EQUILIBRIUM IN ELECTRODELESS DISCHARGE.

PART I. THE DISAPPEARANCE OF HYDROGEN IN ELECTRODELESS DISCHARGE.

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INTRODUCTION.

It has been known for a long time that gases at low pressures in sealed tubes disappear under the influence of electric discharge even in the absence of metallic electrodes.

Various theories have been put forward to account for this behaviour. A. A. Campbell Swinton (*Proc. Roy. Soc.,* (A), 1907, **79**, 134) supports the view that the gas is mechanically held by the glass walls since he found that helium could be liberated back by heating the glass walls. Hill (*Proc. Phy. Soc.,* 1912, **25**, 35) found that the disappearance is due to chemical reaction between the activated gas and the glass.

E. Hiedemann (*Z. physikal. Chem.,* (A), 1931, **153**, 210–40) showed that the clean-up phenomena takes a normal or anomalous course according to the previous treatment of the tube. The normal course is the adsorption of hydrogen atoms on the surface of the tube which corresponds in effect to the results obtained by Johnson (*Proc. Roy. Soc.,* (A), 1929, **123**, 603). The latter author finds that the hydrogen disappeared forms a monomolecular layer on the glass surface. Both the authors have found fatigue in the rate of disappearance and also in the total quantity of gas which disappears. The first experiment on disappearance with a freshly baked tube is the most effective both as regards the rate as well as the quantity of the gas disappeared.

If, however, during the experiments a portion of the apparatus is cooled with liquid air, condensible products are formed. Mierdel (*Ann. Physik.,* 1928, **85**, 612) found a pressure rise on removing the liquid air-bath after the gas had disappeared under the influence of an electrodeless ring discharge. He called this condensible product atomic hydrogen which did not undergo recombination and hence was repeatedly condensible. E. Hiedemann (*Ann. Physik.,* 1931, **8**, 456) however, differs on the ground that the life-period of atomic hydrogen is of the order of a second. Hiedemann considers the condensible product to be a mixture of silicon hydrides, which is formed by the action of hydrogen on the glass walls under the influence of the

discharge. In a subsequent paper (*Z. physikal. Chem.*, (A), 1933, **164**, 20) the same author made investigations on the fatigue phenomenon observed with glass vessel and concluded that the fatigue was due to sodium atoms on the glass walls. He confirmed this by noticing the absence of such a fatigue phenomenon in quartz tubes.

A completely different view is offered by the work of James Taylor (*Nature*, 1928, **122**, 347) who, working with the electrodeless discharge in hydrogen excited by a seven-meter valve oscillator, obtained a condensible product which he found to be water. It had the same volume as that of the hydrogen which disappeared. Its spectrum corresponded to that obtained with water vapour. He explains his results by regarding glass as an electrolyte and the disappearance of hydrogen under the action of the discharge being due to the chemical interaction of the gaseous ions with the electrolytic products and ions of the glass. Thus the SiO_3^- ion decomposes into silica and oxygen which subsequently unites with hydrogen to form water (*Proc. Roy. Soc.*, (A), 1929, **123**, 252).

Srikantan (*Jour. Ind. Chem. Soc.*, 1936, **13**, 79) working in our laboratory reported that under the influence of high frequency discharge hydrogen gas first disappeared completely during the first hour and half and about two-thirds of the gas was desorbed if the discharge was continued for ten hours subsequently. The original pressure was completely regained after heating the tube to 400° C.

It would seem from the diverse nature of observations of different authors and of the explanations given by them that the phenomenon of disappearance of hydrogen in electrodeless discharges is a complicated one and may be due to more than one cause. The present work was undertaken to investigate more fully the nature of the phenomenon by making quantitative measurements.

EXPERIMENTAL.

