

Reactions at the Surface of Hot Metallic Filaments—Part V.¹

Thermionic emission and catalytic activity at the surface of hot metallic wires: $H_2 + CO_2 \rightarrow CO \pm H_2O$ at the surface of platinum, platinum coated with BaO and thoriated tungsten.

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ABSTRACT.

A semi-qualitative investigation has been made on the emission of electrons from the surfaces of platinum and thoriated tungsten and the minimum temperature at which the thermionic emission is perceptible, has been obtained by extrapolation. This minimum temperature is found to be the same as that required to start the interaction of CO_2 and H_2 on these surfaces. Hydrogen is found to be activated at the same temperature, whilst CO_2 is activated at a lower temperature.

The oxidation of methane at the platinum surface is also shown to be similar.

It is concluded that the activation of gases at a catalyst surface is to a large extent influenced by the capacity of the surface to emit electrons at that temperature.

The phenomenon of surface catalysis greatly depends on the adsorption of the reactants and their consequent activation by the association with the surface. The preceding parts of

¹ Cf. Parts I-IV, *J. Indian Chem. Soc.*, 1929 (VI), 6, 931, 949, 959; 1930 (VII), 8, 745.

this paper deal with the kinetics of the interaction of CO_2 and H_2 at various surfaces. The results show the effect of the surface on the reaction and also give us an idea of the relative adsorptive capacities of those surfaces for the gases. But the question how these gases are brought into a reactive state in the presence of a heated catalyst is still left open. The kinetic studies do not help us far in this direction. It appears that in the interpretation of the nature and behaviour of catalysts in gaseous reactions there is some other factor which has not been taken into consideration.

In the course of a discussion on gaseous combustion at the British Association in 1910, Sir J. J. Thomson called attention to the fact that "combustion was concerned not only with the atoms and molecules but also electrons.....In reference to the influence of hot surface in promoting combustion...It was not improbable that the emission of charged particles from the surface was a factor of primary importance.....These electrons might produce very important effects by uniting (perhaps selectively) with moisture, with oxygen and with the inflammable constituent of the gaseous mixture ... The action of surfaces might ultimately be found to depend on the fact that they formed a support for layers of electrified gas in which chemical changes proceed with high velocity."¹

Langmuir² found that chemically indifferent gases have no effect on the electron emission from tungsten but catalytic poisons suppressed the emission of electrons from it. Kruger and Taege³ showed that H_2S , HCN , and CO which are catalytic poisons decreased the photo-electric emission from metals.

Further Thompson⁴ finds that thermionic emission is perceptible at a platinum wire, when its temperature is raised to the same temperature at which the union of hydrogen and

¹ Sir J. J. Thomson, *British Ass. Rep.*, Sheffield, 1910, 501.

² Langmuir, *Trans. Farad. Soc.*, 1921, 17, 641.

³ Kruger and Taege, *Zeit. Electro-Chem.*, 1915, 21, 562.

⁴ Thompson, *Phy. Zeit.*, 1913, 14, 11 (*cf. Kirkby. Phil. Mag.*, 1905, 10, 476).

oxygen begins on the surface. Thompson describes that the influence of excess of oxygen in the mixture is to reduce the temperature of union below that of thermionic emission, whilst the increase of hydrogen in the system does not alter the temperature of union.

While hydrogen is greatly adsorbed by platinum the increase of oxygen in the system would be to displace the hydrogen in preference to oxygen and thus with excess of oxygen the chances of it being adsorbed are greater than that of hydrogen. The reverse is the case with excess of hydrogen.

If it is granted that hydrogen and oxygen must not only be suitably adsorbed but also activated before union, it is evident that the activation of either or both the reactants is brought by the catalyst. The effect of increasing one of the reactants in the mixture shows this. From Thompson's results it follows that at the surface of platinum, oxygen is rendered reactive towards hydrogen at a temperature lower than that at which negative particles are discharged from the surface; whilst the surface activates hydrogen at the same temperature at which thermionic emission is perceptible.

The results of Thompson in conjunction with those of Langmuir, Kruger and Taege show that the activation of gases at catalytic surface has some connection with the emission of electrons from the surface; or at least that the activation of hydrogen is in some way influenced by thermal emission from the surface.

The results described in this paper form an attempt to extend the observation of Thompson to the interaction of CO_2 and H_2 at the surfaces of platinum, platinum coated with barium oxide and thoriated tungsten. Since the adsorptive capacity of platinum and that of coated wire for carbon dioxide would vary, it was of great interest to see if the increase of either of the constituents of the reactive gases would influence the temperature at which the reaction commences.

