REPORT No. 532

THE SOAP-BUBBLE METHOD OF STUDYING THE COMBUSTION OF MIXTURES OF CO AND O_2

By Ernest F. Fiock and Carl H. Roeder

SUMMARY

This investigation, carried out at the National Bureau of Standards at the request and with the financial assistance of the National Advisory Committee for Aeronautics, is a detailed description of the soap-bubble, or constant-pressure, method as applied to the explosive oxidation of CO.

A series of values of the speed of flame in space in various mixtures of CO *and* O_2 *containing a constant percentage of water vapor was obtained by the constant-volume method. These results served as a guide in the perfection of the soap-bubble method.*

The latter has been refined to a degree which makes possible precise determinations of the speeds of flame in space and relative to the active gases, of expansion ratio, and of temperatures attained in mixtures of CO, O_2, *and* H_2O. *Results for this system of gases are reported over a wide range of mixture ratios, and a comparison with previous results by the same method is included.*

THE SOAP-BUBBLE, OR CONSTANT PRESSURE METHOD

INTRODUCTION

A method of investigating gaseous explosive reactions at constant pressure by photographing the travel of the flame when mixtures in soap-film containers are ignited was developed and extensively used at the National Bureau of Standards by the late F. W. Stevens. In numerous published reports (reference 1) he has given the theory of the method and the results that he obtained by its use. The importance of the conclusions that he drew makes further experimental verification desirable. With this purpose in view, a detailed study of the means for increasing the precision of results that can be obtained by the bubble method was undertaken.

THE METHOD

Discussion.—A photograph of the type given in figure 1, showing the travel of flame in an explosive mixture originally contained in a soap film, may be used in the calculation of the speed of flame in the mixture. Since the soap film offers very little resistance to the expansion of the gases, an explosion in such a container takes place essentially at constant pressure. In such explosions the speed of flame in space is constant throughout the entire reaction time. The photographic record also gives a measure of the final volume of the sphere of hot gases at the time the flame has completed its travel. The bubble method therefore yields not only the speed of flame in space but also the

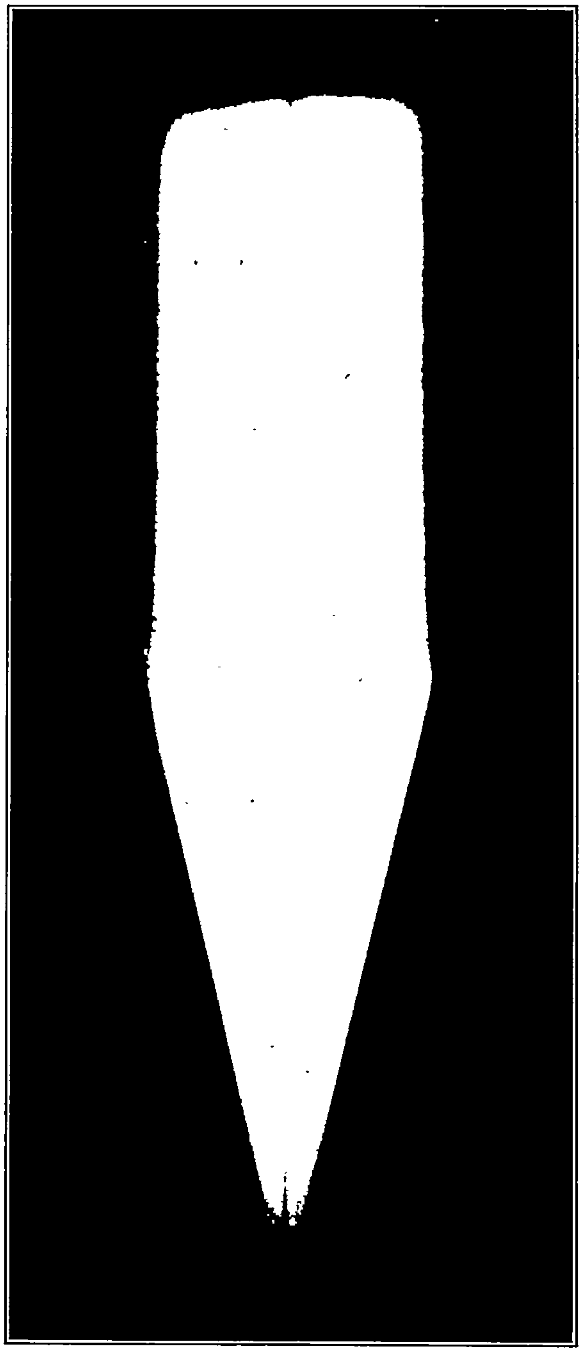

FIGURE 1.—A typical record of a bubble explosion.

expansion ratio. From these data the speed with which the flame moves relative to the unburned gases is readily calculable. In addition, the expansion ratio may be used to calculate either specific heats or equilibrium data if one of the latter is previously known.

In addition to the photographic record of the explosion, a complete bubble experiment requires a knowledge of the initial pressure, temperature, composition of the gas mixture within the bubble at the time of firing, and the horizontal dimension of the bubble at the spark gap. The actual volume of the bubble and its variation in shape from a true sphere are not important, since observation is purposely limited to that part of the flame which travels along a narrow horizontal path centrally embracing the spark gap.

