non-equilibrium atomic hydrogen electrode." The phenomena observed are discussed in terms of a postulated penetration of the metal phase by hydrogen atoms and in relation to mechanisms of desorption of hydrogen atoms from the gold–solution interface.

The work described in the preceding paper indicated that the characteristics of the hydrogen electrode reaction are strongly dependent upon the state of the metal surface upon which the reaction occurs. It was therefore thought that gold could be brought more easily to a standard state than could platinum, and would therefore be more suitable as a substrate for purposes of studying the mechanism of this reaction. Work with gold electrodes was accordingly started, with results of so unexpected and novel a nature as to merit a preliminary report and discussion. This forms the subject matter of the present paper.

The first experiments were made with fine gold electrodes under conditions exactly similar to those used previously for platinum, with no thermal pretreatment in hydrogen, and gave analogous results. Reproducibility was poor, but the following general statements can be made. Rest-potentials, measured with respect to a hydrogen electrode in the same solution, were positive. Measurements of the dependence of electrode potential upon current density were made which yielded Tafel plots the linear sections of which varied on either side of the slope of 0·118 v at 25° and which showed deviations from linearity consistent with an ionisation process increasing with falling current density. There was the same tendency for the Tafel slope to increase as a result of prolonged cathodic polarisation as in the case of platinum, and the same partial reversal of this change by sweeping out the solution with nitrogen. Two Tafel plots of measurements on a gold electrode, conducted by the " discontinuous method," recommended particularly for gold by Hickling and Salt (*Trans. Faraday Soc.*, 1940, **36**, 1226), are shown in Fig. 1 for hydrogen- and nitrogen-saturated solutions. It is noteworthy that polarisation curves for gold electrodes obtained in solutions swept out with hydrogen and nitrogen, respectively, do not appear to approach coincidence at the higher cathodic potentials, as is the case with platinum electrodes. The electromotive sensitivity of a metal to gaseous hydrogen requires a certain facility for atomisation of hydrogen molecules and for ionisation of hydrogen atoms. The loss of sensitivity by platinum with increasing cathodic polarisation can only be due to the suppression of the ionisation process, since it is unlikely that atomisation is ever potential-dependent (cf. Horiuti and Okamoto, *ibid.*, 1936, **32**, 1492; Calvin, *ibid.*, p. 1428). The sensitivity retained by gold under similar conditions shows that this metal is able, if less efficiently than platinum, to catalyse the atomisation of molecular hydrogen and has perhaps a greater facility than platinum in ionising hydrogen atoms. This is perhaps why no depolarisation due to adsorbed hydrogen is normally observed at gold (Hickling, *ibid.*, 1946, **42**, 518). It will become clear, however, that general statements about the properties of a metal may be falsified by the great variations in these properties which may occur as a function of the thermal and mechanical history of the metal. For the particular electrodes under discussion, however, it may be stated that all the " partial processes " of the hydrogen electrode equilibrium can take place at gold, but the balance between them is different from that which applies at platinum.

Heat treatment of a gold electrode in hydrogen gave rise to entirely new properties.

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* Part I, preceding paper.

This operation involved withdrawal of the electrode from the solution into a furnace tube attached to the cell and its restoration to the same solution, after heating and cooling, without exposure to air at any stage. The electrode was, typically, maintained at 750—800° for 6 hr., then at 500° for 17 hr., and finally subjected to slow cooling, in a stream of hydrogen passing up the furnace tube from the cell. This annealing process was designed to bring the electrode to a reproducible standard state. After this treatment, a representative electrode showed a reproducible rest-potential of +400 mv. A " polarisation run " by the usual rapid method gave a very abnormal Tafel plot of the kind shown in Fig. 2, which includes for comparison another plot judged to be normal for untreated, rather active gold. Overpotentials were greater than those recorded for the same electrode in the same solution before annealing (*e.g.*, 550 and 270 mv respectively at 2 mA/cm.^{2}) and greater than any overpotentials previously recorded for gold. Rest-potentials and overpotentials were almost completely insensitive to replacement of hydrogen by nitrogen in the cell, in remarkable contrast to the previous behaviour. It may be noted that the abnormal curve in Fig. 2 resembles those reported by Hitzler and Knorr (*Z. Elektrochem.*, 1949, **53**, 228) for catalytically inactive metals at which, according to these authors, recombination of hydrogen atoms occurs slowly, leading to the establishment at low current densities of an adsorption layer, offering hindrance to the discharge process.

