EQUILIBRIUM IN ELECTRODELESS DISCHARGE.

PART II. ELECTRODELESS DISCHARGE THROUGH WATER VAPOUR AND SILANE.


The present paper deals with the results obtained with a portion of the apparatus kept in liquid air to remove any condensible products from the discharge tube. For this purpose a U-tube $T_2$ was inserted immediately preceding the discharge tube $D$ [Fig. 1 (a) (This Journal, 1937, 20A, page 27)]. This had a further advantage that no grease vapour could have access to the discharge tube when the experiment was in progress.

After introducing the gas at the desired pressure the tap was closed and the liquid air-bath was kept under the U-tube $T_2$. The discharge was then switched on and the rate of fall of pressure of hydrogen was studied. After a certain time the pressure became so low that the discharge automatically ceased: this pressure is below the range of the Pirani gauge (approx. $10^{-4}$ mm.). More hydrogen was let into the tube by opening the tap keeping a liquid air bath under the trap $T_3$ so as not to allow mercury vapour to condense in $T_3$. The tap was again closed and the discharge started. In this way appreciable quantity of the condensible product was obtained before the rate of disappearance had fallen appreciably. The discharge was then stopped and the residual gas pumped off. The liquid air-bath under the trap $T_2$ was removed and the condensible product allowed to warm up and the pressure rise measured by the Pirani gauge.

Experiments described in this part were done with a discharge tube made of quartz with a view to obtain a better yield of the gas condensible in liquid air since in case of the discharge tube made of pyrex the fatigue effect limits its quantity. E. Hiedemann (Z. physikal. Chem., 1933, 164, 20) found no fatigue effect in the formation of condensible product in case of the quartz tube. The tube used in the present case was 2.5 cms. in diameter and 13 cms. in length; the trap $T_2$ was also made of quartz and both of these were joined to the apparatus by means of a quartz-pyrex ground joint.

It was found that when the tube was baked to start with, a definite quantity of the gas first disappeared. Table I gives the amount of hydrogen lost in the beginning of each series, for which no condensible product was obtained.
After this loss if the discharge was continued further, a condensible product was formed which had a definite relation with the hydrogen lost in subsequent runs.

The loss of hydrogen in Table I can be attributed to the adsorption on the walls of the discharge tube to form a monoatomic layer as can be seen from the data given in Table II.

### Table I.

**H₂ lost in mm. mercury.**

<table>
<thead>
<tr>
<th>Pyrex tube</th>
<th>Quartz tube</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2425</td>
<td>0.0725</td>
</tr>
<tr>
<td>0.2000</td>
<td>0.0700</td>
</tr>
<tr>
<td>0.1950</td>
<td>0.0710</td>
</tr>
<tr>
<td>0.2110</td>
<td></td>
</tr>
</tbody>
</table>

After this loss if the discharge was continued further, a condensible product was formed which had a definite relation with the hydrogen lost in subsequent runs.

The loss of hydrogen in Table I can be attributed to the adsorption on the walls of the discharge tube to form a monoatomic layer as can be seen from the data given in Table II.

### Table II.

<table>
<thead>
<tr>
<th>Quartz tube</th>
<th>Pyrex tube</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Volume of the apparatus</td>
<td>110 c.c.</td>
</tr>
<tr>
<td>2. Area for adsorption</td>
<td>98 cm²</td>
</tr>
<tr>
<td>3. Pressure loss at 25°C</td>
<td>0.0725 mm.</td>
</tr>
<tr>
<td>4. Mean surface density of adsorbed H-atoms</td>
<td>$5.395 \times 10^{15}$/cm²</td>
</tr>
<tr>
<td>5. Mean atomic spacing</td>
<td>$1.361 \times 10^{-8}$ per cm.</td>
</tr>
<tr>
<td>6. Diameter of hydrogen atom</td>
<td>$1.06 \times 10^{-8}$</td>
</tr>
</tbody>
</table>

The total number of hydrogen atoms was calculated from the knowledge of the pressure loss in a known volume of the apparatus and the number of molecules at N.T.P. per unit volume. The area of adsorption was taken to be that portion of the tube which was initially baked out and to which the glow of the discharge was confined.

In case of quartz tube the loss of gas for which no condensible product was formed corresponds to the formation of a monoatomic layer of the gas atoms on the surface of the walls.

In case of the pyrex tube we see from Table II that in comparison with the quartz tube the loss is nearly four times as much when calculated for the same area. In this case the adsorbed layer is many molecules thick.