If the speed of flame in space is represented by S', the speed relative to the active gases by S, the initial horizontal dimension of the bubble by R_1, and the corresponding horizontal dimension of the hot products of the reaction at the time combustion is complete by R_2, then the equation

$$\frac{S}{S'}=\frac{R_1^3}{R_2^3}$$

expresses the relation that exists among these quantities (reference 1).

Stevens seems to have considered the speed of flame in space (S') of little importance except as in intermediate in the determination of speed relative to the active gases (S). Values of S, however, he apparently regarded as fundamental properties of the unburned mixtures. In none of his published work did he use his experimental values of R_2 except as intermediates in deriving values of S. His calculations of final temperatures from his observed values of R_2 were left incomplete at his death.

Practically, the bubble method has an obvious advantage over the bomb, or constant-volume, method in that it yields equivalent results without the use of an intricate indicator of pressure. The temperature of the unburned charge remains constant since the adiabatic compression ahead of the reaction zone is constant in amount and negligibly small. The constant-volume method has, however, been used quite successfully without a pressure indicator for the measurement of S' alone.

The most serious disadvantage of the soap-film method lies in the fact that, no matter how carefully the composition of the explosive mixture is controlled before the bubbles are blown, this composition does not necessarily remain unaltered within the film. There may occur either an increase or a decrease in the amount of water in the gas mixture due to evaporation or condensation at the soap film or, if the solution contains besides water some other volatile material (such as glycerin), there will be evaporation of this material into the mixture. Knowledge of the initial composition of the explosive mixture within the bubble becomes therefore somewhat difficult to obtain.

The first part of this report is principally an account showing how initial composition within a bubble may so be controlled that the method will yield more reliable results.

Obviously the method can be used in its present form to study only those explosive combinations which emit sufficient actinic light to form the photographic images. Regardless of the amount of light emitted, the method is not considered adequate for the study of mixtures in which the flame travels in space with a velocity less than about 150 cm per second, because in such cases the hot gases are allowed sufficient time to rise by convection, and interpretation of the photographs is made impossible. There is also an upper limit to the values of flame speed that can be measured with the present equipment, because the camera drum is small (10 cm diameter) and because it is not designed mechanically for extremely high rotational speeds. In the results obtained with CO, the maximum spatial speed observed was approximately 1,000 cm per second. The equipment functions very satisfactorily at this speed and could doubtless be successfully used for speeds up to at least 1,500 cm per second. The present apparatus is not adapted to the measurement of flame velocities attained in detonations.

The bubble method is obviously unsuited to the use of any active gas which dissolves rapidly in the soap solution. The rate of solution of CO, the only gas studied thus far, is quite slow.

For very rich mixtures, bubbles blown in air cannot be used to determine expansion ratios because of the effect of the oxygen of the surrounding air. Such an effect is clearly evident in the photographs, since an increase in the speed of the flame takes place when the reaction nears completion. The final diameter of the sphere of hot gases is obviously meaningless in such cases. The determination of the speed of flame in space in such mixtures is, however, rendered none the less satisfactory by this end effect.

In order to establish the reliability of the soap-bubble method, it was necessary to demonstrate that certain of its characteristics were correctly postulated in the theory. To this end, the behavior of the soap film during an explosion was of interest. If a light source of proper intensity be placed behind the bubble, the trace of its wall can be recorded on the film of the drum camera simultaneously with the explosion itself. Figure 2 is a reproduction of a record of this type. External illumination of the central portion of the bubble was excluded by an opaque disk. In this figure it is shown that there is no measurable change in the diameter of the soap film for a considerable time after ignition. The bubble then expands slowly and bursts when the sphere of hot gases attains a diameter approximately equal to the initial diameter of the bubble. After the bubble bursts the record shows, as faint traces, the boundaries between the hot and cold gases. These traces may be ascribed to refraction or diffraction of the external light in the region of high temperature gradient.

Further detailed information as to the mechanics of bubble explosions has been obtained by photographing such explosions with a high-speed motion-picture camera. Figure 3 is a reproduction of a section of such a motion-picture film. In this case the bubble, before firing, contained an equivalent mixture of CO and O_2 with 2.7 mole percent of H_2O. A source of light of proper intensity was placed behind the bubble so that the image of the soap film could be recorded without obscuring the image of the flame. In frame 1 the bubble, before firing, is shown suspended on the wire ring, with the glass inlet tube at the top and the electrode at the bottom. Frame 2 shows in addition a tiny spot of light at the center, which is probably the image of the igniting spark. Successive frames show the growth of the sphere of flame at a uniform rate (i. e., the diameter increases linearly with time). In frame 7 an increase in the diameter of the bubble, owing to the expansion of the burned gases, can be detected, although this fact may not be evident in the small-scale reproduction. The bubble seems to be intact in frame 14, but in frame 15 the flame has reached the wire suspension ring and the soap film has failed there. Successive frames show the gradual disappearance of the remainder of the film, without any apparent distortion of the sphere of flame.

There is evidence of the existence of the last remnant of the soap film around the electrode in frame 23, but in 24 it has disappeared entirely. The combustion was probably completed at about the time frame 28 was taken and the cooling of the hot gases by the surrounding air is clearly shown in frames 29 and 30.

The remainder of the record, not shown in the figure, shows the hot gases rising out of the range of the camera. Numerous small bodies of greater light intensity than the hot gases can be seen rising with the gases. These are probably droplets of soap solution, the glycerin of which is ignited by the hot gases.

Time is also recorded by the camera, simultaneously with the travel of the flame. The images of the clock dials, which can be seen in the figure, were used to compute the speed of this record as being approximately 1,610 frames per second.

