

ON THE POSITIVE ION EMISSION FROM HEATED NICKEL WIRE IN OXYGEN AND HYDROGEN.*

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Introduction.

The ionization of gaseous molecules or atoms on a metal surface, heated or not heated, has been presumed in various surface phenomena. For instance, the effect of gases upon the emissivity of the thermoelectron¹⁾ or photoelectron²⁾ from metal surfaces has been explained by the presence of the adsorbed ions (positive or negative). According to Finch³⁾ and his coworkers, some metal sheets or gauzes (Au, Ag, Ni, Cu, Pt, etc.) heated in various gases (O₂, H₂, CO, N₂, A, etc.) presented themselves charged electrically. These experimental facts were also ascribed to the ionization of the gases adsorbed on surfaces. Langmuir⁴⁾ and his coworkers investigated the ionization of caesium on the heated tungsten surface comprehensively and found its necessary condition to be

$$\phi > I,$$

where ϕ is the work function of the metal surface and I the ionization potential of the gas, while Richardson⁵⁾ and Rymer⁶⁾ reported about the positive ion emission from heated platinum wire in oxygen. In this case $\phi = 6.3$ volt⁷⁾ ($= 8.46$ in oxygen)⁸⁾ and $I = 13$ volt.⁹⁾ These values contradict the above mentioned condition for the surface ionization.

Now, if such a surface ionization process can be generally admitted in gas-solid systems, it may be of great significance for the mechanism of the surface catalysis. Some investigators¹⁰⁾ have assumed such a process in their theories of

* The main part of this paper is the reprint from the *Proceedings of the Imperial Academy, Tokyo*, 13, 320 (1937).

1) J. A. Becker, *Trans. Am. Elec. Chem. Soc.*, 55, 153 (1929).

2) R. Suhrmenn, *Z. phys. Chem.*, (B), 28, 215 (1935).

De Boer, "Electron Emission and Adsorption Phenomena", 150 (1935).

3) Finch-Stimson, *Proc. Roy. Soc.*, (A) 116, 379 (1927); 124, 356 (1929). 144, 307, 320 (1934).

4) Langmuir-Kingdom, *Proc. Roy. Soc.*, (A) 107, 61 (1925).

5) O. W. Richardson, "The Emission of Electricity from Hot Bodies", 179—233 (1916).

6) T. B. Rymer, *Proc. Roy. Soc.*, (A) 153, 422 (1936).

7) Hughes-Du Brige, "Photoelectric Phenomena", 75 (1932).

8) Cassel-Gluckauf, *Z. phys. Chem.*, (B), 347 (1932).

9) H. D. Smyth, *Rev. Mod. Phys.*, 3, 389 (1931).

10) O. Schmidt, *Chem. Rev.*, 12, 363 (1933).

J. E. Nyrop, *J. phys. Chem.*, 32, 1006 (1928); *J. Am. Chem. Soc.*, 54, 4588 (1932).

the catalysis. But neither the relation between the mechanism of the catalysis and the surface ionization nor even the mechanism of the surface ionization itself has come to full understanding.

On the other hand, if the ionization of gaseous molecules can be regarded as a special case of chemical decompositions as done by Saha and Langmuir, the surface ionization is in itself considered to be a special case of catalytic decompositions on a metal surface.

In order to elucidate the general property of the surface ionization and its relation to the surface catalysis, the author investigated the positive ion emission from heated metal wire in oxygen and hydrogen. In this paper, it is his intention to report that the positive ion emission from nickel wire in both oxygen and hydrogen was recognized and that it was enhanced on the oxidised surface in comparison with the reduced one.

Apparatus:

The apparatus used is shown in Fig. 1. F is a filament of Mond nickel wire (0.25 mm \times 50 cm) which was closely coiled and heated electrically by the battery B_1 . Its temperature

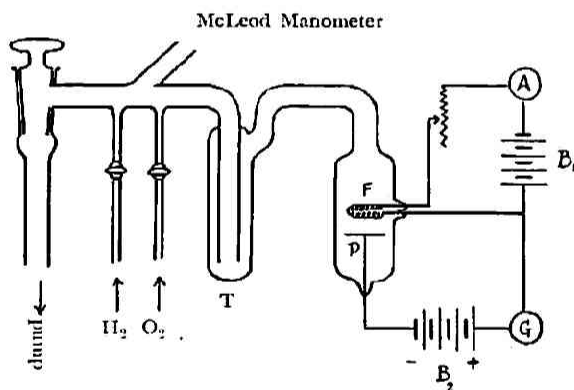


Fig. 1.

was kept between 750°–950°C. throughout the experiment, being measured by means of an optical pyrometer. Correction of the optical pyrometer reading of the filament was difficult to make, for the filament changed its emissivity as it was oxidized. Error for the temperature due to the neglect of the correction is expected to be approximately 80°C. at 950°C. for the reduced state of the filament. And this error should be smaller at lower temperatures or more oxidized state.