FIG. 1.

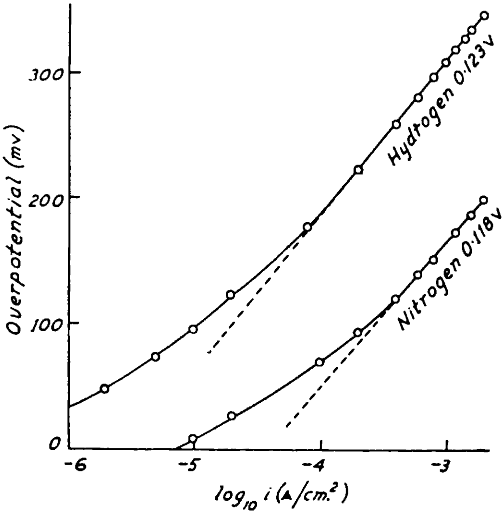
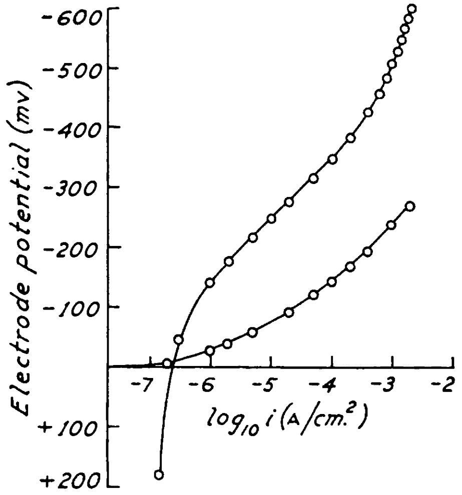


FIG. 2.



It became evident, however, that the annealing process had caused even more radical changes in the properties of the gold, calling for thorough and detailed investigation. Circumstances do not allow this to be pursued immediately; the present report will therefore be confined to a description of the more outstanding phenomena and their provisional interpretation.

For the unannealed electrodes, a rapid growth of overpotential occurred from the instant that a constant current density was established, leading to a steady value showing no further significant change in a period of one hour. The annealed electrodes showed a complex growth of overpotential, which, without detailed analysis, may be described as follows. An initial period of rapid growth passed smoothly into an indefinitely prolonged period of slow growth. Constancy of overpotential was not attained in 6 hr., the longest time for which polarisation was continued. This behaviour must be associated with a continuous and progressive change in the state of the electrode concerned. This is supported by the effect of a sudden reduction in the polarising current density; an immediate fall of overpotential was instantly followed by a period of growth faster than before (cf. Busing and Kauzmann, *J. Chem. Phys.*, 1952, **20**, 1129).

The properties of an annealed gold electrode after prolonged cathodic polarisation were very abnormal. On breaking the polarising circuit, the negative potential of the electrode fell rapidly, linearly with log time, to a value of about —150 to —200 mv with respect to a hydrogen electrode in the same solution. From this point, the potential decayed rapidly at first, then more slowly, passing through zero and eventually returning to its original resting value of +400 mv. These changes were slow enough to allow brief investigations of the properties of the electrode both before and after its potential crossed the reversible hydrogen potential. This was done by connecting the electrode to the hydrogen electrode *via* a microammeter. Whilst the electrode potential was still negative, this connection caused a current, initially of a few microamperes, to flow anodically at the gold electrode. This current slowly decayed, but was temporarily enhanced by stirring. On disconnection, partial recovery of the negative potential took place before resumption of the original slow decay. When the electrode potential had passed spontaneously to positive values, the same operation caused cathodic current to flow at the gold electrode, enhanced by stirring and persisting for the longest period studied, 16 hr. On disconnection, the potential changed immediately in the direction of the final rest-potential, +400 mv. These

FIG. 3.

