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Fig. 1. Schematic of the apparatus

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Abstract

Full Text

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NORMAL FLAME VELOCITY OF THE DECOMPOSITION OF PURE ACETYLENE

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The normal velocity is the principal physicochemical constant characterizing the process of flame propagation in a given combustible mixture. From the magnitude of the normal velocity one can obtain definite ideas about the rate of the chemical reaction in the flame, i.e., about the rate of heat release. From the dependence of the normal velocity on the initial pressure, temperature, and concentration, one can judge the effective order of the reaction, the activation energy, the width of the chemical-reaction zone, and the limiting diameters of flame propagation.

Fig. 1. Schematic of the apparatus: 1 –receiver, 2 –ignition electrodes, 3 –experimental vessel, 4 –separating membrane, 5 –differential manometer, 6 –manometer, 7 –vacuum gauge, 8 –photorecorder, 9 –ionization sensors

Some estimates of the normal flame velocity of the decomposition of pure acetylene were made in works (^{1}, ^{2}). However, the method for measuring the normal velocity used by those authors does not make it possible to obtain reliable values of the normal velocity. Thus, in work (^{1}), during flame propagation the pressure increased, and the flame shape was determined from instantaneous photographs, with the area of the flame surface being equated to the surface of part of an ellipsoid. This method of determining the flame-surface area, as has already been noted repeatedly in the literature, is insufficiently accurate.

In work (^{2}) the normal velocity was determined in vertical tubes of small diameter (from 3 to 20 mm) at initial pressures of 2–10 atm. It is known that the critical diameters of flame propagation in pure acetylene at pressures, for example, of 2 and 4 atm are 30 and 10 mm, respectively (the values refer to horizontal tubes). Therefore, owing to the use in the experiments of work (^{2}) of tube diameters close to and smaller than the critical ones, strong underburning of acetylene was observed, especially at pressures of 2–4 atm, which led to underestimated values of the normal velocity. In addition, determining the flame surface from a direct photograph in such narrow tubes also introduced serious errors.

In the present work, the dependence of the normal flame velocity of pure acetylene on the initial pressure at constant temperature (18-20°) was investigated in the pressure interval 2.5-5.0 atm. The experiments were carried out in an apparatus whose schematic diagram is shown in Fig. 1. The experimental vessel (3) (a steel tube with an internal diameter of 50 mm and a length of 750 mm) and the nitrogen receiver (1) ($V = 120$ l) are separated by a thin polymer film (4), which makes it possible to evacuate and fill

the experimental vessel with acetylene and the receiver with nitrogen. Before ignition, which was carried out by a heated nichrome coil at the end of the tube at a distance of 50 mm from the end face, the film was melted by heating a nichrome wire bent into a ring and glued to the film on the receiver side. In this way an open end of the tube was created for the free outflow of combustion products into the receiver. In view of the large difference between the volumes of the experimental vessel (0.8 liter) and of the receiver with nitrogen (120 liters), the measured increase in pressure during flame propagation along the tube did not exceed 0.05 ata. The initial pressure of acetylene and nitrogen required in the experiment was set by the manometer (6) and equalized according to the reading of the differential manometer (5).

For calculating the value of the normal velocity from the formula

$$U_\mathrm{n} = U_\mathrm{v} \frac{S_\mathrm{t}}{S_\mathrm{p}}$$

(where U_n is the normal velocity, U_v is the visible flame velocity, S_t is the cross-sectional area of the tube, S_p is the flame-surface area) it is necessary to know both the visible velocity of flame propagation and the magnitude of the flame surface. To record the flame on photographic film at the final section of the tube, the intrinsic luminosity of the acetylene-decomposition flame was used. Flame propagation was photographed through a narrow slit (2×250) by an FR-11 photorecorder with continuous time sweep. To determine the flame shape, ionization probes were used. The probes were as follows. Thin (ϕ1 mm) metal rods, tapered at the end to a cone, 100 mm long, were extended from the flange side toward the direction of flame propagation. The distance between probes was 10 mm. The ground electrode passed perpendicular to the probes, leaving a gap between the end of the probe and it of 0.5-1 mm. A constant voltage of 160 V was applied to each probe. At the moment when the flame passed through the ionization gap, the resistance in the latter changed, and this was recorded on an N-102 loop oscillograph in the form of a deflection of the light beam. From the relative positions in time of the beam deflections on the film, curves were constructed for sections of the flame surface by vertical and horizontal planes in which the probes were located. From such sections, full-scale models of the flame shape were made, from which the flame-surface area was determined.

Fig. 3. Dependence of the visible velocity of flame propagation on pressure

Figure 2: Fig. 3. Dependence of the visible velocity of flame propagation on pressure

Fig. 4. Dependence of the normal flame velocity of acetylene on pressure

Figure 3: Fig. 4. Dependence of the normal flame velocity of acetylene on pressure

Fig. 3. Dependence of the visible velocity of flame propagation on pressure

The determination of the visible flame velocity was carried out at initial pressures of 2.5–5.0 ata with an interval of 0.5 ata. In Fig. 2,A, as an illustration, a photorecording of the process of propagation of a decomposition flame in acetylene at a pressure of 3.5 ata is shown. As is seen from the photograph presented, the flame velocity over the section where the photographing was carried out (250 mm) practically does not change (see insert, p. 1282).