The filament was kept positive by the battery B_2 with respect to a nickel plate P which stood against F. In almost all the cases the potential was kept at such a relatively low voltage as 8 volt in order to avoid ionization in the gaseous phase. The distance between the electrodes P and F was varied from few millimeters to a few centimeters. The electric current between the electrodes was measured by means of the galvanometer G whose sensi-

vity was 6.3×10^{-10} Amp. As the lubricating grease for stop cocks Apiezon L was used and the trap T was cooled with liquid air or CO_2 mixture.

The pressure was measured with the McLeod manometer.

Experimental Procedure and Results.

1) Preliminary heat treatment of the filament.

No current was observed between F and P in vacuum till the filament was heated and made positive with respect to the plate. On heating the filament above 700°C , large deflexion of the galvanometer was observed and it faded away during heating and evacuating for long hours (from several hours to a few days).

2) Hydrogen treatment.

When no current was observed after the above mentioned treatment a small quantity of hydrogen (0.1 mm Hg) was introduced and then considerably large current was observed and it faded away in an hour. After repeating such a heat treatment in hydrogen, no current was observed either in vacuum or in hydrogen.

3) Momentary Oxygen Treatment.

After the above repeated hydrogen treatment and evacuation, oxygen was introduced (0.1 mm Hg) for a few seconds and at once evacuated. Then large current was observed in hydrogen as the case with (2) and it faded away in a few minutes. After the momentary oxygen treatment this effect was every time observed, as is seen in Table I. In this case, the galvanometer deflexion also diminished as the hydrogen treatment was repeated until no deflexion was observed on introducing hydrogen. On the momentary oxygen treatment the filament slightly changed its colour and on introducing hydrogen it soon regained its bright colour. The colour change shows that oxidation by oxygen and reduction by hydrogen occurred on the surface of the filament.

4) Continuous Oxygen Treatment.

In the momentary oxygen treatment scarcely any current was observed in oxygen, but on repeating the treatment there appeared measurable current which faded gradually and at the same time the pressure of oxygen was found to decrease. On supplying oxygen, the current

Table I

Treatment	Galva. Deflexion (mm)
Evacuation	0
H_2	0
Evac.	0
O_2	0
Evac.	0
O_2	0
Evac.	0
H_2	90
Evac.	0
H_2	88
Evac.	0
H_2	56
Evac.	0
H_2	0

increased again and this effect was always observed on repeating the experiments as shown in Fig. 2.

5) Rate of the Decrease in Current and Pressure.

The rate of the decreases in current and pressure of oxygen gradually

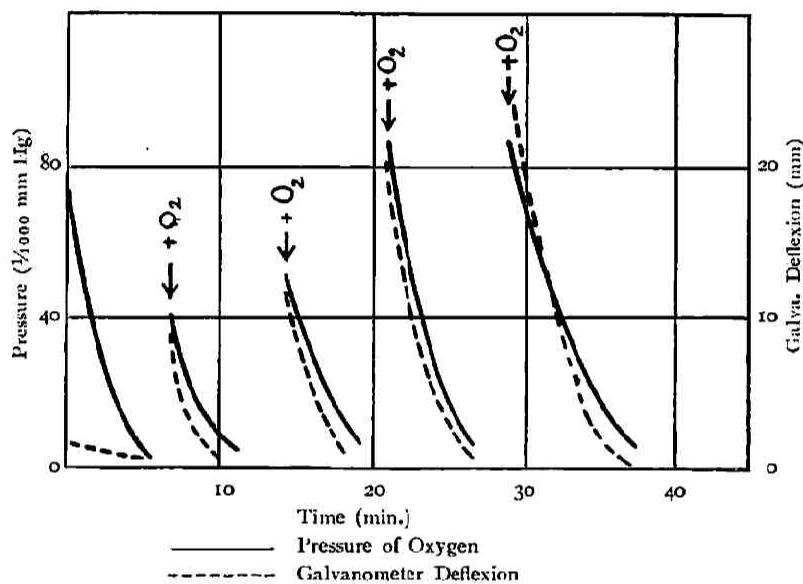


Fig. 2.

lowered as oxygen treatments were repeated, and after long heating in oxygen the rate became conspicuously slower as shown in Fig. 3. These tendencies shown in Figs. 2 and 3 suggest that absorption of oxygen or oxydation occurred on the surface of the filament and the observed current depended upon the