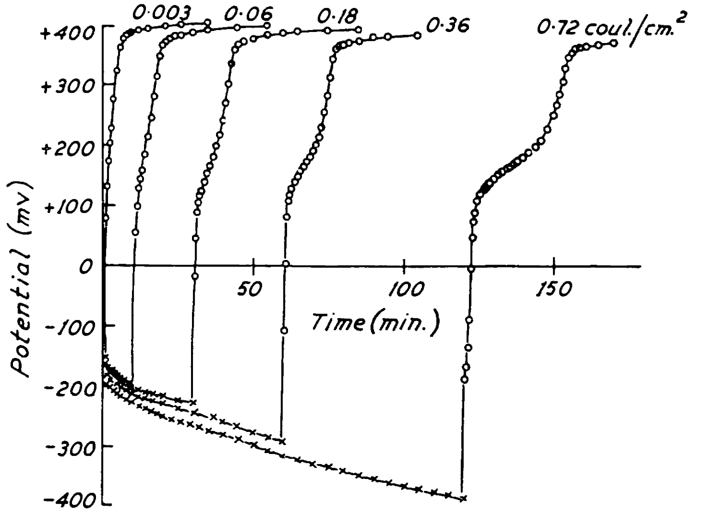
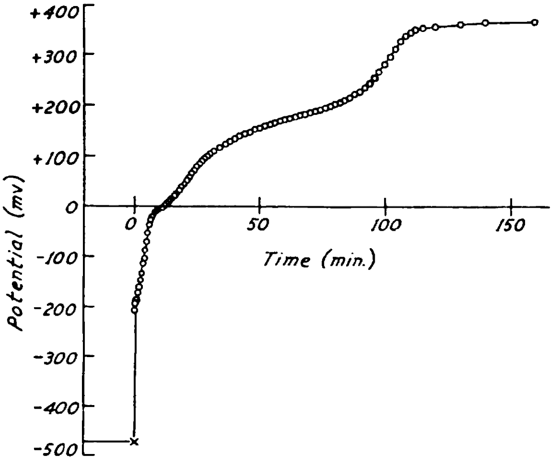


FIG. 4.

