211. *Alternative Electrode Reactions. Part I. Reactions at a Platinum Cathode in Nitric Acid Solutions.*

By Harold J. T. Ellingham.

In the course of electrolysis under constant or gradually varying conditions, it sometimes happens that a reaction which is occurring with high current efficiency at one of the electrodes gives place more or less abruptly and completely to a different reaction, the transition from one to the other being marked by a definite change in the single potential of the electrode. Transitions between reactions which occur at anodes of metals exhibiting active and passive states, *e.g.*, between metal dissolution and oxygen evolution, have been very extensively investigated, but comparatively little attention has been given to transitions between electrode reactions of other types. It has been pointed out, however (Ellingham and Allmand, *Trans. Faraday Soc.*, 1923, **19**, 753), that all such transitions, whether they occur at an anode or a cathode, have a number of common characteristics, and can, in fact, be regarded as constituting a definite class of phenomenon—*transitions between alternative electrode reactions*. In this connexion, no attempt is made to distinguish between transitions involving an alteration of the primary electrode reaction and those in which the change may be confined to a secondary reaction.

An investigation of transitions between alternative electrode reactions of various types has been undertaken with a view to further characterisation of this general class of phenomena. The present paper deals with a cathodic example.

Reactions at a Platinum Cathode in Nitric Acid Solutions.—Faraday (*Phil. Trans.*, 1834, **124**, 96) observed that in the electrolysis of dilute nitric acid solutions between platinum electrodes, hydrogen was evolved at the theoretical rate from the cathode, but with concentrated solutions no hydrogen evolution occurred, the cathodic products being nitrous acid and apparently nitric oxide. By increasing the applied voltage, however, hydrogen could be liberated even from concentrated solutions : the greater the concentration, the higher was the voltage needed for this purpose. In the work of Fromme (*Wied. Ann.*, 1883, **19**, 300) and Ihle (*Z. Elektrochem.*, 1895, **2**, 174) on the Grove–Smee cell there is some indication that these two processes, hydrogen evolution and production of nitrous acid (sometimes accompanied by nitric oxide), may be alternative electrode reactions in the sense explained above. Thus, during gradual dilution of the nitric acid in a Grove cell, the *E.M.F.* remained nearly constant around 1·8 volts until a critical stage was reached whereat it fell sharply to about 0·7 volt. The cathode reaction changed simultaneously from the production of nitrous acid and oxides of nitrogen, characteristic of the Grove cell, to hydrogen evolution, characteristic of the Smee cell. Actually, however, the alternative character of the two reactions has been most clearly indicated by the early experiments of Schönbein (*Pogg. Ann.*, 1839, **47**, 563) on the electrolysis of nitric acid solutions. Indeed, the two reactions seemed to be so distinct that Schönbein was led to postulate two different " states " of platinum in order to account for their separate occurrence. Evidently, the observed phenomena reminded him of those of anodic passivity, and in this respect he anticipated the point of view taken up in the present series of investigations.

EXPERIMENTAL.

Nitric acid solutions of various concentrations have been electrolysed between smooth platinum electrodes, and the cathode potential measured at intervals (A) during a step-wise increase (and subsequent decrease) of the applied voltage, the current density (*C.D.*) being also measured at each stage; and (B) during the maintenance of a constant *C.D.*

These two methods of experiment have proved useful in the study of anodic passivation phenomena. Experiments of type A bring out the general character of the relations between *C.D.* and potential, and hence indicate the conditions for the occurrence of transitions between the alternative electrode reactions; whilst those of type B show how these relations and conditions are affected by the time factor (compare Ellingham and Allmand, *loc. cit.*; W. J. Müller, *Z. Elektrochem.*, 1927, **33**, 401).

The system, Pt(cathode) | HNO_3 solution, does not appear to have been investigated previously on these lines. A few polarisation measurements were made by Ihle (*Z. physikal. Chem.*, 1896, **19**, 577), but the *C.D.*'s employed were not specified.