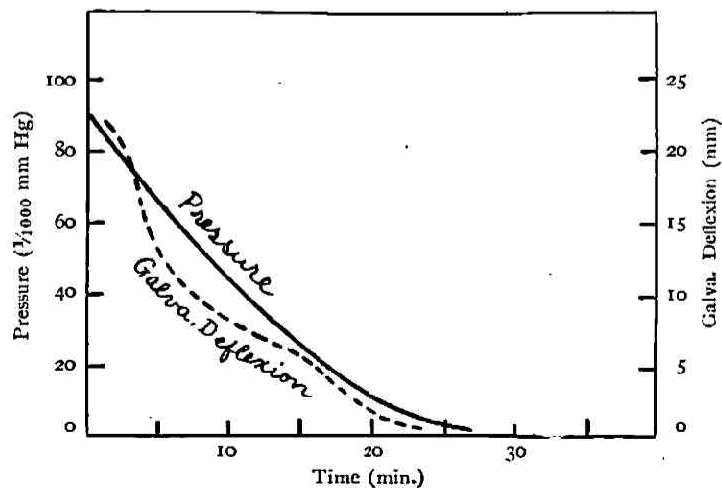


Fig. 3.

amount of oxygen in the gaseous phase.

After such a long exposure of the filament in oxygen, the filament was found to become grayish green. This shows that the filament was oxidised in oxygen and that the oxide contains nickelous oxide (NiO).

6) Current and Voltage.

In the course of the slow change shown in Fig. 3 the accelerating potential was changed variously during a few minutes and the relation between the potential and the current observed is shown approximately in Fig. 4. When the voltage between both electrodes was raised, the current continued to increase and it remained constant at higher voltages than 10 volts.

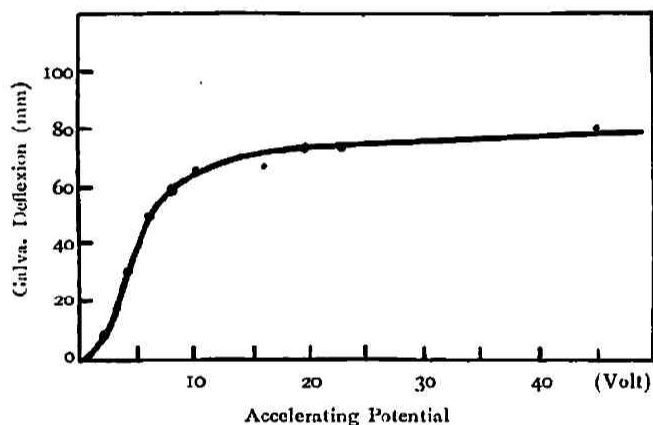


Fig. 4.

This suggests that the observed current is distinguished from the electron current which does not show such a saturation curve in relatively low vacuum as the case above mentioned. Besides, below 1000°C. scarcely any current was observed when the electrodes were interchanged.

Interpretation of the Experimental Results.

As the carrier of the electric current observed in the experiment, such particles as electron, negative gaseous ion, positive gaseous ion, metal ion evaporated and some impurities occluded in the metal or its surface are taken into consideration. But from the facts that no current was observed till the filament was heated and made positive with respect to the plate, the particles negatively charged may be neglected. Moreover, from Experiment (6) it is suggested that electron does not take part in the current.

It is reported by Smith¹¹⁾ that tungsten and molybdenum evaporate as positive ions at high temperatures. But such evaporation should be more remarkable in high vacuum than in the oxygen atmosphere unless the oxides of metals are volatile as in the case of tungsten. Though above 1000°C. the evaporation of nickel was observed, yet at lower temperatures noticeable deposit of the metal on the wall of the vessel was observed neither in vacuum nor in oxygen.

The effect of impurities in the gases or the metal cannot explain the result of the oxygen treatment (4), especially the small current at the first stage of Fig. 2.

From these considerations it is concluded that the current observed may be probably due to positive gaseous ions emitted from the surface of the filament. The procedure (5) suggests that the ions may come from the oxygen molecules which have stricken the surface of the filament and evaporated from it, for the ion current depends upon the total pressure of the oxygen as shown in Fig. 2. As to the current observed in hydrogen, the case is more complex than in oxygen, for the temperature of the filament greatly changes on account of rapid reduction.

When the mechanism of the ion emissions in both hydrogen and oxygen is considered, it should not be neglected that reduction or oxydation proceeds parallel with the ion emission.

Summary.

Positive ion emission from heated nickel wire in oxygen and hydrogen has been recognised in the temperature range between 750° and 950°C. and it has been found that the emission is enhanced by preliminary oxydation of the wire.

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11) P. Smith, *Phys. Rev.*, **35**, 381 (1930).