Detailed examination of the high-speed records led to the following conclusions, most of which are evident from the accompanying record of the explosion of a wet, equivalent mixture.

1. The flame front advances in spherical form.
2. There is no measurable rise of the burned gases until after the flame was completed its travel.
3. The distorting effects of the solid materials within and near the bubble are so slight that they have no influence at the horizontal midsection.
4. The flame traverses approximately one-half of the initial diameter of the bubble before expansion of the bubble wall becomes measurable.
5. The soap film first fails when the flame reaches the ring of gold wire from which the bubble is suspended, and persists much longer at the bottom of the bubble.
6. No measurable distortion of the flame front is produced by the bursting of the soap film.
7. Expansion ceases with the passing of the flame front.

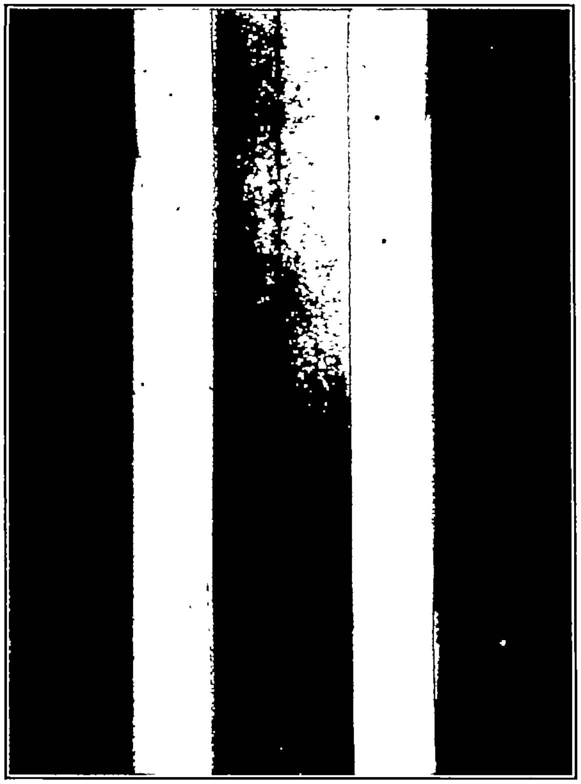

FIGURE 2.—Record of a bubble explosion, showing the expansion of the bubble wall.

The foregoing characteristics were reproduced with remarkable fidelity in all the high-speed records taken. These facts all lead to the conclusion that the mechanics of an explosion in a soap film and the method of interpreting the results therefrom were correctly postulated by Stevens.

Use.—The soap-film container method was used by Stevens in the following manner. The combustible gas (for example, CO) and the O_2 were separately bubbled through bead towers containing H_2O at the temperature of the room. The gases thus humidified were mixed in the desired proportions by volume in a glass cylinder, whence they could be displaced by mercury. From such mixtures bubbles were blown at the center of a hollow cast-iron sphere, 3 feet in diameter. One or both of the diametrically opposite openings, having an area of about 40 square inches each, were left open during the work at atmospheric pressure. The mixtures within the bubbles were ignited at their centers and the travel of each flame front was recorded on a moving film. The initial