From the fact that the visible velocity is constant one may conclude that the flame surface also does not change. Experiments in which the ionization probes were moved forward by the length of the slit did indeed show that the flame shape in the photographed section of flame propagation, for the given pressure, does not change. Photorecordings analogous to that shown in Fig. 2,A were also obtained for all other pressures. Fig. 3 shows the dependence of the visible velocity of flame propagation on pressure.

To determine the flame-front surface for each initial

oscillograms of the ionization current from seven sensors located in horizontal or vertical cross sections were recorded. In all, for each initial pressure, oscillograms were obtained from sensors located in five horizontal and one or two vertical cross sections. In the experiments it was observed that, regardless of the sensitivity of the sweep, a sharp deflection of the beam, i.e., a rapid drop in the resistance of the spark gap, occurs at some single place in the flame. In other words, when a low-sensitivity sweep is replaced by a high-sensitivity one, the position in time of the onset of the sharp beam deflection does not change. Only the character of the deflection changes: it becomes sharper, and sometimes, before the sharp deflection, a certain rise in the ionization current is observed. Thus, it could be assumed that all sensors record the moment at which some single surface passes through them, i.e., the shape of the flame. Processing of the ionization-current oscillograms obtained in the experiments by the method described above showed that the magnitude of the flame surface depends on the initial pressure, decreasing as the latter increases. The magnitude of the flame surface at a pressure of 2.5 ata is 3.8 times greater than the cross-sectional area of the tube, and at 5.0 ata it is 2.5 times greater.

Fig. 4. Dependence of the normal flame velocity of acetylene on

pressure

The results of calculating the normal flame velocity in pure acetylene from the experimentally measured visible velocity and the experimentally determined magnitude of the flame-front surface for various pressures are presented on a logarithmic scale in Fig. 4. It follows from the graph that the normal velocity changes with pressure according to a linear law, the angle of inclination of the straight line being close to 45°, i.e., $U_n \sim P^n$, where $n = 1$.

From the thermal theory of flame propagation it is known that, for gas mixtures, the dependence of the normal velocity on pressure is limited by exponents n ranging from $+0.5$ to -0.5. Experimentally determined exponents always fall within this interval. The dependence obtained in the present work of the normal-velocity magnitude on pressure, with an exponent equal to 1, has not been observed before. Application of the thermal theory to the decomposition flame of pure acetylene leads to the conclusion that the pressure dependence of the normal velocity obtained in the present experiments should correspond to a fourth-order reaction, which is absolutely unrealistic for a reaction proceeding in a homogeneous gas phase. It is evident that an explanation of the experimentally obtained result should be sought in the specific features of the acetylene-decomposition flame, i.e., in the formation, among the decomposition products, of a solid phase—carbon—alongside hydrogen.

As was already indicated above, when high-sensitivity sweeps were used and the pressure was increased, it was found that before the sharp beam deflection there exists a certain increase in the ionization current. From such records and from photographic registrations of the flame it was possible to determine which place in the flame corresponds to the first increase and to the sharp rise of the ionization current. In photographs of the flame (see, for example, Fig. 2A) it is seen that the zone of the chemical reaction in acetylene has a considerable extent and different brightnesses of luminescence across the width of the zone. Against the background of the exposure, the beginning of the zone is clearly visible—the first bright band, which is followed by a broad region of weaker luminescence, also ending in a rather bright boundary (the end of the zone). In view of the slight difference in the brightnesses of luminescence of all three sections, only two of the three boundaries can be obtained sharply at the same time in the photograph. Therefore, in the photograph presented, the luminescence of the end of the zone is only slightly distinguishable from the middle, darker part of the zone.

As shown by experiments in which the recording of the ionization current and the propagation of the flame were synchronized in time, the first band corresponds to the first increase, and the last to the sharp rise of the ionization current. When the ionization current was recorded on a cathode-ray oscillograph, traces were obtained that are shown in Fig. 2b. As can be seen from the oscillogram, the reaction zone in fact has both two maxima and a decline in the magnitude of the ionization current. Similar records are also obtained when a single-probe ionization sensor is used. Estimates of the width of the zone, both from photographs of the flame and from records of the ionization current, give similar values. Approximate estimates of this quantity for pressures of 5.0 and 2.5 atm are 4–5 and 7–10 mm, respectively.

It seems to us that such a two-stage character of the acetylene flame is associated with the presence in the reaction products of both a solid phase and a gaseous phase; i.e., the last stage is associated with a powerful reaction of carbon condensation, while the first is associated with a gas-phase reaction that gives condensation centers and some intermediate product that is absent from the reaction products (for example, acetylene polymers).

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Note: Figure translations are in progress. See original paper for figures.