PHYSICO-CHEMICAL STUDIES WITH AQUEOUS FLUORIDE SOLUTIONS

Part II. Hydrogen and Oxygen Overvoltages in Hydrofluoric Acid

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The current-voltage curves for the electrolysis of aqueous solutions of alkali fluorides and ammonium fluoride show two breaks in each case.\textsuperscript{5,14} The first one undoubtedly refers to the primary decomposition of water. Earlier workers\textsuperscript{8} regard the second break as a mere duplication of the first break, differing from it only by the inclusion of hydrogen and oxygen overvoltages in the measured potential for the second break. From other considerations, however, the second break appears to be due to a different electrode process than that occurring at the first break.\textsuperscript{14} A knowledge of the hydrogen and oxygen overvoltages in hydrofluoric acid solutions at the relevant current densities is necessary to elucidate the point further. No such data are, however, available although hydrogen and oxygen overvoltages and related phenomena have been widely studied in a variety of other solutions and under various conditions.\textsuperscript{2,9,10} In view of the general importance of overvoltage phenomenon in a study of irreversible electrode processes, it appeared desirable to make a detailed study of hydrogen and oxygen overvoltages in aqueous solutions of hydrofluoric acid.

EXPERIMENTAL

A. R. quality Merck's hydrofluoric acid and Kahlbaum's potassium hydroxide and oxalic acid were used in preparing the solutions. All vessels, etc., required for use with hydrofluoric acid were coated with pure paraffin wax if not entirely made of this material.

For the determination of hydrogen overvoltage, hydrofluoric acid solutions were prepared in redistilled water which had been freed from dissolved oxygen by prolonged boiling and subsequent cooling in a current of hydrogen. The solution was further saturated with hydrogen and kept in a hydrogen atmosphere. All other solutions were prepared in redistilled water only.
Pure potassium hydroxide solution kept in wax-coated vessel to prevent contamination with silica from glass was used as the intermediate titrant in preparing the hydrofluoric acid solutions. During titration the alkali was taken in a glass burette as the time of contact with glass was not sufficiently long for detectable quantities of silica to be dissolved; perfectly sharp end-point was obtained. The fundamental standard in preparing the solutions was oxalic acid, and phenolphthalein served as indicator.

A decinormal calomel half-cell checked against a hydrogen electrode was used as the reference electrode. Hence, to prevent contamination of the electrolyte, electrical connection with the reference electrode was made in a side tube connected with the electrolytic cell which was a round-bottomed beaker of about 400 c.c. capacity. The tip of the side tube projecting inside the cell had only a small opening, slightly less than 1 mm. in diameter and this opening was plugged with a tiny roll of hydrofluoric acid-washed filter paper to prevent bubbles of gas evolved on the test electrode from entering into the tube, and thus breaking electrical connection with the reference electrode.

The cell was provided with a close fitting wooden stopper soaked in paraffin wax which carried a hydrogen inlet tube, a thermometer, and a wax tube stopped at the bottom by means of a tight roll of hydrofluoric acid-washed filter paper. This tube enclosed the other electrode necessary for the passage of electric current through the solution, so that access to the test electrode of the depolarising gases evolved at this other electrode was prevented. This other electrode consisted of platinized platinum to avoid its polarisation during electrolysis.

The test electrode was introduced into the cell through another hole in the stopper which was, when not in use, closed by a tight fitting cork carrying the hydrogen-outlet tube; this was protected from the air by a gas-bubbler.

The test electrode was rotated rapidly during measurement to avoid concentration polarisation, and the rotation was made slightly eccentric so as to prevent the electrolyte from being dragged in rotation. The distance between the rotating electrode and the tip of the side tube which served to make electrical contact between this electrode and the reference electrode, was arranged to be as small as possible (about 1 mm.) in order that any appreciable IR drop may not be included in the potential measurements. The device used for rotating the test electrode was similar in principle to that of Harkins and Adams, but differed from it in constructional details. Different electrodes might be fitted interchangeably to this device, as needed.
The following metals were used as cathode materials:—Pt, Ag, Al in the form of thin wires of about 1 mm. thickness (Kahlbaum A. R. quality); Cu, Au, Ni, Co, Cr, Fe and Zn in the form of thin film electrodeposited on copper wires under such conditions that smooth, adherent, thick coatings were obtained.