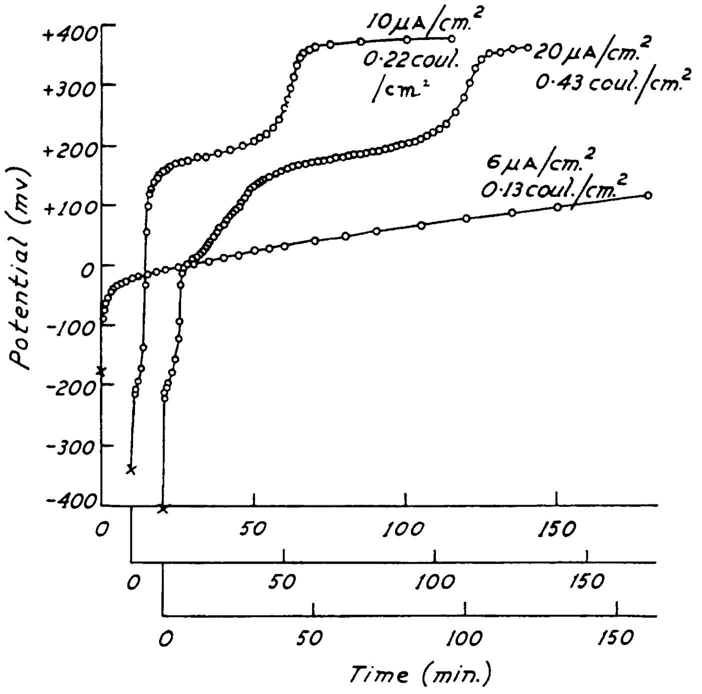


experiments leave no doubt that the potentials through which the electrode passes after cathodic treatment are well-defined potentials, decisively determined by the state of the electrode at each instant. The state of the electrode at any time is, in turn, a function of the stage reached in a slow reaction at the electrode–solution interface, leading finally to a steady resting state.

The course of the slow potential changes after cessation of cathodic polarisation attracted interest, and the following facts have been established :

(1) For a given constant current density of cathodisation, the course of the subsequent open-circuit potential–time curve depended upon the duration of cathodisation. This is illustrated in Fig. 3, which also shows the growth of overpotential during periods of $\frac{1}{2}$, 10, 30, 60, and 120 mins. at a uniform current density of 100 μA/cm.^{2}, and in Fig. 4, which records the change in potential with time after a cathodisation of 6 hr. at the same current density.

FIG. 5.



(2) The form of the open-circuit potential–time curve depended strongly upon current density in the preceding cathodisation up to a certain current density. Above this critical current density, however, this dependence vanished and the curve then became a function of the time of cathodisation alone. This is illustrated in Fig. 5, which shows the changes of potential with time after 6-hr. cathodisations at current densities of 6, 10, and 20 μA/cm.^{2}. It is seen that the last of these curves is nearly identical with that of Fig. 4, relating to 100 μA/cm.^{2}. This effect is believed to be associated with the attainment during the preceding cathodisation of an electrode potential exceeding about —300 mv. If this critical value was exceeded, the subsequent potential-decay curve assumed sensibly the same inflected form.

(3) At no stage of overpotential growth and decay did any annealed gold electrode show any perceptible effect when hydrogen passing through the cell was replaced by nitrogen; it was as if the annealing process had, in some respects, caused the electrode to become isolated from its surroundings.

(4) The observed effects depended upon electrode material in the following way.

Results obtained with a given electrode of fine gold were reproducible with some accuracy. Other electrodes prepared from the same sample of fine gold gave results in close correspondence. A second sample of fine gold, of independent history, furnished electrodes which gave similar, but not identical results. Finally, an electrode of spectroscopically pure gold showed considerable disparity, but in the sense of enhanced abnormality, with even higher overpotentials subject to more protracted decay of the same inflected type.

Two further observations on experimental aspects of this work must be made. During prolonged cathodic polarisation of unannealed gold electrodes, adherent bubbles of hydrogen were formed at localised places on the electrode surface and were not dislodged by vigorous stirring. It is thought to be significant that bubbles were not formed on any of the electrodes after annealing.

Since interest was mainly devoted to the change in electrode properties caused by annealing in hydrogen, all but one of the annealing operations were carried out in a stream of hydrogen that had passed through the electrolytic cell already charged with solution, in which the electrode had already been given preliminary examination. The annealing process therefore occurred in an atmosphere of hydrogen containing water vapour. There is reason to believe that the presence of this water vapour was of significance, for, in a single case, an otherwise similar annealing operation conducted in dry hydrogen had little effect. A systematic study of annealing conditions is clearly required. The range of potentially significant experimental conditions studied in the present work has been unavoidably limited. The invariable appearance of new phenomena as a result of the same specified thermal treatment of the electrodes, however, suggests that these phenomena are of fundamental interest.