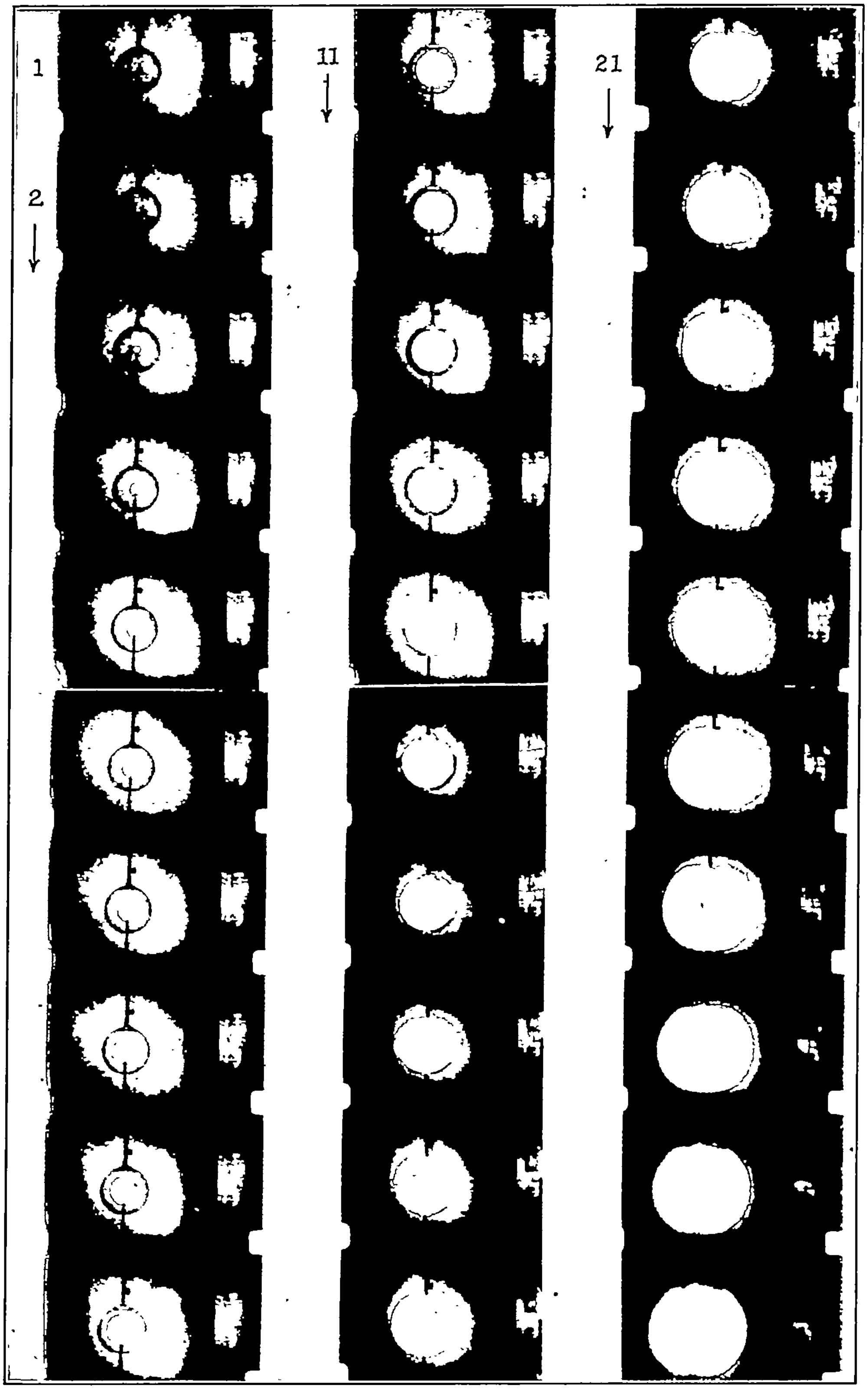

FIGURE 3.—High-speed motion-picture record of a bubble explosion (1,610 frames per second).

temperature and pressure were those of the air within the cast-iron sphere.

The method of saturating the gases with H_2O vapor is open to question, loss of water by condensation when the gases were displaced from the mixing vessel was probable, and the temperature and humidity of the air in which the bubbles were blown were not adequately controlled. Each and all of these factors doubtless contributed at one time or another to produce uncertainties in the amount of water vapor present in the bubbles at the time of firing. It is probable that Stevens underestimated the magnitude of the errors in flame speed that arise from this source and that a considerable portion of the spread of his results may be assigned to this cause.

It should be emphasized that neither the initial diameter of the bubbles nor the final size of the sphere of hot gases need be known for the determination of S' and that as far as the study of the method is concerned, it is probable that measurements of S' are sufficient. At any rate, it is certain that the method cannot be considered successful for any purpose unless satisfactory values of S' can be obtained by its use.

After the completion of the constant-volume series of experiments at pressures below atmospheric, which were described in a previous report (reference 2), an attempt was made to use the bubble method. It was realized that small changes in the concentration of water vapor would produce large changes in the observed values of S'. In the attempt to keep the water-vapor concentration constant in all the bubbles, the following precautions were taken. Since the bubbles were blown in the free air of the laboratory, the temperature of the room was thermostatically controlled to $25 \pm 0.3°$ C., as indicated by a mercury thermometer near the bubble suspension, in order to keep the vapor pressure of the soap solution constant. The gas mixtures were humidified with distilled water to a partial pressure equal to the total pressure of the soap solution at 25° C. Although it was expected that values of S' could be measured to better than ± 10 cm per second, the observed variations were much larger than this.

A detailed study of the purity of the gases, the method of making the mixtures, and of the mechanical details of the recording apparatus indicated that none of these could have been responsible for the observed discrepancies. It was also found that the same values of S' were obtained when the bubbles were blown down over the spark gap (thus leaving it wet) as when the electrode was kept dry by lowering it into the bubble through the gas inlet tube.

Two possibilities remained as to the cause of the observed variations, namely, that the amount of water vapor actually present in the mixtures at the time of firing was not yet adequately controlled, or that some volatile material other than water was entering the mixtures from the soap films and influencing the flame speed. The latter was ruled out experimentally by measuring S' in the glass cylinder, described in reference 2, using first water and then the soap solution itself for humidifying the mixtures. In each pair of several such determinations the observed values of S' differed by less than 10 cm per second, the speed being slightly higher in some cases when water was used and lower in others.

A survey of all the data obtained by the bubble method revealed the following facts concerning the observed values of S': (1) In most cases all comparable experiments made on a single day were in fair agreement. (2) The day-to-day variation was much larger, and showed no uniform trend. (3) Over a period embracing late summer and early winter there appeared a marked general trend toward lower values of S'.

The latter of these facts, in particular, suggested that the humidity of the laboratory air might be exerting an influence upon the amount of water vapor initially present in the bubbles. If such an explanation were the true one, it would be compatible as well with above-mentioned points 1 and 2 because the humidity in the laboratory would not be likely to change greatly in any single day nor to show a regular trend from day to day over a short time interval.

In order to examine experimentally the effect of the humidity of the air outside the bubble upon the water-vapor content of the mixture inside, two measurements of S' in equivalent mixtures of CO and O_2 were made. The first of these, made when the air in the room had a temperature of 25° C. and a relative humidity of 0.4, gave $S'=660$ cm per second. Before the second measurement was made, steam was liberated in the room until it began to condense in the cooler places. The relative humidity was increased to over 0.9 and the temperature had increased to 31° C. A determination under these circumstances gave $S'=940$ cm per second, an increase of over 40 percent. From the known vapor pressure of the soap solution and the effect of water vapor on S' in equivalent mixtures at atmospheric pressure (see reference 2), it was calculated that the change in temperature alone could not account for more than one-fourth of the observed change in S'. The remainder, 210 cm per second, must be due solely to the effect of the humidity of the air surrounding the bubbles.