It was also thought interesting to repeat the above

experiment with thoriated tungsten wire, since thoriated tungsten is usually preferred to platinum as a suitable substance for giving a source of electrons. The electron emission from thoriated tungsten takes place with great ease at temperatures even far below that required for dull red heat. So experiments were made with CO_2 and H_2 to see if the reaction between them started just at the temperature at which thermionic emission is perceptible as in the case of platinum. Great difficulty was experienced in mounting the wire in the cell with suitable leads. Welding on directly to copper or platinum leads could not be done for the thoriated tungsten easily burns off. After many trials of different methods the following one was found to be workable :

No. 24 copper wire was taken for the leads. A tiny hole was bored along the axis of the wire with No. 80 drill. The clean end of the thoriated tungsten wire was put inside the hole and the wire was pressed in position in a vice, thus forming a good contact. When the wire was stretched along the axis of the tube the two copper leads passed through the glass ends CC (see Fig. 1). The ends CC were closed with molten shellac. But when the reaction was proceeding the cell got appreciably warm and the shellac softened. So it was found necessary to put a water jacket around the cell and water was kept circulating throughout the experiments.

Experimental.

The apparatus used in these experiments is given in Fig. 1. The glass cell D is about 12 cms. in length and 2 cms. in diameter. In general the filament A was welded on to suitable leads CC, which are sealed in the ends of the vessel D so that the wire is stretched in the middle of the cell. It was found that the wire stretched like that at the axis of the tube sagged down a great deal when it was heated and came with in a millimeter or two of the other electrode. So the wire was

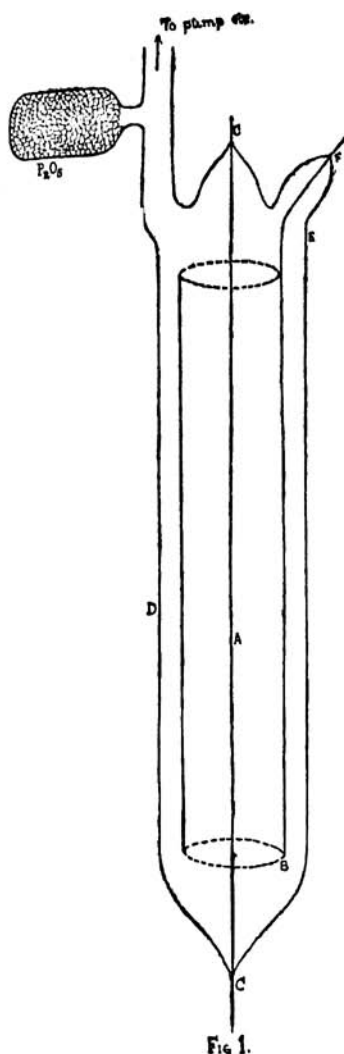


FIG. 1.

twisted into a small spring at one of its ends, and this prevented the two electrodes from coming together. B is a copper foil rolled into a cylinder with a narrow slit, for observation; it forms the positive electrode. A stout copper wire E is soldered on to it, which is in itself welded to a piece of platinum which runs through the glass wall at F.

The cell is connected to a small bulb of P_2O_5 and to a system of pump and manometer. A Geissler tube was connected to the apparatus in order to test the degree of vacuum obtained before an experiment is started. In all the experiments described below the cell was exhausted till no discharge passed through the Geissler tube.

The heating current is supplied by the 110 mains regulated by a system of rheostats. In order to measure the thermionic current the electrode B is connected to the +ive of the high tension batteries

(usually 80 volts or 40 volts) through a sensitive galvanometer. The -ive of the high tension is connected on to the -ive of the mains.

Methods of working.

Thermionic emission—The apparatus is first exhausted till no discharge passes through the Geissler tube. The wire

was heated by a small current and then the high tension was switched on. Slowly the temperature of the wire was raised. To find out the temperature of the wire, its resistance was noted by means of an ammeter in series and a voltmeter across. So long as the resistance of the wire in any set of experiments was constant, the temperature would be constant. By slowly adjusting the heating current the resistance of the wire was varied. The thermionic current flowing through the galvanometer was noted at various temperatures of wire. In some experiments it was necessary to glow out the wire in vacuum at a high temperature of about 1000°C before consistent readings could be obtained. The thermionic current is expressed as deflections on the galvanometer scale, 1 division = 10^{-6} amps.