Apparatus.—The electrolysis cell, which was supported in a thermostat, consisted of a rectangular glass jar provided with a cover fashioned from a block of paraffin wax. In all except certain preliminary experiments, the cathode consisted of a stout platinum wire bent into the form of a flat spiral and sealed into a glass tube which was supported so that the spiral was in a vertical plane. The anode was a piece of platinum foil. The total volume of electrolyte was always 70 c.c., but 10 c.c. of this were contained in a small cylindrical porous pot standing on the bottom of the cell and completely surrounding the anode. The anode plate and the spiral portion of the cathode were just submerged, their effective surface areas being 3·0 and $0{\cdot}52_6$ sq. cm. respectively. The catholyte was stirred by means of a glass stirrer. The gaseous products of electrolysis were allowed to escape freely through an opening in the cover of the cell.

In experiments of type A the electrolysing current was furnished by two lead accumulators. In those of type B, however, current was taken from the 110-volt D.C. lighting circuit. By using such a comparatively high voltage supply and a correspondingly high resistance in the circuit, the current strength remained practically constant even when the back-*E.M.F.* of the electrolysis cell changed by about 1 volt as a result of the transition from one cathode reaction to the other.

One limb of a capillary solution bridge was cemented into the wax cover of the cell in such a position that its lower end, which was drawn out slightly and bent at right angles, pressed closely against the cathode coil. The other limb of this bridge and the connecting tube of a normal calomel electrode dipped into a small beaker containing nitric acid of the same concentration as that in the cell.

The *E.M.F.* of the system

$$\mathrm{Pt}\left(\begin{matrix}\text{cathode of the}\\ \text{electrolysis cell}\end{matrix}\right)\Big|\ \mathrm{HNO_3}\ \text{solution}\ \vdots\ N\text{-}\mathrm{KCl,Hg_2Cl_2}\ \Big|\ \mathrm{Hg}$$

was measured by the compensation method, a metre slide-wire being used, with a capillary electrometer as null instrument. Values of this *E.M.F.* are referred to as cathode potentials on the normal calomel scale. Actually, the *E.M.F.* readings should be corrected for liquid-junction potential in order to obtain the true cathode potential, but the magnitude of this correction cannot be estimated when concentrated nitric acid solutions are used. Through neglect of the correction, which is probably of not inconsiderable magnitude, cathode potentials in nitric acid solutions of different concentrations are not strictly comparable. For our purpose, however, it is sufficient that *changes* of cathode potential in a solution of given concentration are properly measured by changes in the uncorrected values of the *E.M.F.*

Nitric Acid.—" Pure " nitric acid (Hopkin and Williams) was distilled from silver nitrate and potassium nitrate, and then redistilled alone from a Jena-glass retort. After a rapid current of air had been drawn through the product until it was quite colourless, stock solutions of various concentrations were made up by dilution.

Experiments of Type A. First Series.

The electrodes were put into the electrolyte 30 mins. before electrolysis was begun in order that they might attain a steady potential. 0·2 Volt was then applied across the electrodes, and at successive 5-minute intervals the applied voltage was increased to a value 0·2 volt above the *P.D.* prevailing at the end of the previous period. When a suitably high *P.D.* had been attained, the voltage was decreased in similar steps. Readings of current strength, cathode potential, and *P.D.* between the electrodes were taken 4 mins. after each increase (or decrease) of applied voltage.

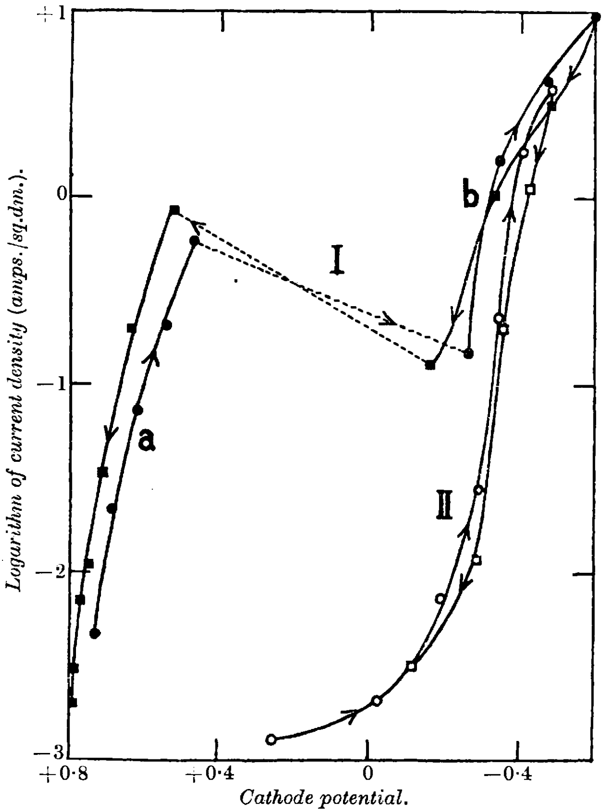
Relations between cathode potential, e_c (volts), and cathodic *C.D.*, d_c(amp./sq.dm.), under these conditions are shown for two typical cases in Fig. 1, where $\log d_c$ is plotted against e_c. This method of plotting is adopted in order to be able to cover a very wide range of *C.D.*, and because for many electrode reactions e_c is approximately a linear function of $\log d_c$.

