Probe Studies of Rarefied Flames

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We have investigated the changes in the probe current in relation to the location of the probe within a rarefied flame. An assumption is introduced pertaining to the mechanism of ionization in the reaction zone of a flame.

Physicists are interested in two phenomena taking place within flames--radiation and ionization. Spectrum investigations have given us means for studying a large number of molecules, atoms, and radicals present in flames, and also allowed us to gain an understanding of some elementary processes taking place in a flame. Ionization of flames is less thoroughly understood. For the investigation of this phenomenon we have employed the method devised and described by J. J. Thomson and G. P. Thomson[1], and by H. A. Wilson.[2] Andrew, Axford, and Sugden,[3] and later Shuler and Weber[4] have developed a new method based on the measurement of the damping of ultrashort radio waves passing through the flames. All the investigations of flame ionization have been carried out at atmospheric pressure. Only recently, Rossikhin, Protopopov, Martyniuk and Tsikora[5] investigated electrical conductivity of a non-stationary flame under the pressure of 200-400 mm Hg, while Jost and Wagner[6] have studied ionization of a cold flame under the pressure of 200-700 mm Hg.

In our present work we have investigated electrical properties of flames under pressures of 30-50 mm Hg by means of a probe similar to that used by Heumann[7] in his studies of flames burning under atmospheric pressure.

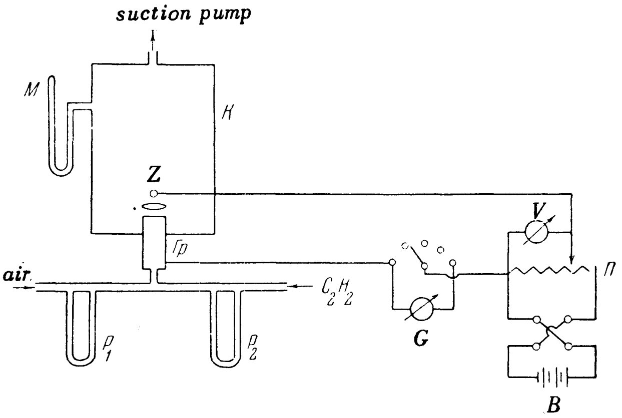

FIG. 1. Schematic drawing of the apparatus: *K*-camera of burning, *M*-manometer, P_1 P_2 -rheostats, *Z*-probe, *V*-voltmeter, *G*-galvanometer, *B*-batteries.

Figure 1 shows the schematic drawing of the apparatus; camera of combustion is cylindrical in shape and is made of 3 mm thick iron. Its diameter is 30 cm, and its height 40 cm. The metallic hearth is covered by a removable copper lid coated with nickel. The lid contains several openings of

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[1] J. J. Thomson and G. P. Thomson, *Conduction of Electricity through Gases*. 3rd ed., Cambridge, 1928.

[2] H. A. Wilson, Revs. Mod. Phys. 3, 156 (1931); *Modern Physics*, Blackie, 1944.

[3] E. R. Andrew, D. W. E. Axford, And T. M. Sugden, Trans. Farad. Soc., 44, 427 (1948).

[4] K. E. Shuler and J.Weber, J. Chem. Phys., 22, 491 (1954).

[5] S. Rossikhin, A. K. Protopopov, L. A. Martyniuk and I. L. Tsikora, Nauchn. Zap. Dnepropetrovsk Mining Institute, 41, 9 (1953).

[6] W. Jost and H. G. Wagner, Naturwiss 40, 435(1953).

[7] T. Heumann, Spectrochimica Acta. 1, 293 (1940).

2 mm diameter. The inflammable mixture is ignited by means of an induction coil. We have investigated the inflammable mixture of C_2H_2 and air, with the volumetric concentration of the former, $c = 7$ per cent. The rarefied flame may be divided into three parts: the bright-green part in the shape of a disc with a diameter of 40 mm and thickness of 5-7 mm (this part is known as the zone of reaction); the part between the zone of reaction and the surface of the hearth; and the region above the zone of reaction. The last has a barely visible violet tinge.

The probe, which was in the form of a platinum sphere of 0.95 mm diameter, was moved along the height of the flame, and its location was fixed by means of a viewing tube. The system of the probe and the hearth was subjected to a current of known intensity.

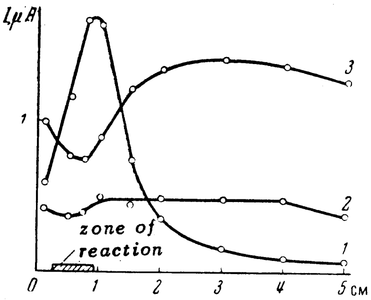

FIG. 2. Dependence of the probe current on the position of the probe in the C_2H_2-air flame burning at a pressure of 30mm Hg

Figure 2 shows the curves which depict the relationship of the current to the location of the probe.* Curve 1 was produced at the probe potential $V_1 = -5V$, curve 2 at the potential $V_2 = 0$, curve 3 at the potential $V_3 = +5$ V. The flame was burning under the pressure of 30 mm Hg. Investigation of the curves indicates that the maximum current in case of a negative probe occurs at the zone of reaction, and that it does not coincide with the maxima of the positive and the zero probe; for the latter two the maxima lie above the zone of reaction. Diffusional flow of electrons and negative ions onto the zero probe invariably produces a stream of positive ions.