Before each set of experiments described below the apparatus was well exhausted and the filament was glowed out at about 1000°C and care was taken to see that the Geissler tube showed no discharge passing through.

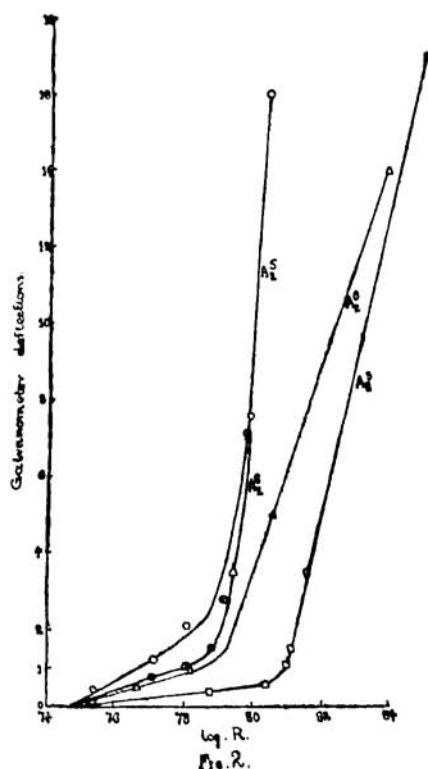
Interaction of CO_2 and H_2 —In these experiments that part of the apparatus used for measuring thermionic current was cut off; only the main heating circuit with ammeter and voltmeter being used. Pure dry CO_2 and H_2 (as in the previous experiments) were let into the exhausted apparatus at suitable pressures. A small heating current was put on for 15 minutes or 1 hour, according to the rate of reaction at that temperature. The resistance of the wire was noted and maintained steady. The resistance of the wire was kept remarkably steady with the rheostats alone, since the temperature at which the experiments were conducted was low and strong convection currents were not set up in the cell as there was no sudden cooling of the cell (as in the previous experiments) and the cell was of small dimensions. After some time, noted by the watch, the current was switched off; sufficient time was allowed to cool down the gases to the laboratory temperature and the water formed to get absorbed by

the P_2O_5 . The fall in pressure was noted. It was taken to be proportional to the reaction rate in that interval. Thus the reaction rate of the interaction of CO_2 and H_2 with varying quantities of the gases was noted at various temperatures.

A. Platinum wire 12 cms. long, 0.01 cm. diameter.

The platinum wire used in these experiments is an old sample used in the first experiments of part I of this thesis to study the reaction between CO_2 and H_2 .

To find out the temperature at which thermionic emission is just perceptible or commences, curves were drawn for each of the experiments performed with this wire. The logarithms of the resistance were plotted against the galvanometer deflection. These graphs (Fig. 2) were straight lines, at low



resistances of the wire, which when produced cut the x-axis sharply; but at higher resistances they suddenly took a bend and went straight almost parallel to the y-axis; this is perhaps due to large currents being set up owing to ionisation due to collision with the residual gases in the tube. On extrapolation for zero thermionic current, these graphs cut the x-axis at a point corresponding to 5.56 ohms. The temperature of the wire corresponding to this is 975° C, calculated from a knowledge of the resistance of the wire at zero degree and its temperature co-efficient.

Experimental data on the kinetics of the interaction of CO_2 and H_2 on this surface are given in Figs. 3 and 4. Extrapolation for zero reaction for experiments A_3 and A_2 gives the resistance of the wire as 5.58 ohms, *i.e.*, at a temperature of 979° C interaction of CO_2 and H_2 begins at the surface of platinum.

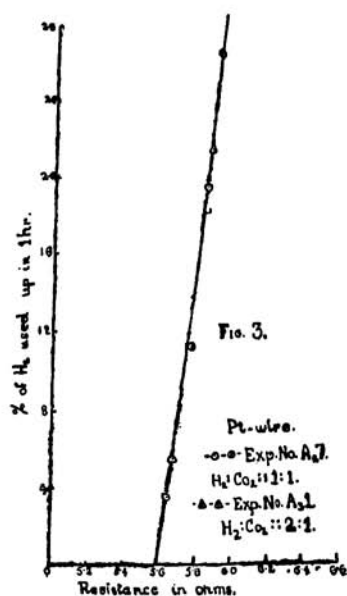


FIG. 3

It is seen that for equimolecular proportions of CO_2 and H_2 (Fig. 3) the reaction begins at the same temperature at

which thermionic emission is perceptible and the increase of H_2 in the system does not alter the temperature at which reaction starts. But on plotting data for the resistance and the percentage of the hydrogen used up for Exps. No. A₄ the graph (Fig. 4) does not agree with the previous one. The resistance of the wire when the reaction starts is 3.75 ohms. The temperature at which the reaction starts is 520°C. The increase of CO_2 in the system is to lower the temperature, when the reaction begins, below that at which thermionic emission is perceptible.