Curve I, for 3·40*N*-acid, consists of two distinct branches, branch *a* corresponding to reduction of nitric acid to nitrous acid, and branch *b* to hydrogen evolution as the predominant cathode reaction. The transition from *a* to *b* and *vice versa* involves a sudden jump of potential of about 0·6 volt. In curve II, for

2·05N-acid, however, there is a direct passage from a residual current region at very low *C.D.*'s to a hydrogen evolution branch corresponding with *b* in curve I.

In the lowest part of branch *a*, curve I, the polarisation tends to decrease slightly during the 5-minute period allowed at each setting of the potential divider, but in the uppermost part of this branch there is a tendency for the polarisation to rise, and very slight evolution of gas (nitric oxide) can be observed. Eventually, at a certain setting of the potential divider, the rise in polarisation suddenly accelerates and the transition to branch *b* is completed in a few seconds. Vigorous hydrogen evolution then sets in, and thereafter the polarisation increases gradually at any given setting of the potential divider. This is the normal increase of hydrogen over-potential with time. When the reverse transition occurs

FIG. 1.



I. 3·40N-HNO_3. II. 2·05N-HNO_3.

during step-wise decrease of the applied voltage, hydrogen evolution ceases abruptly and the polarisation falls to a value lower than that at which the $a \longrightarrow b$ transition began. No gas evolution occurs after the $b \longrightarrow a$ transition, but a few hydrogen bubbles usually remain on the cathode.

With more concentrated solutions, curves similar to I were always obtained, and, the higher the concentration, the greater were the *C.D.*'s at which the transitions occurred. Evolution of nitric oxide before the $a \longrightarrow b$ transition was more marked with more concentrated solutions but the current efficiency of its production never became high.

The form of these curves is closely similar to those obtained for anodes of metals exhibiting active and passive states, branch *a* corresponding with the former state and branch *b* with the latter. The " hysteresis " between the ascending and descending curves (Fig. 1, I) is a well-known feature in anodic passivation and activation. It is clear, therefore, that at a platinum cathode in nitric acid solutions of sufficient concentration there are two electrode reactions which are alternative in the sense defined above. In no case did the log d_c–e_c curves exhibit more than two branches apart from the residual current line at very low *C.D.*'s (compare chromic acid solutions; Liebreich, *Z. Elektrochem.*, 1921, **27**, 94; 1923, **29**, 208).