To recover the adsorbed gas the pyrex tube was baked out in the same way as described in Part I. It was found that the quantity of the gas obtained in this way was nearly $2/3$ of that lost, in conformity with experiments described in Part I.

Experiments were carried out after the loss of the gas due to adsorption had reached the limit given in Table I. Table III shows
the relation between the amount of hydrogen lost in subsequent runs and the corresponding amount of the condensible vapour formed.

The figures in the fourth column have been obtained on the assumption that the condensible product is water vapour. It has been shown by Campbell (Proc. Phy. Soc., 1920–21, 33, 287) that the calibration curves for gases other than hydrogen lie very near each other; and in the present case the values of pressures of water vapour corresponding to the indications of the Pirani gauge were computed from an approximate curve drawn on the basis of data given by Campbell (loc. cit.). In the first and second columns the correction for cooling due to liquid air has been applied. The pressure values obtained on this assumption lend quantitative support to the view that one volume of water vapour is formed for one volume of hydrogen disappeared.

**Table III.**

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Starting pressure of H₂ mm.</th>
<th>End pressure of H₂ mm.</th>
<th>H₂ lost in mm.</th>
<th>Pressure of condensible product in mm. H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pyrex Tube</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.4750</td>
<td>0.0040</td>
<td>0.4710</td>
<td>0.4800</td>
</tr>
<tr>
<td>2</td>
<td>0.5650</td>
<td>0.2150</td>
<td>0.3500</td>
<td>0.3400</td>
</tr>
<tr>
<td>3</td>
<td>0.2150</td>
<td>0.0200</td>
<td>0.2250</td>
<td>0.2250</td>
</tr>
<tr>
<td>4</td>
<td>0.1275</td>
<td>0.0005</td>
<td>0.1275</td>
<td>0.1250</td>
</tr>
<tr>
<td>5</td>
<td>0.0975</td>
<td>0.0005</td>
<td>0.0975</td>
<td>0.0950</td>
</tr>
<tr>
<td><strong>Quartz Tube</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.1325</td>
<td>0.005</td>
<td>0.1275</td>
<td>{ 0.2450</td>
</tr>
<tr>
<td></td>
<td>0.1250</td>
<td>0.0075</td>
<td>0.1175</td>
<td>}</td>
</tr>
<tr>
<td>2</td>
<td>0.1350</td>
<td>0.015</td>
<td>0.1200</td>
<td>0.120</td>
</tr>
<tr>
<td>3</td>
<td>0.1925</td>
<td>0.085</td>
<td>0.0075</td>
<td>{ 0.0425</td>
</tr>
<tr>
<td></td>
<td>0.1175</td>
<td>0.085</td>
<td>0.0325</td>
<td>}</td>
</tr>
</tbody>
</table>
The Identification of the Condensible Product.—The vapour pressure of the condensible product was determined as follows. A low temperature bath was prepared by cooling light petroleum in a Dewar vessel with liquid air till it just solidified. When this bath was put under the U-tube nearly all the product was condensed. The temperature was measured by means of a copper-constantan thermo-couple which had been calibrated beforehand. The temperature of the petrol bath was allowed to rise slowly and the corresponding pressures were measured on the Pirani gauge.

Fig. 1 shows the results. The indication of the Pirani gauge were converted into pressures of water vapour. Curve 1 is the vapour pressure curve of water at low temperatures as given in the literature. The round points in Curve 2 represent the vapour pressures of the condensible product and the crosses on the same curve refer to the readings obtained when water vapour was actually introduced into the apparatus. This was accomplished by introducing 5 c.c. of air freed from carbon dioxide and saturated with water vapour at room temperature through the siphon. Liquid air was kept under the trap T1 to condense the water vapour, and the residual air was pumped off and the pressure-temperature determinations were done as before. It will be seen that both the
Experimental curves are very nearly superimposed proving the identity of the vapour. The apparent recovery of only two-thirds of the gas lost is due to the fact that water vapour and hydrogen affect the readings of the Pirani gauge in that ratio.

Discharge through the Condensible Product.—If the discharge is passed through the condensible product obtained in the above experiments without the liquid air-bath, there occurs a rise in pressure in the system and most of it becomes non-condensible in liquid air. The results of such experiments are given in Table IV.