It has been shown by Hinshelwood and Prichard¹ that excess of CO_2 in the system actually displaces H_2 from the surface of platinum so that the reaction velocity increases rapidly but after a certain stage the displacement of H_2 is so marked that a further amount of CO_2 actually poisons the wire.

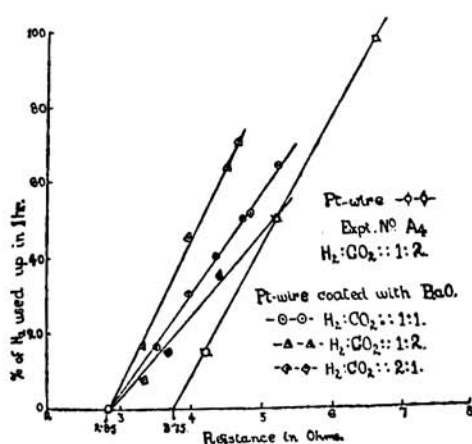


FIG. 4.

So it is obvious that in the interaction of CO_2 and H_2 with stoichiometric proportion of the gases the hydrogen is normally adsorbed on the active centres of the surface and that is activated or rendered reactive at the same temperature at which thermionic emission commences. If displacement of

¹ Hinshelwood and Prichard, *J. Chem. Soc.*, 1926, 127, 806.

H₂ from the surfaces by CO₂ takes place with excess of CO₂ in the system it has to be concluded that CO₂ is activated at a temperature far lower than that at which thermionic emission is perceptible (*cf.* Thompson).¹

Note :—In this paper the expression “ *the temperature at which thermionic emission is perceptible* ” has been used often. It must be understood, however, that it is *not claimed* that below this temperature thermionic emission ceases. Theoretically and practically also sometimes, thermionic emission is possible at low temperatures. In a similar manner catalysis on cold surfaces is also a theoretical possibility. Hence there is an obvious danger in taking the terms literally. All that is claimed is that it is only a condition obtained from the graphs. The similarity of conditions in the two different phenomena is only emphasised.

In Thompson's experiment also, hydrogen was activated at the same temperature at which thermionic emission is perceptible. In order to see if such a result is common only to those reactions concerned with hydrogen as one of the reactants, a few experiments were made to extend this to other reactions. The oxidation of methane by oxygen in the presence of platinum wire was undertaken. The reaction is explosive; so the temperature of the wire was raised very slowly and care was taken to see at each stage if there is any slow combustion taking place. 100 m. m. of each of the gases were put in. As soon as the temperature of the wire reached about 965°C the reaction went off with an explosion and unfortunately the wire snapped off. Considering the explosive nature of the reaction at this temperature the voltmeter and the ammeter readings had to be taken very quickly; so the temperature of the wire noted-965°C-is only approximate; but still it could be taken as fairly agreeing with the previous one.

¹ Thompson, *loc. cit.*

B. *Interaction of CO₂ and H₂ at a platinum surface coated with BaO.*

In order to verify the idea that if CO₂ is adsorbed on the surface in presence of H₂, and is activated at a far lower temperature than H₂, it was thought to substitute for platinum a surface which was more conducive to the adsorption of CO₂ than hydrogen. Such a surface was realised in practice by coating the platinum filament with a thin layer of barium oxide, as mentioned before.¹

On plotting (Fig. 4) as before the resistance and the percentage of H₂ used up in 1 hour it is seen that the least temperature at which the reaction starts is very low and the graphs when extrapolated for zero reaction cut at the same point corresponding to 2.85 ohms. The approximate temperature corresponding to this being 380°C (calculated from a knowledge of the resistance of the wire at zero and its temperature co-efficient of resistance). Since CO₂ is greatly adsorbed by BaO, the increase of H₂ or CO₂ does not alter the temperature of which the reaction starts. However it is far lower than that on the surface of plain platinum.

C. *Thoriated Tungsten.*

The wire used in these experiments was 10 cms. long and 0.085 m.m. in diameter. The experimental procedure was the same as in the previous case. A great deal of care had to be taken to exhaust the apparatus well for minute amounts of air would oxidise and burn off the wire.