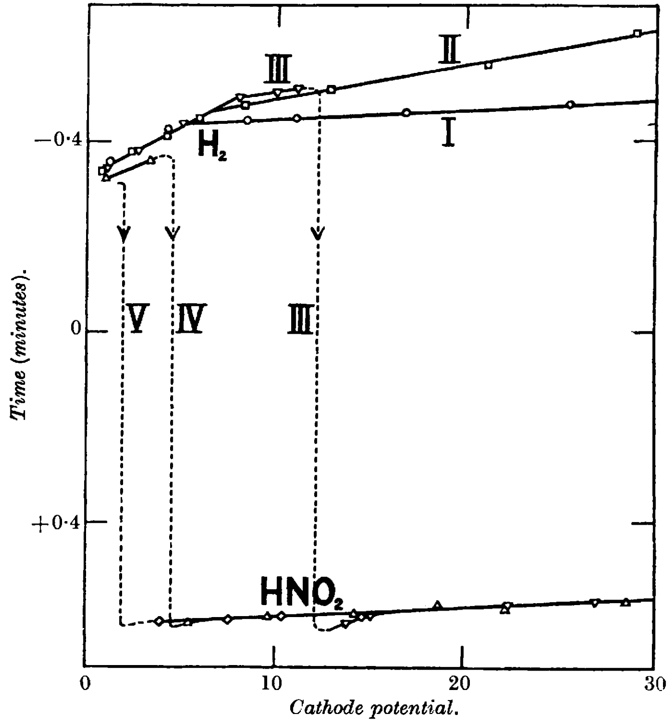
In the course of these experiments it was observed that the approximately steady potentials acquired by the coiled-wire electrode during immersion in the solution before electrolysis were dependent, not only on the nitric acid concentration, but also to some extent on the cathodic treatment to which this electrode had been subjected in the previous experiment. Such effects persisted even after the electrode had been exposed to the air for several days. In order to avoid any possibility that differences in previous treatment might affect the reproducibility of the cathode potentials during electrolysis, the following procedure was adopted in all further work : immediately after each experiment the cathode was immersed for 15 minutes in 68% nitric acid, washed in running water, and left over-night exposed to the air before being used again. In all cases the potential of the electrode was measured at intervals during the 30-minutes immersion in the electrolyte before electrolysis, in order to ensure that a steady value had been reached.

Experiments of Type B.

By analogy with anodic passivation, it was expected that in the electrolysis of a moderately concentrated nitric acid solution at a suitably chosen constant *C.D.*, reduction to nitrous acid would occur first and eventually give place suddenly to hydrogen evolution.

Actually, however, in numerous experiments at various constant *C.D.*'s this sequence of electrode reactions was never observed. Hydrogen evolution was always the initial process. If the *C.D.* exceeded a certain critical value, which seemed to be determined mainly by the concentration of the solution, this process continued indefinitely, but if the *C.D.* were below this value, hydrogen evolution suddenly gave place to the reduction process after electrolysis had been continued for a certain time—the " transition time." After this $b \longrightarrow a$ transition had occurred, nitrous acid (unaccompanied by nitric oxide) was produced continuously, and no reversion to hydrogen evolution ever took place. The temporary evolution of hydrogen at the beginning of electrolysis was first noticed by Schönbein (*loc. cit.*), but has received little further attention (*vide infra*).

FIG. 2.



Current density (*amp./sq.dm.*) : I, 19·5; II, 11·7; III, 6·8; IV, 3·5; V, 1·4.

The cathode potential–time curves for the electrolysis of 6·24*N*-nitric acid at various constant *C.D.*'s are shown in Fig. 2. At *C.D.*'s above about 8 amps./sq.dm., hydrogen evolution continued uninterruptedly throughout electrolysis, even though the current was passed for several hours. At lower *C.D.*'s, however, the $b \longrightarrow a$ transition always occurred after a certain time : the lower the *C.D.*, the shorter was the transition time. Observed transition times ranged from a few seconds to about 20 minutes. A tendency for the cathode potential to assume abnormally positive values for a few minutes immediately after the transition is indicated particularly by curve III.

The critical *C.D.* above which hydrogen evolution continues without interruption becomes much greater with more concentrated solutions.

For a given concentration and *C.D.*, the transition time was scarcely affected by varying the rate of stirring or by using a special type of cathode designed so as to ensure regular distribution of *C.D.* over its surface. On the other hand, solutions of a particular concentration made up from different batches of nitric acid sometimes gave notably different transition times at a given *C.D.* Of substances which might be present in varying amounts as impurities and give rise to these differences, potassium and ammonium nitrates were found to be without effect. The addition of a small amount of nitrous acid (added as potassium nitrite) produced, however, a marked decrease in transition time at any given *C.D.*, and thus increased considerably the critical *C.D.* above which uninterrupted hydrogen evolution occurred. At sufficiently low *C.D.*'s the initial evolution of hydrogen could be suppressed entirely. Reference to this action of nitrous acid has been made by Gladstone and Tribe (J., 1879, **35**, 172) and by Ihle (*loc. cit.*).