The Apparatus.—Fig. 1 (*a*) represents the general scheme of the apparatus. D is the discharge tube, made of pyrex, 2 cms. in diameter and 10 cms. in length. T_2 is a trap which is cooled with liquid air to obtain the condensible gas formed by the discharge in hydrogen. A_1, A_2, A_3 are small side tubes with constrictions at the top which were subsequently joined to the apparatus to seal off the condensible products formed in the apparatus. In order to obtain pressure changes of larger order of magnitude it was necessary to have the volume of the rest of the apparatus as small as possible compared with that of the discharge tube itself. Consequently, the liquid air trap T_1 used to arrest mercury vapour, the diffusion pump, the Toepler pump, etc., were cut off from the discharge tube by means

of a tap of large bore after the discharge tube had been thoroughly evacuated and filled with the gas. For the same reason a pressure-gauge of smaller dimensions which was subject to no other objection was required. The Pirani gauge was considered to be the most suitable for the purpose. This gauge is very sensitive within the range of pressures at which the work was carried out.

Fig. 1a.
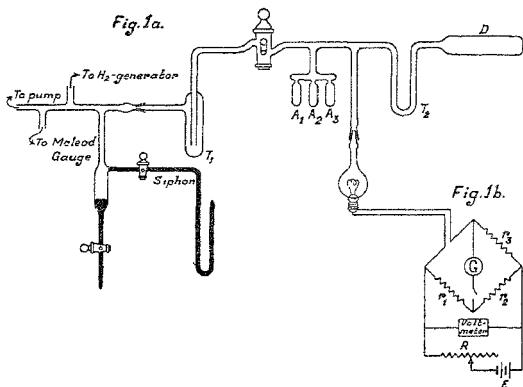
Fig. 1b.

The Pirani gauge was made out of a Mazda 110 volt 10 watts galvanometer lamp which formed the fourth arm of a Wheatstone's circuit [Fig. 1 (b)] and the voltage required to keep the temperature of the filament constant at 60°C. at different pressures as measured by McLeod gauge was recorded by a voltmeter and the calibration curve for different gases was prepared (Fig. 2).

For evacuating the whole apparatus a two-stage steel mercury diffusion pump was used. The diffusion pump was backed by an ordinary Toepler pump, the advantage being that the gases could be collected if desired.

An additional siphon arrangement [Fig. 1 (a)] was joined to the apparatus so that gases collected in tubes could be easily transferred to the apparatus when required. A small mercury manometer was also incorporated in the system as a guide for preliminary evacuation.

The whole apparatus including the trap T_1 was made of pyrex and it was joined to the line leading to the pumps, the McLeod gauge, etc., by means of a ground joint.
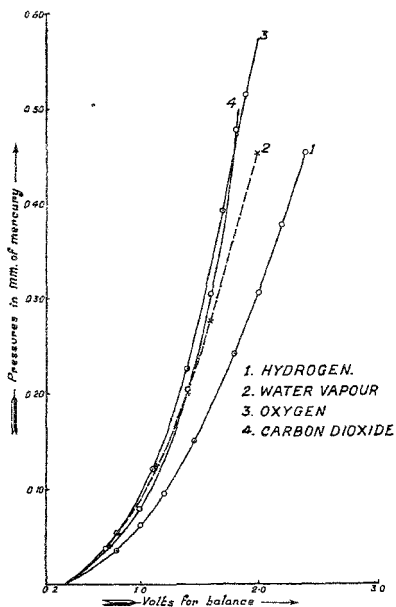
FIG. 2

The Oscillator.—The gas in the discharge tube was excited by placing the latter in the high frequency field of a magnetron oscillator. Fig. 3 shows diagrammatically the whole of the oscillating circuit. The magnetron valve (E 396) is placed between the poles of an iron-cored electromagnet with the electrode axis perpendicular to the direction of the lines of force. The filament is heated at 4 volts by means of a step-down transformer (110 V–6 V) supplied from 110 volts 25 cycles mains. The high tension was applied from a 1000 volts D.C. generator having a rheostat in series on its input side for regulating the voltage, through a smoothing circuit.