This effect of humidity has since been repeatedly observed at constant temperature. Earlier experiments upon the effect of allowing the bubbles to stand at full size for different time intervals showed very little change in S'. These tests, however, happened to be made in midsummer when the natural humidity and the observed values of S' were high. Similar experiments later, in an atmosphere of controlled low humidity, showed that the observed value of S' decreases as the time of life of the bubbles is increased.

The probable mechanism by which the external humidity influences the amount of water vapor within the bubbles may be briefly stated as follows: For all cases in which the partial pressure of water in the outside air is less than the partial pressure of water from the soap solution, water evaporates from the soap film during the formation and life of the bubbles. This evaporation produces a cooling of the film and consequently a partial condensation of the water within the bubble. Obviously such a mechanism requires time and the amount of water removed will be a function of the life of the bubbles.

The cause of the discrepancies in the earlier experimental values of S' has since been removed by building a thermostatically controlled box around the bubble suspension. The partial pressure of water within this box is kept at a value equal to the vapor pressure of the soap solution at the temperature of the box, so that there can be no continued evaporation from the soap films that form the bubbles. This further refinement in the control of the initial composition of the explosive mixtures has made it possible to reproduce the observed values of flame speed (S') to within ±5 cm per second in practically all of the records taken since its adoption.

As previously stated, Stevens formed the bubbles that he photographed within a large cast-iron sphere. Inside this sphere was an open cup containing soap solution, and drops of the solution doubtless were thrown onto the walls with each explosion. Therefore the humidity of the air in which his bubbles were blown was probably subject to much less variation than that of the free air in the room. Considerable error in his values of flame speed must have arisen because the temperature of the sphere was not controlled and because one or both of its windows were left open during his work at atmospheric pressure. A search of his records has failed to reveal his opinion as to the effect of the humidity of the surrounding air.

PRESENT APPARATUS AND PROCEDURE

Apparatus.—The apparatus in the form in which it is now being used will be described without reference to the intermediate stages through which it has been developed.

The photographic recording system was used without modification of its form as described in reference 2. The CO was prepared and purified as there described, and stored in three glass flasks of 19 liters total capacity. The oxygen was prepared by electrolysis of a KOH solution in a small generator built so that air could not come in contact with the electrolyte. Oxygen from the generator was passed over anhydrous magnesium perchlorate to remove most of the water, then through a furnace, the central tube of which was filled for a length of 15 cm with copper-oxide wire at a temperature of over 500° C. The gases emerging from the furnace were condensed in a liquid-air trap, from which the oxygen was evaporated into an appropriate storage tank. From this tank, the O_2 passed through a P_2O_5 tube on its way to the mixing chamber.

The gases were mixed in a 2-liter glass flask, well lagged, and having the bulb of a "calorimetric standard" mercury thermometer at its center. Mercury was used to displace the gases from this flask in such a way that the pressure of the gases exceeded that of the atmosphere by only the small increment necessary slowly to expand the soap-film containers. Since the gas mixtures were never saturated with water vapor, the danger of condensing liquid in the mixing vessel was avoided.

Connections were provided from the mixing chamber through stopcocks, to the storage tanks for CO and O_2, to a small reservoir of distilled water, to the closed-end mercury manometer described in reference 2, to a similar 2-liter flask filled with mercury for displacement of the final mixture, to the tube through which the bubbles were blown, and to the vacuum pump.

The bubbles were blown at the center of a cubical chamber 30 inches on a side. This chamber was a double-walled wooden box provided with a heater, a thermoregulator, and a circulating fan. Windows and sliding doors were provided at the places where access to the interior was necessary. The inside of the box was thoroughly coated with paraffin. The whole served as a chamber within which the temperature and partial pressure of water vapor could be kept constant.

Figure 4 is a photograph of a bubble suspended and ready to be fired. The glass tube at the top served for the introduction of the explosive mixture. The suspension ring (4 cm diameter) of gold wire increased the stability of the bubbles. The sparking device, seen coming up to the center of the bubble, was made of nickel wires fused to 1 mm spheres at the gap. The central wire led downward through a glass capillary tube, which was in turn surrounded by a thin metal tube. The second electrode was soldered to this metal tube and the circuit to the gap was completed through it. A drop of soap solution placed over the lower end of the glass inlet tube furnished the material for the wall of the bubble. This suspension offers no resistance to lateral expansion of the bubbles and but a very small amount in the vertical direction.

In the present series of observations, the initial horizontal dimension of each bubble was made 9 cm by admitting explosive mixture until the shadow of the bubble cast upon a white screen reaches fiducial marks originally located by substituting an object of known size at the position later to be occupied by the bubble. It is believed that the value of the initial radius (R_1) can be more accurately determined by this method (9 cm at bubble = 32 cm on screen) than if it were determined by measuring a photograph (about one-fourth actual size) of the bubble, as was done by Stevens. The present procedure has the added advantage of simplifying the reduction of the results, since the value of R_1 is constant throughout all the calculations.