Differences in the behaviour of different samples of nitric acid solution were therefore probably due to varying traces of nitrous acid, although tests had shown that such traces must have been extremely small in the solutions employed. Attempts were therefore made to remove nitrous acid more completely before electrolysis. Addition of urea led to less positive potentials after the transition (nitrogen was being evolved), but the transition time was increased only very slightly. It seems that the action of urea in removing nitrous acid from the original solution must have been notably incomplete (compare Joss, *J. Physical Chem.*, 1927, **30**, 1252); for a very marked increase in transition time could be brought about merely by drawing a current of air through the solution for 20 minutes before the electrodes were introduced (30 minutes before the beginning of electrolysis). Thus, with 8·23*N*-nitric acid the transition time became 9 minutes at 3·5 amps./sq.dm. as compared with 6·75 minutes at 15·8 amps./sq.dm. With 6·15*N*-nitric acid the *C.D.*

required to give a transition time of 16 minutes fell from 7·1 to 0·07 amp./sq.dm. as a result of this air treatment, and with less concentrated solutions uninterrupted hydrogen evolution occurred at all except extremely low *C.D.*'s. All such experiments showed that the removal of traces of nitrous acid led to a remarkable decrease in the critical *C.D.* above which cathodic reduction to nitrous acid cannot set in. With nitric acid concentrations up to 6*N* (about 30% HNO_3) this critical *C.D.* fell to practically negligible values : with more concentrated solutions the fall was as great as could be expected in view of the ease with which such solutions yield traces of nitrous acid under the influence of light.

It is concluded that the cathodic reduction of nitric acid to nitrous acid is an extremely slow process unless traces of nitrous acid are already present as catalyst.

Experiments of Type A. Second Series.

Further experiments in which the applied voltage was increased (and afterwards decreased) in steps of 0·2 volt at 5-minute intervals were carried out exactly as in the first series, except that the cathode had been subjected to the preliminary treatment described above (p. 1570), and the solution to the air treatment adopted in later experiments of type B. Introduction of this latter procedure tended to decrease the *C.D.* at which the $a \longrightarrow b$ transition occurred (" transition current density," *T.C.D.*) in solutions less concentrated than 5*N* : at concentrations below 4*N* the *a* branch of the log d_c–e_c curve was suppressed altogether.

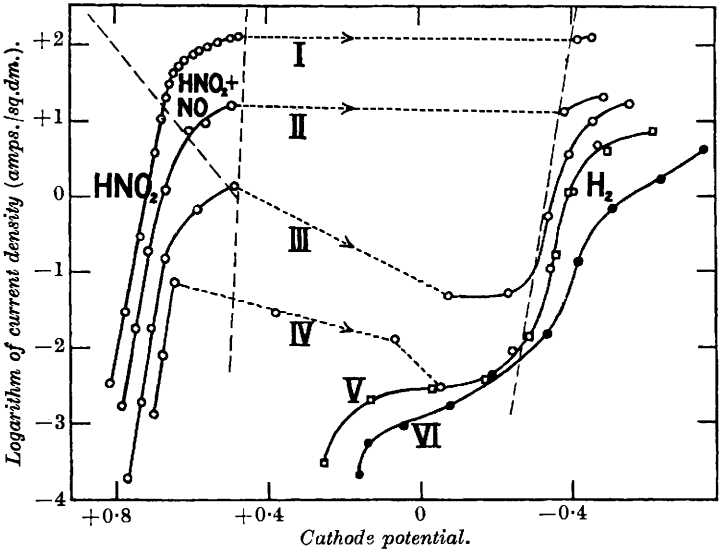
Fig. 3 shows the ascending log d_c–e_c curves for nitric acid solutions of various concentrations at 25—26° when the stirrer was rotated at 170 r.p.m. The *T.C.D.* is seen to increase rapidly with concentration. With the more concentrated solutions the *a* branch of the curve bends over before the transition, and there is a range of conditions, indicated on the figure, in which evolution of nitric oxide accompanies nitrous acid formation. With the less concentrated solutions the transition is relatively sluggish, and unstable potential values lying between the two branches of the curve are sometimes obtained (curve IV). The curves for 3·09*N* and less concentrated solutions are very similar to that for 2*N*-sulphuric acid under the same conditions.