Discussion

Positive rest-potentials, and high overpotentials, increasing with time during cathodic polarisation at constant current density, and subject to slow and inflected decay on open circuit after polarisation, have all been observed before and have been attributed to the presence of poisons (Volmer and Wick, *Z. phys. Chem.*, 1935, **172**, *A*, 429; Bockris and Conway, *Trans. Faraday Soc.*, 1949, **45**, 989; Bowden, *ibid.*, 1927, **23**, 571). The technique of the present work minimised the incidence of poisoning, which was not evident in the behaviour of the electrodes before annealing. The effects were, moreover, evoked by the annealing process alone and were of a magnitude out of all proportion to any conceivable poisoning effect. It is probable, however, that the thermal treatment in hydrogen had a similar effect to that of poisons in destroying catalytically active centres on the surface of the electrode. That this treatment radically altered the surface of the metal was confirmed by examination of the electrode under the reflecting polarising microscope. Before annealing, the surface was apparently structureless, except for what appeared to be mechanical scratches and scores, but afterwards it showed a definite crystalline structure with well-marked grain boundaries. It is probable that the presence of hydrogen exerted an additional effect. Thus, Hammett and Lorch (*J. Amer. Chem. Soc.*, 1933, **55**, 70) have shown that platinum is deactivated by gentle heating in hydrogen. This they attributed to the "burning out" of active centres by the great energy effect of the reaction $H_2 \rightleftharpoons 2H$ initially established at these centres. A similar mechanism may operate during the annealing of the gold electrodes in hydrogen, with the additional possibility of the co-operation of the reaction $H_2O \rightleftharpoons H_2 + \frac{1}{2}O_2$, due to the water vapour present under the conditions of our experiments, in the de-activating process. It is known that heating in moist hydrogen exerts a passivating effect on platinum (Ershler, Deborin, and Frumkin, *Acta Physicochim.*, 1938, **8**, 565).

The possibility that this treatment might lead to the firm adsorption of OH radicals on the gold has been considered. It is known, however, that oxygen or oxide films on gold exert a depolarising action at quite high positive potentials (Armstrong, Himsworth, and Butler, *Proc. Roy. Soc.*, 1933, *A*, **143**, 89; Deborin and Ershler, *Acta Physicochim.*, 1940, **13**, 347; Hickling, *Trans. Faraday Soc.*, 1946, **42**, 518). Such films could hardly resist prolonged cathodic polarisation so as to effect a permanent change in electrode properties. Simultaneous adsorption of H and OH to any significant extent would be highly metastable (cf. Bennewitz and Schieferdecker, *Z. phys. Chem.*, 1931, **157**, *A*, 32). It is therefore thought that this treatment undoubtedly altered the properties of the gold itself, for it is known that this metal is susceptible to significant structural changes at temperatures as low as 450° (Chung Fu Ying and Farnsworth, *Phys. Rev.*, 1952, **85**, 485).

Whatever detailed interpretation may be found for the processes occurring during annealing, there is no doubt of their effects upon the gold electrodes in causing profound deactivation. Beforehand, their behaviour was consistent with rate-limitation of cathodic hydrogen deposition by slow discharge. This implied that hydrogen-atom recombination occurred without significant hindrance and this is confirmed by the sensitivity of the electrodes to gaseous hydrogen. This sensitivity must be due to catalysis of atomisation which must be associated with catalysis of recombination. Afterwards, the complete insensitivity of the electrodes to gaseous hydrogen, and their ability to sustain very high positive rest-potentials, indicate clearly that catalytic activity had been lost. In this state of the electrodes, cathodic hydrogen evolution no longer followed any clear-cut kinetic law. It is obvious that the overpotentials, slow in build-up and decay, were composite, being partly due to the hindrance of a reaction step and partly due to the accumulation of electromotively active cathodic products. There is a close analogy with the case of palladium, at which the hydrogen overpotential is the sum of two contributions (Hitzler, Knorr, and Mertens, *Z. Elektrochem.*, 1949, **53**, 228), one of which is transferable through a palladium membrane and the other not (Frumkin and Aladjalova, *Acta Physicochim.*, 1944, **19**, 1). It is also known that the destruction of active centres on the surface of, *inter al.*, palladium, by poisoning, increases the cathodic production of atomic hydrogen (Kobosew and Monblanowa, *ibid.*, 1936, **4**, 395; Farkas, *Trans. Faraday Soc.*, 1936, **32**, 1667) and the transferable overpotential.