Procedure.—The mixtures were prepared as follows: The mixing chamber was emptied of mercury, closed from the atmosphere, and evacuated. It was then connected to the flask containing distilled water at a constant temperature below that of the room. The reasons for the choice of the particular temperature employed will appear subsequently. After about 15 minutes the temperature of the water reservoir and that of the water vapor in the mixing vessel were observed and the reservoir was closed off. The temperature of the liquid determined the pressure of the water vapor in the mixing vessel and the temperature of the vapor, in conjunction with the perfect gas law, was used in calculating its mass. Dry CO was then admitted to the chamber to a chosen value of pressure as indicated by the manometer. The temperature and pressure of the mixture of CO and H_2O were recorded after a steady state had been reached. Similarly the dry electrolytic O_2 was admitted and the final steady temperature and pressure observed. The mole fraction of each constituent could then be calculated from the pressure-temperature data with the aid of the gas law. At least 1 hour was allowed for complete mixing before blowing a bubble.

The soap solution used in the final series of measurements had approximately the following composition by weight: triethanolamine oleate, 1 part; glycerin, 8 parts; distilled water, 32 parts. The vapor pressure of this solution at 29.4° C. was found to be 25.2 mm Hg. Since this pressure is due largely to water, the partial pressure of the water in each of the explosive mixtures was regulated to very nearly this same value, with the idea that less time would be required for establishing equilibrium between the soap film and the contained gas mixture. In other words, the water reservoir was maintained at a temperature of 26° C. for each mixture, since the vapor pressure of water is 25.21 mm at this temperature.

After flushing out the small portion of the line that could not be evacuated (ca. 0.2 cm ^{3}), a drop of soap solution was placed over the lower end of the glass inlet tube and the bubble was blown by letting mercury into the mixing vessel. A delicate needle valve in the flow line made it possible to stop the flow quickly when the bubble reached the desired size (9 cm diameter.)

A sliding door on the camera side of the thermostat was opened and the explosion was initiated and recorded by the procedure outlined in reference 2.

With these precautions the spread of the results has been reduced to a value that might reasonably be expected from an examination of the constitutent observed quantities.

THE EFFECT OF MIXTURE RATIO UPON FLAME SPEED, EXPANSION RATIO, AND TEMPERATURE ATTAINED, AT CONSTANT WATER-VAPOR CONCENTRATION

INTRODUCTION

In a previous report (reference 2), and in the preceding sections of this report a detailed description of the apparatus and technic evolved for the investigation of the explosive oxidation of CO by the constant-volume method and by the constant-pressure, or bubble, method has been given. The following sections are concerned with the experimental results obtained for various mixtures of CO and O_2 at constant water-vapor concentration, and the comparison of these results with previously published data.

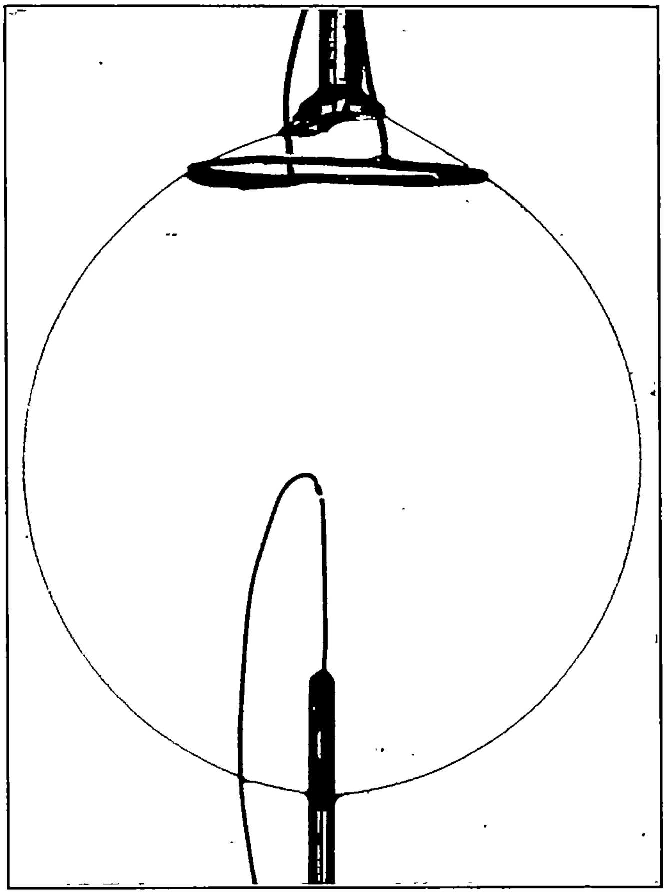

FIGURE 4.—Bubble suspended and ready to be fired.

COLLECTION OF EXPERIMENTAL DATA

Prior to the start of the final series of bubble experiments, a series of values of S' was determined, using the cylindrical constant-volume apparatus described in reference 2. In every case the mole fraction of water vapor was adjusted to 0.0269 ± 0.0001, and the total pressure to 760 mm Hg. In other words, the temperature of the water used for humidifying the mixtures was adjusted to 22.5° C., at which the vapor pressure of water is 20.44 mm. In a few of these experiments soap solution at 25° C., at which temperature its vapor pressure was observed to be 20.5 mm, was substituted for the water in the humidifier. This change produced no measurable change in the flame speed. The mole fraction of CO was varied during this series from 0.2471 to 0.8553, 46 determinations in all being made. Table I gives the observed values of S' and the corresponding CO concentrations.