The reproducibility of the curves was reasonably good under these carefully controlled conditions. Moreover, the *T.C.D.*'s were scarcely affected by increasing the interval between successive voltage increments from 5 to 10 minutes. Fig. 4 shows, however, that an increase of temperature caused a notable decrease in polarisation on the *a* branch of the curve, and greatly increased the

T.C.D. (curves VI, III, and I). The use of a platinised platinum cathode instead of the smooth electrode produced a very large increase in the *T.C.D.* These effects correspond with those observed in the polarisation of other electrode systems.

The effect of altering the rate of stirring, however, was the reverse of that for other electrode reactions. Increasing the rate of stirring *increased* the polarisation on the *a* branch of the curve and lowered the *T.C.D* very considerably. Thus, with 6·15*N*-nitric acid the *T.C.D.* was 33, 16, and 3 amps./sq.dm. when the stirrer was rotated at 0, 170, and 250 r.p.m. respectively. No other case of this kind appears to have been described. With other electrode reactions an increased rate of stirring always tends to decrease the polarisation. Since more vigorous stirring tends to maintain a higher concentration of soluble reactants and a lower concentration of soluble products in the layer of solution in immediate contact with the electrode, it leads normally to an increase in the velocity of the electrode reaction and hence to a decrease in the polarisation at any given *C.D.* The only condition under which the polarisation might rise with increasing rate of stirring would seem to be when one of the soluble products of the reaction, which is being swept away from the electrode surface by the action of the stirrer, is also a catalyst for the reaction. In the present case the strong catalytic action of

FIG. 3.

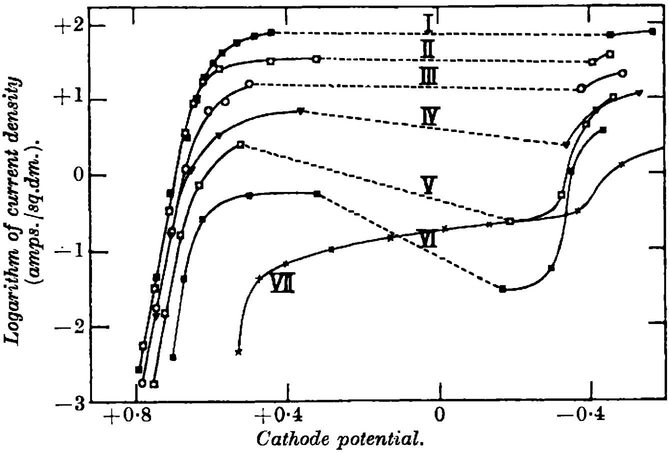


I, 8·23*N*-HNO_3; II, 6·15*N*-HNO_3; III, 5·13*N*-HNO_3; IV, 4·11*N*-HNO_3; V, 3·09*N*-HNO_3; VI, 2*N*-H_2SO_4.

nitrous acid on the cathodic reduction of nitric acid to nitrous acid is evidently the cause of the observed anomalous influence of stirring (curves II, III, and V).

Addition of 5 g. of urea per litre of 6·15N-nitric acid had little effect upon the lower part of the log d_c–e_c curve, in spite of the fact that evolution of nitrogen occurred in this region, but above about 1 amp./sq.dm. the polarisation was notably increased, and the *T.C.D.* was lowered from 16 to 7 amps./sq.dm. On the other hand, addition of 5 g. of potassium nitrite per litre of 6·15N-nitric acid had practically no effect on any part of the curve or on the *T.C.D.*

FIG. 4.



6·15N-HNO$_3$.
Normal stirring : I, 40°; III, 25°; VI, 3°.
25° : II, *no stirring*; V, *fast stirring.*
IV, 6·15N-HNO$_3$ + urea, 25°, *normal stirring.* VII, 2N-H$_2$SO$_4$ + HNO$_2$.

With 4·11N-nitric acid, however, a similar addition of nitrite increased the *T.C.D.* from 0·07 to 1·5 amps./sq.dm. With still more dilute solutions, addition of nitrite led to the appearance of an *a* branch of the log d_c–e_c curve, which is normally absent, but this branch bends over at quite low *C.D.*'s and passes without definite transition into the *b* branch. A closely similar curve is given by 2N-sulphuric acid to which nitrite has been added (curve VII, Fig. 4).