The conclusion is reached that annealed gold forms a " non-equilibrium atomic hydrogen electrode." Its behaviour can only be explained in terms of a cathodic generation of hydrogen atoms which are unable to escape from the metal by any facile mechanism: combination, ionisation, evaporation, or electrochemical desorption. All the signs are present of a metal which becomes, over long periods, increasingly saturated with hydrogen which can only be dissipated in some slow process, or combination of processes, reflected in the slow and characteristic decay of overpotential. This statement, which summarises the main result of the present work, is of possible importance in relation to current ideas on hydrogen overpotential. It is amplified and supported in the discussion which follows.

The growth of overpotential at an annealed gold electrode has been observed oscillographically, but cannot be analysed in detail at present. It is clear, however, that during the later stages of this growth the electrode must pass through a succession of states, developing one from another. Early in this development, hydrogen atoms accumulate upon the electrode surface. The processes by which these atoms leave the surface increase in rate and, normally, this would soon establish a kinetic steady state. But if these processes are very slow, then at all but the lowest current densities the accumulation of hydrogen atoms may become extensive and lead to a progressive change in the properties of the electrode surface. This may occur by a " burning out " or obstruction of the few remaining active centres. If the rate of dissipation of hydrogen atoms has an upper limit, not dependent upon potential, there will be a critical rate of discharge. For rates of discharge less than the critical, a steady state will be possible; for higher rates, accumulation of atoms may proceed unchecked and lead to progressive saturation. Since rate of discharge is a function of cathodic potential, this is consistent with the observation that has been made that there is a critical potential attainment of which during polarisation greatly modifies subsequent electrode behaviour.

In the later stages of overpotential growth, development is slow enough to suggest the participation of bulk, rather than purely surface phenomena. It is believed that atomic hydrogen penetrates the gold lattice. Gold does not normally dissolve hydrogen (cf. Barrer, " Diffusion in and through Solids," Cambridge Univ. Press, 1951, p. 146), although silver does so. Since gold and silver have cubic close-packed structures of similar dimensions, there seems to be no theoretical reason (cf. Fowler and Smithells, *Proc. Roy. Soc.*, 1937, *A*, **160**, 37) why hydrogen should not dissolve in gold. Recorded solubilities relate to equilibria with gaseous hydrogen under such conditions that the equilibrium concentration of hydrogen atoms is very small. Very different behaviour may be expected if the surface of the metal phase, in such a state that it is unable to catalyse atom recombination, is provided with a relatively enormous disequilibrium concentration of pre-formed hydrogen atoms. Benton's statement (*Trans. Faraday Soc.*, 1932, **28**, 202) that activated adsorption must always precede solution is perhaps relevant in this connection. This is well established by the recent proof that an evaporated film of spectroscopically pure gold, otherwise indifferent to hydrogen, takes up atomic hydrogen with avidity (Pritchard and Tompkins, personal communication), an interesting result which appears to be opposed to the view that chemisorption of hydrogen on clean metals is not activated (Eley, *J. Phys. Colloid Chem.*, 1951, **55**, 1017).

The view that bulk absorption is involved in our experiments is supported by the dependence of electrode properties, as judged by overpotential decay, on time of cathodisation and their independence of current density above a certain minimum. If these properties depend upon the amount of hydrogen absorbed, they will in turn depend solely on the period of time for which the surface concentration of hydrogen atoms has been maintained at its saturation value.