Here again the pressure indications of the Pirani gauge have been converted into absolute values on the assumption that the condensible product is water vapour and that it is decomposed by the discharge into hydrogen and oxygen. Column one gives the pressure of the product before the start and column two gives the final pressure of the condensible product which was found by the difference between

<table>
<thead>
<tr>
<th>Expt. No.</th>
<th>Starting pressure mm.</th>
<th>Final pressure mm.</th>
<th>Amount decomposed in mm.</th>
<th>Pressure of non-condensible gas obtained mm.</th>
<th>Ratio of 4 and 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.275</td>
<td>0.075</td>
<td>0.200</td>
<td>0.320</td>
<td>1.60</td>
</tr>
<tr>
<td>2</td>
<td>0.225</td>
<td>0.050</td>
<td>0.175</td>
<td>0.265</td>
<td>1.52</td>
</tr>
<tr>
<td>3</td>
<td>0.130</td>
<td>0.042</td>
<td>0.088</td>
<td>0.127</td>
<td>1.44</td>
</tr>
<tr>
<td>4</td>
<td>0.135</td>
<td>0.035</td>
<td>0.080</td>
<td>0.1175</td>
<td>1.47</td>
</tr>
<tr>
<td>5</td>
<td>0.125</td>
<td>0.04</td>
<td>0.085</td>
<td>0.1275</td>
<td>1.50</td>
</tr>
</tbody>
</table>

The pressure values in column four have been obtained from the Pirani gauge on the assumption that the gas consisted of a mixture of two volumes of hydrogen and one of oxygen. Finally column five gives the ratio of the pressure of non-condensible product to the condensible product, the latter being completely decomposed by the action of the discharge. The last reading (Expt. No. 5) shows the results obtained by passing a discharge in water vapour itself and the indications of the Pirani gauge were
subjected to the same conversion as before. It will be seen that the behaviour of the condensible product is quite similar to that of water vapour in this respect, and further the assumption that it decomposed into hydrogen and oxygen seems to receive the support from the values given in column five.

A small glass boat filled with phosphorous pentoxide was kept in the discharge apparatus a little further off from the tube and the experiment was started to prepare the condensible product. When a sufficient quantity of hydrogen was lost the residual gas was pumped off and the liquid air-bath under T₂ was removed. The Pirani gauge showed a gradual rise in pressure as the temperature increased but the pressure immediately dropped to zero as indicated by a sudden kick in the galvanometer due to the absorption of the vapour by phosphorous pentoxide.

Spectroscopic Observations.—Fig. 2 shows photographs of the spectra of the glow when the tube filled with particular gas or vapour had been placed in the high-frequency field. Spectrograms 1 and 2 have been taken with a constant deviation glass prism spectograph and the rest with a small Hilger quartz spectrograph. Spectrograms 1 and 3 show the spectrum of pure hydrogen at 0.15 mm. pressure taken with the glass and the quartz spectrographs respectively, when the experiment was started with a liquid air bath under the U-tube. It will be seen that both primary and secondary spectra are prominent in the visible and after 3760 Å there is continuous spectrum. 2 and 4 have been obtained when there was mercury in the apparatus. It is seen that both the secondary spectrum of hydrogen in the visible and the continuous spectrum in the ultraviolet have been wiped out by mercury. 5 is the photograph of the spectrum emitted when the condensible product formed by the action of discharge in hydrogen, had been subjected to the discharge without the liquid air trap. In addition to hydrogen spectrum, it shows the mercury lines and carbon monoxide bands probably as impurities. There is a prominent band at 3064 Å which is due to ‘OH’ radical. 6 and 7 have been photographed when a discharge was passed through water vapour and carbon dioxide respectively. The above-mentioned band is present only in the 5th and 6th spectrograms.

The fatigue effect observed in case of pyrex tube is shown in Fig. 3. In case of quartz tube, however, the fatigue is not so prominent (Fig. 4). Curves 1 in both the figures show the results obtained when the tubes were freshly baked. Curves 2 were obtained when the pyrex tube was baked initially but the quartz tube was not. Curves 3 and 4 represent the results obtained when both the tubes were not baked. Curve 5 in case of pyrex tube shows the limit where no gas would disappear and no further condensible product could be obtained. Such a limit has not been obtained in the quartz tube.
After a course of several experiments on the disappearance of hydrogen the quartz tube became slightly smoky in the space between the two exciting coils and a slightly yellowish deposit was noticeable at a spot under one of the coils, which could not be removed even when the tube was baked at 800°.

In all the tests carried out to identify the nature of the condensible product no indication as to the presence of any silicon hydride was obtained. This is contrary to the results of E. Hiedemann (loc. cit.). The formation of silane could not be expected as it has a vapour pressure of 0.25 mm. at liquid air temperature and the gas, if at all formed, was probably immediately decomposed by the discharge. The following experiment was done by subjecting silane itself to the action of the discharge.