It was seen that a fresh wire gave no thermionic emission even when the filament was heated to visible redness. It is not surprising in view of the fact that a new wire is never so good an emitter as an 'old' one. So the reaction between CO₂

¹ Brikantan, *J. Indian Chem. Soc.*, 1929, [VI] 6, 959

and H_2 was first studied and then the wire was used to measure thermionic emission.

Since the temperature coefficient of resistance for this wire was not found out, the temperature at which thermionic emission is perceptible or at which the reaction commences was not calculated. Only the corresponding resistances of the wire were noted. The results are given in the following Tables.

TABLE I.

$CO_2 : H_2 :: 1 : 1.$

Resistance of wire in Ohms ...	16.19	19.57	23.0	25.0
% of H_2 used up in 1 hour ...	nil.	nil.	10.3	42.8

TABLE II.

+ 80 Volts on plate.

Exp.						
A	{ Resistance in Ohms. ...	25.31	27.38	30.56	31.47	
	{ Galvanometer deflections. ...	0.2	0.6	1.0	4.0	
B.	{ Resistance in Ohms. ...	25.62	27.69	28.48	29.12	29.83
	{ Galv. deflections. ...	0.2	1.0	1.2	1.9	2.4

On plotting the data from the above Tables it was seen that the thermionic emission was zero or just perceptible when the resistance of the wire was 22.65 ohms. The two values from Table I were on a steep line which cut the axis corresponding to 22.5 ohms. Hence it appears as in the case of platinum that the catalytic reaction between CO_2 and H_2 on the surface of thoriated tungsten commences at the temperature at which thermionic emission is just perceptible.

The few results described above clearly indicate that the activation of gases at a catalyst surface is to a large extent

influenced by the capacity of the surface to emit electrons at that temperature.

A few experiments were undertaken to see if the reaction between CO_2 and H_2 would proceed in the presence of a platinum foil and an oxide coated one when exposed to radiations from mercury vapour lamp. 100 m.m. of each gas were taken in a small quartz tube in which about a square centimeter of the platinum foil was suspended. The system was irradiated for 8 hours continuously. The results were negative. Perhaps working at low pressures might be helpful.

D. Further work.

A possible criticism that might be advanced against the experiments described above is that the methods of evacuation adopted are far too inefficient for any measurement of thermionic emission and that the results might have been vitiated by large currents set up due to ionisation by collision. While admitting the validity of such a criticism, it has to be noted that the object of the work was not to make any measurements on thermionic emission *per se*. A qualitative study of the process was only attempted. Further this imperfect evacuation was advantageous inasmuch as the ionisation currents set up, only served to enhance the value of the currents measured and hence render the measurements more sensitive on a comparatively less sensitive instrument.

However, in order to meet the above criticism as far as it lay within the experimental facilities available a thorough evacuation of the apparatus was attempted.

The apparatus was evacuated by means of a Langmuir pump backed by the Topley; and liquid air trap was introduced between the pumps and the cell. Before each experiment the tube was thoroughly baked out at 400°C for 5 hrs.

while the pumps were continuously worked during the whole course of the experiments.

The vacuum obtained was much better than that in the previous experiments. A spiral type of McLeod gauge was used to measure the pressures. Before each set of experiments it was noticed that the apparatus was evacuated to the same degree.

However as measurements of thermionic currents were started it was observed that gases were evolved, perhaps due to the degassing of the anode by the electronic bombardment. This greatly interfered with the measurement of the currents. Therefore the wire was glowed out with 80 volts across the electrodes while the apparatus was baked out as mentioned above.

However it was found advantageous to make measurements, as quickly as possible soon after the procedure described above. The pressures during these experiments were of the order of 10^{-6} m.m. Still it is not claimed that ideal vacuum conditions were attained as in absolute measurements of thermionic currents.

A piece of platinum wire 10 cms. long and 0.01 cm. in diameter was taken for these experiments.

The results show that the conclusions arrived at in the first section of this paper are fully confirmed. In this case the temperature of the wire at which the thermionic emission is perceptible is 770°C , and the temperature at which the reaction between hydrogen and carbon-dioxide is perceptible is 765°C .

This work was done in the laboratories of the Indian Institute of Science, Bangalore, and I take the opportunity of recording my heart-felt thanks to Prof. H. E. Watson for his interest and kind criticism. My thanks are also due to Mr. S. K. Jatkar, M.Sc.