The oscillatory circuit was made from a 1/16″ copper wire bent in the form shown in the figure. It was connected at its ends to the anode leads of the valve by means of binding screws. In some experiments the oscillatory circuit consisted of a Lecher wire system bridged at the other end, the mid-point of the bridge being connected to the

positive of the H. T. supply. However, it was found that more power could be put into the discharge tube by using the form of the oscillatory circuit as shown in the figure than by simple Lecher wires; hence it was used in the present work throughout.

The usual operating data for the circuit is as follows:—

Filament volts	..	..	3.5
,, current	..	..	2.2 amps.
Anode volts	..	..	500–600
,, current	..	..	30–40 ma.
Field strength	..	..	400 lines per sq. cm.

The wave-length was measured on a Lecher wire system inductively coupled when the circuit was oscillating under the above-mentioned conditions. The positions of the current nodes were detected by means of a vacuum thermocouple and a galvanometer. The value of the wave-length found from a number of such determinations was 1.8 metres.

Fig. 3
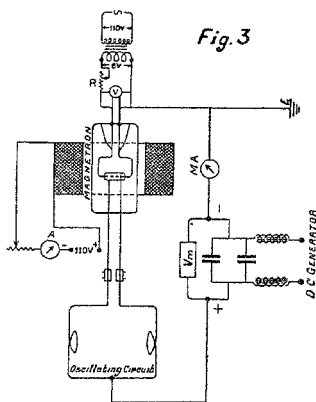
Hydrogen was prepared by electrolysing a solution of barium hydroxide between two platinum electrodes in a U-tube. It was led over platinised asbestos heated electrically to a temperature of 200°C., then through a U-tube filled with calcium chloride to remove water-vapour. It was stored in a tube filled with phosphorous pentoxide which was isolated from the calcium chloride tube by means of a capillary tap; the storage tube was joined to the main apparatus through a capillary tap at the other end.

To start with, the whole apparatus was evacuated and rinsed with hydrogen a number of times to ensure absence of impurities. Liquid air was kept under the trap T_1 during the whole process to trap mercury vapour.

Before starting an experiment, the discharge tube D was baked out at 500°C. in an electric furnace. After filling the tube with the gas at the desired pressure the tap was closed and the discharge was started by switching on the oscillating circuit. The colour of the glow was red in the beginning when pressure was 0.2 mm. and became more intense when the pressure fell to about 0.1 mm. The primary hydrogen spectrum was very strong compared with the secondary spectrum. At still lower pressures, however, the secondary spectrum became comparatively prominent and the colour of the discharge was more violet than red. Mercury lines were sometimes faintly observed in a direct vision spectroscope when liquid air was not put under the trap T_2. The pressure at which the glow ceased was of the order of 10^{-4} mm. as judged from the indications given by the Pirani gauge.

It was found that when the rate of disappearance was negligible the tube became hot due to the passage of the discharge, but not so much when the disappearance of the gas was comparatively faster. Whenever the disappearance was rapid the colour of the discharge was scarlet red with intense Balmer lines, and when it was slow due to fatigue, the colour was whitish red showing more prominently the secondary spectrum.

The first set of experiments was done at the earlier stage of the present investigation using the oscillator described by Srikantan (*loc. cit.*) and the apparatus did not include the trap T_2 and side tubes A_1, A_2 and A_3. The procedure adopted was to fill the discharge tube at a known pressure and start the discharge. The progressive fall of pressure was given by the Pirani gauge whose readings were taken at definitive intervals after stopping the discharge and allowing the tube to cool. To know the total amount of the gas that could be made to disappear, further quantities of the gas were supplied by opening the tap, and the discharge again started. This was done till no more gas disappeared after continuing the discharge for two to three hours.

The method employed for recovering the gas that disappeared, by heating the tube at various temperatures, was as follows: The tube was put in the furnace at 450°C. The amount of gas evolved at any one temperature was known from its pressure as given by the Pirani gauge, taking the temperature correction for the heated part into consideration. When there was no further rise in pressure, the tap was opened for a while to pump off all the gas that was in the discharge tube and the process repeated till there was no indication of pressure rise.

Table I gives the results of three series of experiments; the first series of these experiments was done with a push-pull oscillator of 10 metre wave-length; it was less powerful than the magnetron oscillator which was used for the second and the third series.