The nature of the potential changes after cathodisation also suggests a bulk phenomenon; there is a superficial resemblance to desorption isotherms of hydrogen from palladium, in which discontinuities may arise solely because of maintenance of the rate of surface desorption by faster diffusion from the interior (Ubbelohde and Egerton, *Trans. Faraday Soc.*, 1932, **28**, 284). Discontinuous overpotential decay has also been observed with platinum (Bryant and Coates, *Discuss. Faraday Soc.*, 1947, **1**, 115), tantalum, niobium, and molybdenum (Bockris, *Trans. Faraday Soc.*, 1947, **43**, 417), in which metals, with the possible exception of molybdenum, hydrogen is soluble (Smithells, "Metals Reference Book," Butterworths, 1949). It is believed that the potential changes in question do in fact represent a discontinuous desorption of hydrogen atoms. The further discussion is based upon this view.

Desorption isotherms with successive discontinuities may occur when adsorbed molecules escape from a non-uniform surface consisting of a discrete number of areas of differing heat of evaporation (Taylor, *ibid.*, 1932, **28**, 131), and some of the desorption isotherms of hydrogen from metals observed by Benton and White (*J. Amer. Chem. Soc.*, 1931, **53**, 3301) show resemblances to our potential–time curves. The loss of hydrogen atoms from a metal–solution interface, however, is likely to differ from the case of evaporation into the gas phase. On the assumption that the hydrogen atoms are firmly held at the gold surface (Farkas, *Z. phys. Chem.*, 1929, **5**, *B*, 474; Deborin and Ershler, *loc. cit.*), two mechanisms of desorption require examination.

The state of the adsorbed atoms, held by short-range forces, may be viewed in terms of Lennard-Jones's discussion (*Trans. Faraday Soc.*, 1932, **28**, 333). Each atom is held in a potential field which has a deep hollow along a normal to the surface passing through a gold atom and which is wavy in two dimensions parallel to the surface. Evaporation from the surface and migration about it are therefore both activated processes, of which migration is by far the easier. This suggests that desorption occurs mainly by recombination, which probably only takes place when two atoms meet close enough to a gold atom for the latter to act as third body. The frequency of such encounters, leading to desorption, will depend upon the two-dimensional geometry of the surface concerned in two ways; first, in an obvious way upon the geometry itself, and secondly, because the geometry largely controls the activation energy of migration. This will tend to differentiate one kind of surface from another as a substrate for the recombination reaction. Not only are markedly different specific reaction rates (*i.e.*, rates per unit surface concentration of atoms) to be expected for recombinative desorption at different crystal planes, but also different maximum rates, for each kind of plane has a different upper limit to the number of hydrogen atoms it can accommodate. This will widen the disparity between the planes. It is known that different crystal planes of metals do differ in significant properties: adsorptivity and work function (Johnson and Shockley, *Phys. Rev.*, 1936, **49**, 436; Martin, *ibid.*, 1938, **53**, 937) and in hydrogen overpotential (Allbrecht, *Z. Elektrochem.*, 1951, **55**, 173).

Reasons have already been given for thinking that progressive bulk saturation of the gold occurs as a result of prolonged cathodisation. Whether this is due to lattice penetration, or to the entry of hydrogen atoms to interior surfaces along lattice defects or grain boundaries, a reservoir of atoms will be provided for the replenishment of the surface planes. In either case the migration of hydrogen atoms from the interior will be an activated process occurring more easily in preferred directions (cf. Barrer, *op. cit.*, p. 200), probably parallel to the crystal planes of denser packing.

Events following cathodic polarisation may be traced on the basis of these postulates. Immediately the polarising circuit is broken, activation overpotential very rapidly vanishes according to well-known laws. There may then occur a relief of a degree of surface supersaturation by evaporation of hydrogen atoms, leading to a temporary steady state, during which the rate of replenishment of hydrogen atoms is adequate to keep all surfaces operating at the maximum rate of recombinative desorption. With continued decline of the internal concentration of hydrogen atoms, however, there must eventually be a decrease in the rate of desorption. Reasons why this should occur in a non-uniform manner have already been indicated, and the simplest assumption is that rate of desorption from one kind of plane is maintained by lateral migration from another. If, however, the surface planes are replenished by diffusion from the interior, there is a further factor promoting non-uniformity. Crystal planes of low reticular density, less efficient in promoting recombinative desorption, are necessarily intersected by other planes of higher reticular density, along which migration of atoms is relatively mobile. These will serve, therefore, for the more efficient replenishment from the interior of the less active surface planes. Conversely, the surface planes of closest spacing and greatest activity can be no more, and perhaps less, efficiently replenished. Conditions may then arise where rates of recombination at the different surface planes approach equality, but at one plane rate-limitation may be due to the recombination and at another to replenishment. A steady state would then arise.