The Anode Reaction.—In all experiments with pure nitric acid solutions, the anode potential varied continuously with *C.D.* over the whole range explored. It is concluded therefore that oxygen evolution is the sole reaction at a platinum anode in nitric acid solutions. With solutions to which nitrite had been added, however, the anode potential remained at relatively very low values until a certain *C.D.* was reached, whereat there was a sudden transition to the normal value for oxygen evolution. Evidently anodic oxidation of nitrous acid to nitric acid was occurring at the lower *C.D.*'s.

Equilibrium Potentials.—The steady potentials assumed by the spiral electrode during simple immersion for 30 minutes in the nitric acid solution before electrolysis ranged from + 0·84 volt for 3·08*N*- to + 0·92 volt for 8·23*N*-acid, with reference to the normal calomel electrode (*vide supra*). These values are about 0·05 volt more positive than those of Ihle (*loc. cit.*), doubtless as a result of more complete removal of nitrous acid. Addition of nitrite lowered the equilibrium potential and greatly decreased the time required for its establishment.

Discussion.

In the electrolysis of nitric acid solutions the primary cathode reaction under all conditions is regarded as

$$H^{\cdot} + \ominus = (H) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where (H) represents atomic hydrogen occluded in the platinum. This process may be followed by either of the alternative secondary reactions

$$HNO_3 + 2(H) = HNO_2 + H_2O \quad . \quad . \quad . \quad (2a)$$

$$2(H) = H_2 \text{ (gas)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2b)$$

depending on the conditions of electrolysis.

Reaction (2*b*) will occur only if (2*a*) cannot proceed at a sufficient rate to remove (H) as fast as it is produced by (1). The experimental results described above show that the velocity of (2*a*) is very low, even for moderately concentrated nitric acid, unless nitrous acid is already present as catalyst. The *C.D.* which can be maintained by reaction (2*a*) in a solution of given nitric acid concentration will therefore be determined mainly by the concentration of nitrous acid which is established in the layer of solution in immediate contact with the cathode.

In experiments of type A the *C.D.* increases very gradually, and during each of the earlier stages the nitrous acid concentration in the diffusion layer builds up sufficiently to allow for a further increase of *C.D.* with very little rise in polarisation. At a certain stage, however, the reaction

$$3HNO_2 = HNO_3 + 2NO + H_2O \quad . \quad . \quad . \quad (3)$$

limits the rate of increase of nitrous acid concentration at the cathode surface. Nitric oxide begins to be evolved and the polarisation increases more markedly with *C.D.* At a certain *C.D.*, dependent on the nitric acid concentration, the concentration of nitrous acid in the diffusion layer will reach a maximum value, thus setting a limit to the velocity of reaction (2*a*). With further increase in *C.D.*, the activity of atomic hydrogen in the cathode surface will rise at a rapidly increasing rate, and the potential will therefore change sharply to more negative values until reaction (2*b*) can set in. This is the probable mechanism of the $a \longrightarrow b$ transition.

That the progress of reaction (2*a*) at moderate *C.D.*'s is dependent on the maintenance of an intact diffusion layer over the cathode surface, is demonstrated by the marked fluctuations of potential caused by the escape of bubbles of nitric oxide just before the transition, and by the increase in polarisation and the lowering of the *T.C.D.* produced by an increased rate of stirring.

The higher the nitric acid concentration, the greater will be the maximum concentration of nitrous acid in the diffusion layer, and hence the greater the *T.C.D.* With the more concentrated nitric acid solutions this limiting nitrous acid concentration is so high that it can hardly be increased by moderate additions of nitrous acid to the solution before electrolysis. With more dilute nitric acid, however, the limiting nitrous acid concentration in the diffusion layer may be notably raised by such an addition, since the concentration gradient will become much less steep. After the transition the diffusion layer will be largely broken up by hydrogen evolution, and the *C.D.* which reaction (2*a*) can maintain will therefore fall to a comparatively very low value.