The first series consists of four experiments carried out at different initial pressures. Columns 1 and 2 represent the starting and end pressures respectively in each case; the third represents the loss which has been totalled up at the end. The fourth column gives the pressure of the gas that could be restored by the heat treatment, and finally, the fifth column gives the ratio of the gas restored to that of the gas lost, the mean value of which is 0.64. The second and the third series of experiments have been carried out in the same manner.

TABLE I.

Pyrex Discharge tube.

	Initial press. mm.	End press. mm.	H₂ lost mm.	H₂ recovered mm.	Ratio of 4 : 3
	1	2	3	4	5
1. Push-pull Oscillator λ = 10 m. metres	0·155	0·0225	0·1325	0·1900	0·68
	0·0225	0·015	0·0075		
	0·101	0·080	0·021		
	0·4975	0·3825	0·1150		
			0·2760		
2. Magnetron Oscillator Lecher Wire coupled λ = 1·8 m.	0·275	0·08	0·1950	0·154	0·60
	0·080	0·013	0·0670		
			0·262		
3. Magnetron Oscillator coupled with looped wire λ = 1·8 m.	0·285	0·076	0·209	0·133	0·64

The value of the pressure of hydrogen (which was recovered by heating) given in the fourth column, has been obtained after applying the temperature correction for the heated portion of the apparatus.

The results bring out the "fatigue phenomenon". The tube absorbs hydrogen under the influence of the discharge upto a certain limit. This fatigue is manifested in the rate of disappearance of hydrogen as shown in Fig. 4, where the progressive fall of the pressure with time at different stages is given.

Curve I corresponds to the experiment No. 1 of the first series in Table I, which was carried out with a baked out tube.

Curve II corresponds to the experiments in the second series. It will be seen that the rate is much slower than in Curve I, although the tube had been baked out initially.

Curve III corresponds to the third series. Here the rate is quicker because of the increased output of the oscillator but the fatigue is evident from the fact that the end pressure is much higher than in Curve II.
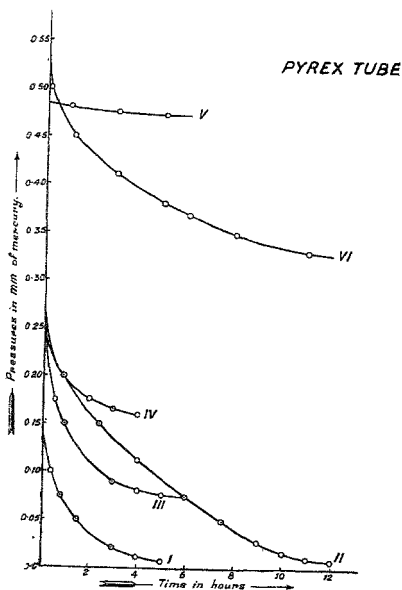

FIG. 4.

Curve IV shows the course of disappearance without baking the tube which was in the same condition as at the end of the third series of experiments, and the fatigue in this case is evident both in the rate as well as in the end pressure.

Curve V shows the effect of higher initial pressure, when the tube was not baked. It will be seen that the curve is practically horizontal and the limit of disappearance is reached.

However, if the tube was initially baked and the experiment started at higher initial pressure, the course followed is that shown in Curve VI.

It is quite evident that the rate of the disappearance depends upon (i) the initial treatment of the tube and (ii) the oscillator input. The higher the input of power, the quicker is the disappearance. The final pressure which is reached at the end of an experiment mostly depends upon the total amount of the gas that has been taken by the tubes.

SUMMARY.

The disappearance of hydrogen in a degassed pyrex tube under the influence of high frequency electrodeless discharge was followed by a sensitive Pirani gauge. Both the rate of disappearance of the gas as well as the amount depend upon the previous history of the tube. A fatigue effect is evident. The apparent quantity of gas recovered by subsequent heating is approximately two-thirds of that lost under the influence of the discharge, as measured by the Pirani guage.

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