Discharge through Silane, SiH₄.—Silane used was prepared by Watson, Rao and Ramaswami in our laboratory. When the oscillator was switched on the discharge passed through the gas with a reddish glow and the pressure rose from 0.145 to 0.27 mm. The spectrum was quite similar to that of hydrogen, the secondary spectrum being more prominent. In addition to this a brown deposit of elliptical form was formed on the walls of the tube. Liquid air was kept under the
trap T₂ from the very beginning. If the discharge was continued further, the pressure began to fall gradually and water vapour was detected when liquid air was removed. This means that silane completely decomposes into hydrogen and silicon according to the equation

$$\text{SiH}_4 = 2\text{H}_2 + \text{Si}$$

and that hydrogen forms water vapour.

**Discussion.**

The ‘clean-up’ phenomenon in hydrogen when a trap cooled with liquid air is maintained is a two-fold process: (1) the adsorption of a definite amount of the gas on the walls of the tube and (2) formation of water vapour. The loss due to the first cause corresponds to the formation of a monoatomic layer on the surface of the quartz tube and a layer four molecules thick in case of the pyrex tube. The gas thus adsorbed can be liberated back by subsequently heating the tube; but in no case the whole of the gas could be recovered in contradiction to the result obtained by Srikantan (*loc. cit.*) but in agreement with the observation made by the Research Staff, General Electric Co., Ltd. (*Phil. Mag.*, 1921, 41, 685). The fatigue effect can be explained if it is assumed that as more and more gas is adsorbed, the surface becomes less and less available for further deposition of atoms.

In another paper (*Phil. Mag.*, 1924, 48, 553) the same authors have discussed the nature of such adsorption. They think that molecules are adsorbed by reaction with the walls of the vessel but could not make any suggestion as to the nature of reaction.

The loss due to the formation of water vapour is evidently a case of the chemical nature of the disappearance phenomenon. The compound formed under the present conditions has been proved beyond doubt to be water vapour in agreement with the results obtained by Taylor (*loc. cit.*). The question arises as to the origin of oxygen in quantities sufficient for the formation of water vapour. Taylor regards glass as an electrolyte and proposes that oxygen comes from the decomposition of the SiO₂ radical into SiO₂ and O, which subsequently unites with one molecule of hydrogen to form one molecule of water vapour. But this hypothesis does not explain why in his experiments oxygen disappeared more readily than hydrogen. Moreover, he actually maintains a constant d.c. potential of the order of 500 volts to electrolyse glass. In the present case, where the high-frequency discharge is passed through the tube it is difficult to assume how electrolysis can occur.

In the case of experiments with the quartz tube a possible explanation seems to be that hydrogen under the influence of the discharge
becomes excited, and attacks silica to form water vapour. The property of the discharge is to impart the gas through which it passes active chemical properties and to cause it to enter into chemical combination. It puts the molecules and the atoms of the gas into “excited” state, thus enhancing their chemical activity. The explanation suggested is that hydrogen, when excited, attacks SiO₂ according to the equation.

\[ \text{SiO}_2 + 2\text{H}_2 = 2\text{H}_2\text{O} + \text{Si} \]

to form water vapour.

An indication in the direction of this explanation is given by the fact that the quartz tube became smoky in appearance and developed a yellowish deposit at a certain spot. This yellow deposit has a faint resemblance to one obtained by decomposition of SiH₄ and it is quite likely that it is also silicon.

The fatigue effect which limits the formation of water vapour in the case of pyrex tube could be explained by simply considering that less SiO₂ radicals are available for hydrogen to combine with owing to the increased thickness of the adsorbed layer.

SUMMARY.

The general nature of the clean-up phenomenon by high-frequency discharge shows that the gas is first adsorbed on the walls of the tube forming a monoatomic layer on a quartz surface. The apparent further loss of gas is due to formation of water vapour. The observation made in Part I that only two-thirds of the gas lost, could be recovered, has been shown to be due to the fact that the effect of water vapour on the Pirani gauge is two-thirds that of hydrogen.

The water vapour itself is dissociated to the extent of 70% by the action of the discharge.

No silicon hydride could be detected. Silane itself decomposed completely into silicon and hydrogen by the action of the discharge. Other silicon hydrides are probably less stable.

Department of General Chemistry,
Indian Institute of Science,
Bangalore.

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