TABLE I

SPEED OF FLAME IN SPACE BY THE CONSTANT-VOLUME METHOD

[Mole fraction of water=0.0269]

Mole fraction of CO	Speed of flame in space S'	Mole fraction of CO	Speed of flame in space S'	Mole fraction of CO	Speed of flame in space S'
	cm/s		*cm/s*		*cm/s*
0.2471	211	0.6293	863	0.6983	860
.2746	278	.6339	863	.6988	856
.3033	337	.6384	864	.7045	856
.3373	417	.6441	872	.7195	838
.3671	478	.6461	868	.7318	813
.4004	554	.6491	871	.7463	786
.4303	615	.6548	871	.7622	752
.4645	672	.6555	873	.7772	709
.4922	710	.6592	873	.7931	653
.5417	773	.6616	873	.8060	573
.5459	777	.6624	871	.8160	507
.5474	785	.6637	875	.8280	402
.5644	801	.6694	871	.8441	284
.5921	837	.6767	870	.8553	148
.5978	844	.6805	869	----------	----------
.6141	850	.6844	868	----------	----------

The results emodied in this table are shown graphically in figure 5. The square of the mole fraction of CO has been plotted along the axis of abscissae because, by this device, the resulting curve is more nearly symmetrical. The observed points lie, in almost every case, within less than 10 speed units of the smooth curve that has been drawn through them, and the majority of them are within 5 units. As indicated by this curve, the maximum speed in space (S') occurs not at chemical equivalence (i. e., when the mole fraction of CO is 0.649), but slightly on the rich side, at a point where the mole fraction of CO is 0.662.

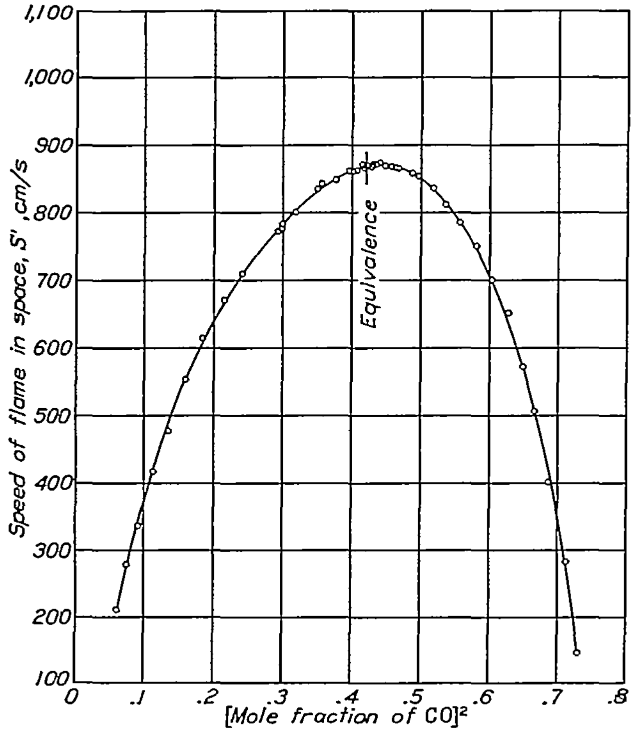

FIGURE 5.—Speed of flame in space by the constant-volume method (mole fraction of water=0.0269).

Before passing to the results by the bubble method, a few points of general interest, as brought out in the constant-volume experiments, will be recounted. The light intensity, as indicated by the density of the photographs, falls off with the flame speed on either side of equivalence. The afterglow persists for a much longer time than that required for the travel of the reaction zone in all mixtures except those extremely rich in CO. At the lean extreme the afterglow seems to be emitting more actinic light than was emitted by the flame front. At the rich extreme no afterglow is visible on the photographs. At both extremes the flame front appears on the records as a line of much greater density than the image produced by the hot gases which are surrounded by the expanding reaction zone. These facts are recorded because they are so strikingly brought out by an examination of the photographs, even though they may seem to be of little immediate importance.

The data obtained in these constant-volume experiments served as a valuable guide in the perfection of the bubble method which was subsequently undertaken. When the details of the latter had been worked out, however, and the method put into satisfactory operation, the season had advanced into the summer and the temperature in the laboratory could no longer be kept consistently below 25° C. The series of bubble experiments was therefore run at a higher temperature (29.44° C. or 85° F.). Although such a series did not give values directly comparable with the values of S' by the constant-volume method, correlation can be made at equivalence through the data of reference 2, and the results themselves are of as much value at one arbitrarily chosen value of water-vapor concentration as at another.

The vapor pressure of the soap solution at 29.44° C. was found to be 25.2 mm. The water used for humidifying the gas mixtures was therefore kept at 26° C., at which temperature its vapor pressure is 25.21 mm.

The chamber in which the bubbles were blown, which was kept saturated with vapor from exposed soap solution, was regulated to 29.44° C. at the start of each set of explosions. This temperature rose slightly with each successive explosion, and it was deemed unnecessary to wait for the box to cool to its initial temperature during the taking of 3 or 4 records for any particular mixture. Instead, the individual values of S' were finally corrected to an initial temperature of 29.44° C. by successive approximations involving the preliminary values of S' from the bubble experiments, the values of S' from the constant-volume experiments at a lower water concentration, and the observed departure of the initial temperature from 29.44° C. In practically all cases the magnitude of the applied correction was less than five speed units, and the final results were changed but very slightly by adopting this procedure.