Hydrogen required for the work was prepared by electrolysis of 15% potassium hydroxide solution in the usual type of hydrogen generating apparatus of suitable capacity, and passed through alkaline pyrogallol to free it from any traces of oxygen, then through two wash bottles each containing the same solution as the electrolytic cell, for saturating the gas before it entered the latter.

The polarising current was drawn from a number of storage batteries. It was determined by measuring the fall of potential across a suitable standard resistance in the circuit and was read on a sensitive unipivot galvanometer which could be used, by means of suitable shunts, to read small as well as large currents. A potentiometer of the "Land und Seekabelwerke" type in conjunction with a sensitive L & N type galvanometer was used for measuring the required potentials. The Standard Weston cell, used in adjusting the potentiometer for measurement, was checked against one having the Bureau of Standards' Certificate.

For the determination of hydrogen overvoltage the electrolytic cell, kept at 25°± 0.1° C. in an electrically controlled thermostat, was swept out with hydrogen; then with the current of hydrogen still continuing, it was filled with the oxygen-free solution, the side tube and the anode compartment being filled first. During this operation some air got into the cell; this was, however, soon replaced by the current of hydrogen and the bubbling of hydrogen was continued overnight to remove all possible traces of dissolved oxygen before taking readings. Hydrogen was passed continuously during a measurement and between successive measurements also in order to keep the solution always saturated with hydrogen so that any air which might have entered the cell at the time of introducing the cathode is easily swept out before the polarisation potential is measured.

The cathode to be used was polished with the finest grade emery powder on chamois leather, then rubbed clean with wet filter-paper, rinsed thoroughly with redistilled water, wiped dry with clean filter-paper, and attached to the rotating device. The apparent area exposed in each case was 1 sq. cm. The Pt cathode was flamed before being polished and washed, as otherwise difficulty was experienced in obtaining reproducible results with this metal. The cathode was prepared in the method described above.
for each determination. In cases where the cathode was affected in such a way that its surface could not be renewed by this treatment, a fresh cathode was used for each determination. This procedure had to be adopted specially in the case of Al.

The current indicating galvanometer was adjusted to read the desired current just before making a determination. This adjustment could be made without polarising the electrolytic cell. The external variable resistances were adjusted to give the required current and the polarising circuit was completed by introducing the cathode into the cell. This method of 'striking' the current with the cathode was followed in order to prevent purely chemical attack, if any, before the electrode is polarised.

The polarisation potential was measured at the end of two minutes. During this time the current was kept constant by adjusting the variable resistances in the circuit. The adjustment of the potentiometer was checked and electrical connection between the reference calomel electrode and the polarised electrode was made just before measuring the polarisation potential.

The procedure of measuring the polarisation potential within a few minutes of starting of the current was followed because, in the first instance, all the metals used except Pt, Ag and Al, were in the form of electrodeposited films on which overvoltage has been shown by Hickling and Salt to attain its maximum value in a few minutes. In the present case this state was generally reached in about two minutes. This was found to be the case with Al also. In the case of Pt and Ag, however, the overvoltage was still increasing after 2 minutes; but, apart from the consideration of preventing the condition of the surface from altering in various ways by continued electrolysis, the procedure of measuring the polarisation potential at the end of two minutes had to be followed in these cases also for the following reason. Due to paraffin wax being a bad conductor of heat, long continued electrolysis caused local heating inside the wax-coated electrolytic cell, and particularly inside the anode chamber which was entirely made of paraffin wax. Even at a c.d. of about 0.1 amp./sq. cm., this local heating became so serious that the wax tube which constituted the anode chamber melted away round about the anode on electrolysing for about 10 minutes only. On this account also readings could not be taken at current densities higher than those used.

After measuring the polarisation potential at any c.d. the cathode was removed from the cell, thus stopping the current, and the polarisation allowed to decay completely before taking the next reading, which was
otherwise found to be affected. Moreover, unless the electrode is initially in virgin condition for each c.d., the readings obtained at different current densities would refer to different initial states of the electrode and electrolyte, and hence would not be comparable. Usually about an hour's rest was sufficient for the decay of polarisation set up at any of the current densities used.

Determinations were usually made starting with the lowest c.d. and ending with the highest c.d. used, taking a number of readings, usually 5 or 6, at each c.d. It was immaterial, however, whether the readings were taken in an ascending or descending or any other order of c.d. if the procedure mentioned above is followed. In fact in those cases where the cathode gets attacked at the lower current densities used, measurements were made in the descending order of current density.