The adsorption of hydrogen atoms on metals, however, may be so strong that there is no tendency for recombinative desorption to occur (Roberts, *Trans. Faraday Soc.*, 1939, **35**, 941). Although this statement does not apply directly to the metal–solution interface, it is necessary to envisage an electrochemical desorption process as a possibly easier alternative, since the potential barrier to the removal of a hydrogen ion may be lower than that opposing the removal of an atom. There can be no doubt that hydrogen atoms adsorbed at a metal–solution interface have some tendency to ionise; the system can be regarded as an acid (Frumkin, *Z. phys. Chem.*, 1932, *A*, **160**, 116; Horiuti and Polanyi, *Acta Physicochim.*, 1935, **2**, 505), with the bare metal as the conjugate base. Different crystal planes represented in the surface will be undoubtedly of different " acid strength," and it may be supposed that ionisation occurs preferentially at an area of lower adsorption energy. But, clearly, no desorption process accompanied by a net transfer of charge will fit the case. This is avoided if a simultaneous discharge of hydrogen ions from solution occurs at an area of greater adsorption energy. This is intrinsically probable; it will be accompanied by a flow of local current within the electrode and will provide a mechanism for the stepwise loss of total hydrogen by whatever process. If, however, desorption of hydrogen as a molecule is favoured whenever a hydrogen ion is discharged at a site adjacent to an adsorbed atom, this will tend to keep the area concerned half covered with hydrogen atoms. If the extent of covering becomes less, the probability of discharge without desorption increases; if it becomes more, the reverse. This again would clearly favour the occurrence of steady states. It may be noted that the evidence of the behaviour of these annealed gold electrodes is against the occurrence of what is generally implied by " the electrochemical mechanism."

Explanation of the overpotential decay of the annealed gold electrodes in terms of these theories of hydrogen-atom desorption involves the assumption already tacitly made that the hydrogen atoms are potential-determining, but not in accordance with the Nernst equation. This is consistent with the basic postulate that a non-equilibrium atomic hydrogen electrode is involved, for the Nernst equation can apply only to a system in equilibrium.

The results of this preliminary work and its interpretation raise a number of points of interest that require further investigation. Although atomic hydrogen plays a minor part in current theories of hydrogen overpotential and cathodic hydrogenation, its essential participation in many striking phenomena at electrodes other than palladium cannot be doubted (as, for example, in the remarkable " iron pillow " experiment of Fink, Urey, and Lake, *J. Chem. Physics*, 1934, **2**, 105). It is possible that atomic hydrogen should receive more general attention in this connection. This view was emphasised some years ago (Hickling and Salt, *Trans. Faraday Soc.*, 1942, **38**, 474) and can still be supported. It is hoped to follow this matter in a further communication.

EXPERIMENTAL

The preparation of materials and experimental procedure were as described in the preceding paper, except for the following. The solution-preparation flask was fitted with an ancillary gold electrode at which pre-electrolysis was carried out, 850 coulombs being passed, under suitable conditions, in the course of 24 hr. The solution was then transferred to the cell by hydrogen pressure. Further pre-electrolysis of the solution in the cell (20 coulombs in 20 hr.) was then conducted by means of a second ancillary gold electrode, replacing the platinised platinum electrode in compartment *B* (cf. Fig. 3 of preceding paper).

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