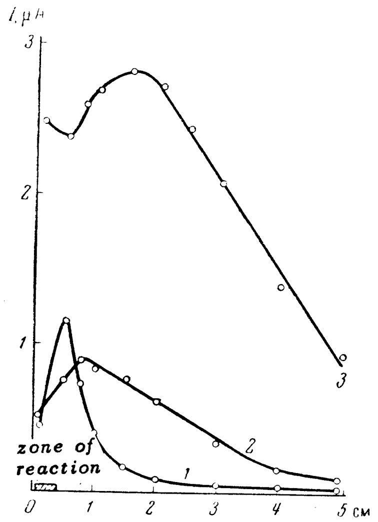

FIG. 3. Dependence of the probe current on the position of the probe in the C_2H_2-air flame burning at a pressure of 50mm Hg

Figure 3 shows curves which depict the relationship of the current to the location of the probe under the pressure of $p = 50$ mm Hg, with all other conditions remaining unaltered. Comparison of Figs. 2 and 3 shows that: 1) with the increase of pressure the current on the negative probe diminishes; 2) as the pressure mounts higher the current on the positive probe increases pronouncedly while the current on the zero probe increases less markedly; 3) the distance between the maxima of currents on the negative, the positive, and the zero probes diminishes with the increase of pressure.

This experimental material can be explained if we accept the assumptions listed below.

1. Formation of the positive and the negative electrons takes place in the zone of reaction. The most plausible reaction leading to the formation of the positive and the negative ions appears to be

$$M + OH' \rightarrow M^{+} + OH^{-}, \qquad (1)$$

where M represents carbohydrogen molecules or radicals of the type C_nH_m and C_n, with a considerable store of inner energy; OH' represents excited hydroxyl. Potential of excitation of the band $OH\lambda = 3064$ is equal to 4 ev; for the other bands of OH, potentials of excitation were quite high. According to the data obtained by Smith and Sugden,[8] electronic affinity of OH is equal to 3 ev. Carbohydrogen molecules and radicals present in the zone of reaction are known to have ionization po-

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*Current of curve 1 is opposite in direction to the currents of cuves 2 and 3.

[8] H. Smith and T. M. Sugden, Proc. Roy. Soc. A211, 31 (1952).

tentials of 8 to 12 ev. It should be noted that, according to the rule, radicals have ionization potentials smaller than the ionization potentials of the corresponding molecules. For this reason the energy reaction (1) becomes acceptable.

2. Ion-radical OH enters the reaction fairly rapidly, and produces a more complex molecule containing an extra electron,

$$M_1 + OH^- \rightarrow M_1OH^- \qquad (2)$$

or else produces free electrons

$$M_1 + OH^- \rightarrow M_1OH + e. \qquad (3)$$

3. Positive ions are formed in response to the process of polymerization, as a result of which particles with diameters of the order of 100-500 Å can be produced. Figures 2 and 3 show that the stream of positive ions flowing onto the probe diminishes sharply after the departure from the zone of reaction. This is caused by the diminution of mobility of the positive ions.

This analysis of the experimental data can be countered by the following possible processes: 1) thermoelectronic emission from the probe, 2) thermoeffect produced in the electric circuit, 3) photoeffect, 4) exothermal reactions originating on the surface of the probe, 5) removal of the conduction electrons from the surface of the probe by the excited particles.

A thermocouple introduced into the rarefied flame gives a temperature reading of ~ 1000° K. The probe placed in this flame assumes the same temperature. Under this condition the current of thermoelectronic emission off the probe is smaller by several orders than the current observed.

Thermoeffect on the electric circuit has also no conspicuous influence on the probe current; this has been proven by the work of Heumann[7] who has studied various interferences in detail.

The probes were made of material in which work of emission is high and which is consequently characterized by a short limiting wavelength of the photoeffect. For example, the limiting wavelength for platinum is $\lambda_0 = 1900$ Å, and for nickel $\lambda_0 = 2490$ Å. The reducing part of the flame's rays falls within the visible region and is near the ultraviolet; for this reason the photoeffect plays no great part in our work.

Any important influence exercised by the exothermal reactions on the probe current is eliminated by the fact that with the increase of pressure, the current on the negative probe diminishes.

The most conspicuous influence can be produced by the excited radicals, atoms and molecules. In the first place such an influence could be exercised by the excited hydroxyl. When the molecules or atoms of a negatively charged gas collide with a metallic surface, the removal of an electron and formation of a negative ion is quite possible. To have this process accomplished it is necessary to satisfy the condition

$$E_c + E_B \geqslant \varphi, \qquad (4)$$

where E_c is the affinity of the particle for an electron, E_B is the energy of excitation, φ is the work function for the metallic surface. For most metals the latter is of the order of 4--5 ev. For this reason condition (4) for the excited hydroxyl is fulfilled. While dealing with experimental data we should take into consideration the possibility of the process of removing the electrons from the probe by the excited hydroxyl.

A layer of gas forms around a probe placed in the flames. Excited particles are not produced in this layer. If the thickness, l, of this layer satisfies the condition $l > r\lambda$, the removal of the electrons from the probe by the excited particles does not take place (λ represents the mean free path of the gas molecules, r the number of collisions necessary for the deactivation of an excited particle). According to the data of Gaydon and Wolfhard,[9] $r = 40$--100 for the excited hydroxyl.

On the bases of these deductions the current on the negative probe should diminish with the diminution of pressure, which fact was indeed observed in our experiment. However, the inspection of curves on Figs. 2 and 3 shows that the process of removal of the electrons is not of paramount importance. If this process were of stronger influence than the others, then the current on the zero probe would have the direction opposite to that observed in the experiment.

In conclusion we would like to express our deep gratitude to V. S. Rossikhin for his valuable help in this work.

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[9] A. G. Gaydon and H. G. Wolfhard, Proc. Roy. Soc. (London) A194, 169 (1948); A208, 63 (1951).

Translated by R. G. Huzarski
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