After finishing the series of measurements with one metal, the potential difference between the reference calomel electrode and a hydrogen electrode in the same solution and under similar conditions as used for measuring the polarisation potentials was determined. The difference between the measured polarisation potential at any current density and the potential of the reference calomel electrode as measured against the hydrogen electrode in the same solution is the hydrogen overvoltage at that current density.

Hydrogen overvoltages were thus determined on Pt in N solutions of hydrofluoric, sulphuric, formic and acetic acids, and on Pt, platinized Pt, Ag, Au, Cu, Ni, Co, Cr, Fe, Al and Zn in N/5 hydrofluoric acid solution at 25°± 0·1° C. at current densities ranging from 5×10⁻⁵ to 1×10⁻¹ Amp./sq. cm.

Similarly oxygen overvoltages were determined in an oxygen atmosphere on Pt in N and N/5 solutions of hydrofluoric acid. The oxygen overvoltage at any c.d. is equal to the difference between the anode polarisation potential at that current density measured against calomel electrode and the potential of this calomel electrode against an oxygen electrode in the same solution. Since a perfectly reversible oxygen electrode cannot be realised in practice, its potential has been obtained indirectly as the difference between the theoretically calculated value for the electromotive force of the reversible H₂—O₂ cell, 1·23 volts,¹ and the measured potential difference between the calomel electrode and a hydrogen electrode in a solution of the same concentration as used for the measurement of oxygen overvoltage.

The results are tabulated below and V—log i curves for different cases are shown in Fig. 1. Usually the results were reproducible to within
**Table I**

Hydrogen overvoltage in aqueous solutions of HF and other acids at 25° C.

<table>
<thead>
<tr>
<th>Current Density in millamps per sq. cm.</th>
<th>Hydrogen overvoltage in centivolts</th>
<th>N H₂SO₄ acid</th>
<th>N HF acid</th>
<th>N Formic acid</th>
<th>N Acetic acid</th>
<th>N/5 HF acid</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Platinized Pt</td>
<td>Ag</td>
<td>Fe</td>
<td>Ni</td>
<td>Cr</td>
<td>Au</td>
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<tr>
<td>0.05</td>
<td>0</td>
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<td>0</td>
<td>0</td>
<td>0</td>
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<td>4</td>
<td>6</td>
<td>8</td>
<td>10</td>
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<tr>
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<td>280</td>
<td>320</td>
</tr>
<tr>
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<td>300</td>
<td>360</td>
<td>420</td>
<td>480</td>
<td>540</td>
</tr>
<tr>
<td>50.00</td>
<td>150</td>
<td>600</td>
<td>720</td>
<td>840</td>
<td>960</td>
<td>1080</td>
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</table>

**Fig. 1.** Hydrogen and Oxygen overvoltages at 25°C.
Physico-Chemical Studies with Aqueous Fluoride Solutions—II

± 0.002 v. to ± 0.02 v. (varying from the lowest to the highest c.d. used), although sometimes, specially at the higher current densities, the reproducibility was much poorer. Moreover, very nearly the same values were obtained on different samples of the same metal prepared in the same way. The reproducibility at any c.d. was, however, different for different metals.

DISCUSSION

The linear relation, \( V = a + b \log i \), between overvoltage and the logarithm of current density is found to hold good below current densities of about 0.005 amp./sq. cm., but at greater current densities the overvoltage values are increasingly higher than required by this relation. This deviation from linearity may be due to (i) concentration overpotential, and/or (ii) resistance overpotential being included in the measured potential. The former does not seem to be included in measurements even at these current densities, since increasing the speed of rotation of the polarised electrode above that at which measurements were made (about 2000 r.p.m.) did not produce any significant effect in the measured potential. From the following considerations, however, it appears reasonable to attribute this deviation to the inclusion of resistance overpotential in the measured potential. Thus, the differences between the measured potentials at these current densities

<p>| TABLE II |</p>
<table>
<thead>
<tr>
<th>Oxygen overvoltage on Pt in aqueous solution of HF acid at 25° C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current density in milliamp./sq. cm.</td>
</tr>
<tr>
<td>Overvoltage in centivolts — N HF acid</td>
</tr>
<tr>
<td>Overvoltage in centivolts — N/5 HF acid</td>
</tr>
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</table>