In experiments of type B, where a moderate *C.D.* is established immediately, reaction (2*b*) must occur until a sufficient concentration of nitrous acid can accumulate at the cathode surface to enable reaction (2*a*) to maintain the given *C.D.* The establishment of this condition is opposed, however, by the action of hydrogen bubbles in sweeping nitrous acid away from the cathode surface. At moderate *C.D.*'s this stirring action is so effective that alterations in the rate of rotation of the mechanical stirrer scarcely affect conditions at the cathode surface. Unless the nitric acid is very concentrated or contains already a moderate amount of nitrous acid, it is only at very low *C.D.*'s that the nitrous acid concentration at the cathode surface can rise sufficiently to permit the occurrence of the $b \longrightarrow a$ transition. It should be noted, however, that owing to the autocatalytic character of reaction (2*a*) its velocity can rise very sharply when once a certain critical value has been exceeded, so that the transition, if it occurs at all, sets in very suddenly and goes to completion in a very short time. The activity of atomic hydrogen in the cathode surface is thereby decreased suddenly from a very high to a very low value, and the rate of production of nitrous acid is temporarily very high. This causes an exceptionally low polarisation (exceptionally positive potential) just after the transition.

A comparison of some results of Ihle (*Z. physikal. Chem.*, 1896, **19**, 572) with those of the present investigation indicates that during hydrogen evolution the formation of ammonia may become an important secondary reaction. At the very negative cathode potentials established at high *C.D.*'s it is probable that nitrous acid formation is largely supplanted by production of ammonia, so that the $b \longrightarrow a$ transition will be still less likely to occur.

Theory of Metal Dissolution.—The well-known catalytic action of nitrous acid on the dissolution of certain metals in nitric acid solutions (Millon, *Compt. rend.*, 1842, **14**, 902; Veley, *Proc. Roy. Soc.*, 1890, **46**, 216; 1891, **48**, 458; 1893, **52**, 27) may be a particular case of the catalysis of reaction (2*a*). When any metal is put into any acid solution the reaction

$$M + 2H^{\bullet} = M^{\bullet\bullet} + 2(H) \quad . \quad . \quad . \quad . \quad . \quad (4)$$

(in the case of a bivalent metal) tends to take place, and, if there were no secondary reaction to remove atomic hydrogen from the metal surface, would proceed to an equilibrium condition. The baser the metal, the greater would be the activity of atomic hydrogen at equilibrium. In non-oxidising acid solutions the baser metals can dissolve continuously because this equilibrium activity is greater than that at which hydrogen gas can be evolved by reaction (2*b*), unless this gas evolution is prevented by the metal having a high hydrogen over-potential. With the nobler metals, however, the equilibrium corresponding to (4) is actually attained when only a minute trace of metal has dissolved, and no further action occurs.

In nitric acid solutions of moderate concentration, reaction (2*a*) is an alternative secondary process capable of removing atomic hydrogen from the metal surface. With a very base metal, such as magnesium, the vigorous progress of reaction (4) corresponds to the rapid production of atomic hydrogen by electrolysis at a high *C.D.*: reaction (2*a*) cannot proceed fast enough to oxidise this hydrogen, so that evolution of hydrogen gas is the predominant reaction. With a metal such as zinc, which although moderately base has a high hydrogen over-potential, production of ammonia may become important, and nitrous oxide may be produced by decomposition of the ammonium nitrate formed. With nobler metals, however, the equilibrium activity of atomic hydrogen in the metal surface is lower, and conditions correspond to electrolysis at a lower *C.D.*: reaction (2*a*) removes the hydrogen as fast as it is formed, yielding nitrous acid and its decomposition product, nitric oxide. Since this reaction is strongly catalysed by nitrous acid, reaction (4) will be correspondingly accelerated, *i.e.*, nitrous acid will appear to catalyse the dissolution of such metals. The observation of Drapier

(*Compt. rend.*, 1914, **158**, 338), that rotation of a copper rod in a nitric acid solution decreased its rate of dissolution, is analogous to the abnormal effect of stirring on polarisation in experiments of type A above.

Summary.

In the electrolysis of nitric acid solutions between platinum electrodes there are two alternative reactions which can predominate at the cathode : (*a*) reduction of nitric acid to nitrous acid (which may yield nitric oxide by decomposition) ; (*b*) evolution of hydrogen. Reaction (*a*) is strongly autocatalytic, the current density which it can maintain being determined by the nitrous acid concentration established at the cathode surface. This explains the observed variations of cathode potential during electrolysis under various conditions, and may account for the well-known catalytic action of nitrous acid on the dissolution of certain metals in nitric acid.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, S.W.7.

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