<p>| TABLE III |</p>
<table>
<thead>
<tr>
<th>Values of ( b ) in the Tafel equation ( V = a + b \log i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen overvoltage</td>
</tr>
<tr>
<td>N H(_2)O(_4) acid</td>
</tr>
<tr>
<td>Pt</td>
</tr>
<tr>
<td>0-10</td>
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</tbody>
</table>
densities and the corresponding values obtained by extrapolating the initial straight portions of the \( V-\log i \) curves to the higher c.d. region are almost in the same ratio as the current densities themselves. Values for these current densities in N HF acid are lower than those in N/5 HF acid in the case of hydrogen as well as oxygen overvoltage. Platinized Pt which is known to have a very small overvoltage even at very high current densities also showed an enormously increasing overvoltage in N/5 HF acid solution at current densities higher than 5 milliamp./sq. cm. as observed in the case of other surfaces. In the case of sulphuric acid, deviation of the above type was almost unnoticeable even at current densities ten times as great as that in the case of hydrofluoric acid. This is quite consistent with the much larger hydrogen-ion concentration and conductivity of N sulphuric acid as compared to those of N or N/5 HF acid solution. On account of comparatively weak ionisation in N or N/5 HF acid, inclusion of resistance overpotential in measurements is, in fact, not unexpected even at current densities as low as 5 milliamp./sq. cm. in view of the method of measurement employed. Owing to the presence of this complicating factor results at current densities upwards of that mentioned above hardly deserve to be listed in the table and hence are shown graphically only; this also made it superfluous to take readings at current densities higher than \( 1 \times 10^{-1} \) amp./sq. cm.

In the case of Pt deviation from the linear \( V-\log i \) relation occurs in the low c.d. region also (cf. Fig. 1). As pointed out by Bowden and Agar\(^4\) this is due to the rate of electroosolution of hydrogen being comparable to that of its electrodeposition under the conditions prevailing in the present case.

The slopes of \( V-\log i \) graphs, \( i.e., \) the values of \( b \) occurring in the overvoltage equation \( V= a+ b \log i \) are very small in the case of hydrogen overvoltage on Fe, Cr, Al and Zn. This is due to the fact that the low polarisation under which this effect is observed is not sufficient to overcome the spontaneous chemical reaction between these metals and HF acid.\(^3\) The consequent spontaneous evolution of hydrogen in quantities much greater than that due to the polarisation upsets the electrochemical equilibrium so that the measured polarisation potential is almost independent of c.d. in this region. Moreover, due to spontaneous chemical attack, the metal surface gets covered with a layer of the corresponding fluoride by which the nature as well as the physical condition of the surface gets changed so that the values measured would not refer to the metal surfaces themselves.

The values of \( b \) for other cases are given in Table III. It is evident that except for hydrogen overvoltage on Pt in N solution of sulphuric and
hydrofluoric acids, the values of $b$ for hydrogen as well as oxygen overvoltage are, in general, about twice the value usually obtained in other cases by other workers. As pointed out by Bowden this may be ascribed to the fact that hydrogen-ion concentration being low in the case of N/5 HF acid, the solution layer next the electrode gets depleted of hydrogen ions; moreover, the conductivity of N/5 HF acid is itself low; under these conditions the measured potential includes an appreciable fall of potential in the solution. For hydrogen overvoltage on Pt in N HF acid, however, the value of $b$ is not far removed from the usual value; but, even in this case, absolute overvoltage values are higher than in N sulphuric acid (Table I) or in other concentrations of sulphuric acid, hydrochloric acid, etc., studied by other workers. This is due to the fact that although hydrogen-ion concentration and conductivity of N solution are greater than those of N/5 solution of HF acid, these are still not enough for the results to be independent of slight resistance errors. The hydrogen overvoltage values obtained in the case of N formic and acetic acids are also in conformity with the above view. Formic acid, having the same order of ionisation as hydrofluoric acid in N solutions, gives results similar to hydrofluoric acid; while N acetic acid with much weaker ionisation gives a higher value for $b$ than is the case with N HF acid. Moreover, deviation from linearity occurs much earlier and is much greater in N acetic acid than in N hydrofluoric acid.

From Table I it is evident that hydrogen overvoltage values in N/5 solution are greater than in N solution of HF acid. This apparent variation of overvoltage with concentration may also be explained in a similar way. In the case of oxygen overvoltage the values at the two concentrations of HF acid are the same in the initial stages where the Tafel equation is obeyed.

It thus appears that results obtained with HF acid solutions are fundamentally similar to those obtained with other acids, the deviations found being only apparent and attributable to causes arising from weak ionisation of HF acid.

The nature of the two breaks occurring in the current voltage curves for the electrolysis of aqueous solutions of alkali fluorides and ammonium fluoride between bright Pt electrodes can now be considered in the light of these results. The first break occurs at a c.d. of about 0.06 milliamp./sq. cm., and the second break at a c.d. of about 0.7 milliamp./sq. cm. In the first instance, as is evident from Tables I and II the measured potential even for the first break must include an oxygen overvoltage value, although the hydrogen overvoltage at this c.d. is negligible. Again in passing from lower to higher c.d. in this range, hydrogen overvoltage on Pt in N HF acid
Hiralal Shrivastava

increases by 0.08 v. and oxygen overvoltage increases by 0.19 v. The total increase of overvoltage at the two electrodes is therefore 0.27 v. This is much lower than the difference between the potentials for the two breaks which is at least 0.60 v. taking Crockford and Loftin's figures, and 1.0 v. from the present author's results. Due to the greater ionisation and conductivity of salt solutions the hydrogen and oxygen overvoltages in these solutions are expected to be somewhat lower than reported here for N/HF acid. The electrode process at the second break cannot, therefore, be regarded as a duplication of that at the first break, namely, the primary decomposition of water, and differing from it merely by the inclusion of increased values for the hydrogen and oxygen overvoltages in the measured potential for the second break. This is quite in conformity with the conclusions already arrived at with regard to the nature of the second break from other considerations. The nature of the reactions at the second break, however, merits further work if more light is to be gained on the point, and work in this direction is in progress.

In conclusion the author wishes to express his indebtedness to the C.P. Government for a research scholarship which enabled him to undertake this investigation, and to Dr. A. N. Kappanna of the College of Science, Nagpur, for invaluable help and advice during the course of the work. To Sir J. C. Ghosh, Director of the Indian Institute of Science, Bangalore, the author owes a deep debt of gratitude for the interest taken in this work and facilities provided.

Summary

Hydrogen overvoltage measurements have been made at 25°C. at current densities ranging from $5 \times 10^{-4}$ to $1 \times 10^{-1}$ amp./sq. cm. on platinized Pt, Pt, Ag, Fe, Ni, Cr, Au, Cu, Co, Zn and Al in oxygen-free N/5 aqueous solution of HF acid, and on Pt only in N solutions of HF, H$_2$SO$_4$, formic and acetic acids. Oxygen overvoltage has been determined on Pt at 25°C. at current densities ranging from $5 \times 10^{-3}$ to $6 \times 10^{-3}$ amp./sq. cm. in N and N/5 aqueous solutions of HF acid. Except Pt, Ag, and Al, the metals were used in electro-deposited form. Reproducibility of results varied from ±0.002 v. to ±0.02 v. according to current density. At current densities below 5 milliamp./sq.cm. the linear relation $V = a + b \log i$ between overvoltage and current density is found to hold good. For hydrogen overvoltage $b = 0.20$ to $0.23$ for non-attackable metals in N/5 solution and 0.145 for Pt in N solution of HF acid; for attackable metals the value of $b$ is very small. For oxygen overvoltage on Pt in N and N/5 solutions of HF acid $b = 0.175$. At current densities upwards of 5 milliamp./sq.cm. the measured potential becomes increasingly larger than
required by this relation. From an examination of the results obtained it
appears that the behaviour of HF acid with respect to overvoltage pheno-
menon is essentially the same as those of H₂SO₄ and other similar acids,
the observed departures being attributable to causes arising from weak
ionisation of HF acid. Results for hydrogen and oxygen overvoltages on
Pt indicate that the second break in the electrolysis of alkali and ammonium
fluoride solutions may be due to electrode processes other than the primary
decomposition of water.

REFERENCES

2. Bowden and Agar .. Ann. Reports, 1938, 35, 90.
7. Dole .. Ibid., 1936, 70, 275.
10. .. Ibid., 1941, 37, 319, 333, 450, 1942, 38, 474.