For each gas mixture the bubbles were allowed to stand for observed time intervals of from 1 to 15 seconds at full size before being fired. Within the first 15 seconds no systematic variation of S' with time was observed. The effect of standing for longer intervals was also negligible except in a comparatively short range of mixture ratios on each side of equivalence where the observed values of S' decreased with the length of time the bubbles remained at full size. The magnitude of this decrease in S' fell off rapidly on both sides of equivalence.

All measurements taken from the negatives were corrected for the fact that the spherical object approached the camera lens as the reaction zone progressed. The constants of the lens were determined by calibration at this Bureau.

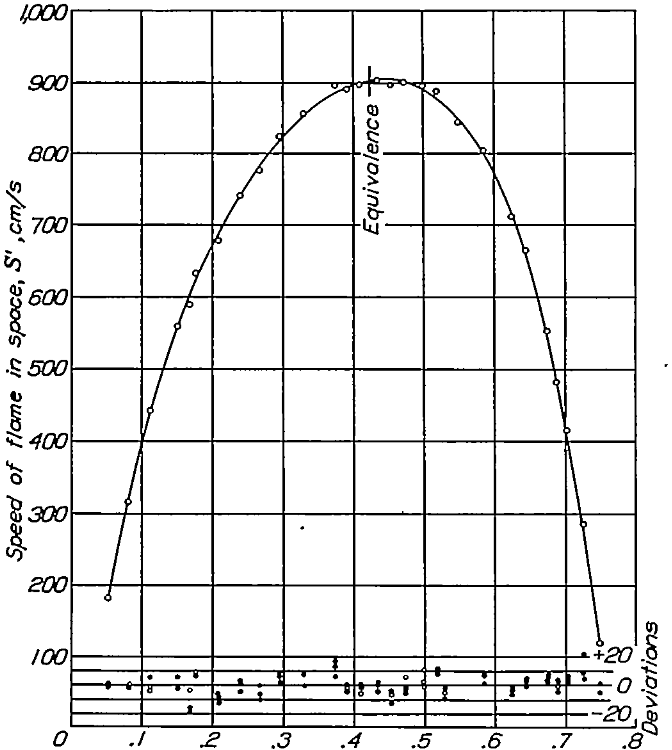

FIGURE 6.—Speed of flame in space by the bubble method (mole fraction of water=0.0331).

The curve given in figure 6 shows the variation of S' with composition for mixtures of CO and O_2, each containing a mole fraction of water of 0.0331. This curve was plotted from the mean observed values of S' for each experimental mixture. The deviation chart at the bottom of this figure shows the variation of the individual determinations of S' from the smooth curve, here represented as the straight base line. Attempts to find a simple empirical equation adequate to express the relation between the observed values of S' and composition were unsuccessful. A large-scale plot of the data embodied in figure 6 was therefore used for obtaining smoothed and interpolated values of S'.

A direct comparison of the values of S' obtained by the bubble method with those by the constant-volume method is impossible because the water content was different in the two series. With the aid of the data given in reference 2, a correlation can be made at equivalence. A value of 908 cm per second is obtained from the constant-volume measurements by applying corrections for the difference in water-vapor content and total pressure. This value is directly comparable and in satisfactory agreement with the value 902 cm per second obtained by the bubble method for an equivalent mixture containing 3.31 mole percent of H_2O at a total pressure of 750 mm. This agreement at equivalence, as well as the marked similarity of the curves shown in figures 5 and 6, is considered as important evidence that the technic of the bubble method has been rendered satisfactory.

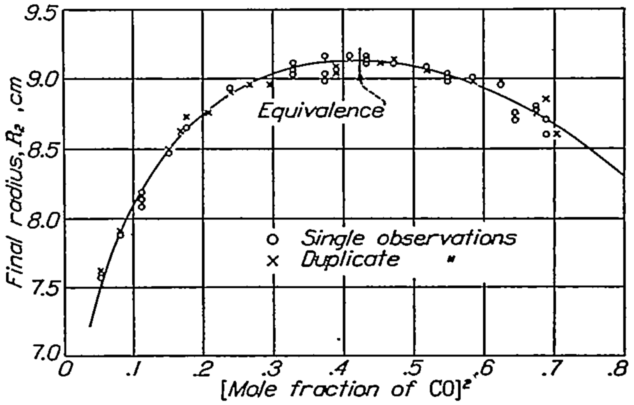

FIGURE 7.—Final radii by the bubble method.

The observed relation between final radius (R_2) and composition can be expressed very well by the equation

$$R_2^2=-48.71\,n^4-78.62\,n^2+154.05\,n+25.18,$$

in which n represents the mole fraction of CO. In figure 7 the solid curve is the locus of this equation, and the plotted points show the deviations of the individual determinations of R_2 from the equation. The smoothed and interpolated values that were used subsequently were calculated from the equation.

The speed of flame relative to the active gases (S) was calculated from the equation

$$S=S'\left[\frac{R_1}{R_2}\right]^3$$

(reference 1).

In all experiments the initial radius R_1 was made 4.50 cm. Corresponding values of S' and R_2 were taken from the curve shown in figure 6 and the empirical equation, respectively. The resulting relation between S and composition is shown graphically in figure 8. A numerical summary of all these results appears later in table II.

COMPARISON WITH THE RESULTS OF STEVENS

It has been pointed out that the theory and the mechanics of a soap-bubble explosion were correctly postulated by Stevens. Much credit is due him for his efforts to emphasize the importance of the speed of flame relative to the active gases rather than the more frequently observed speed in space.

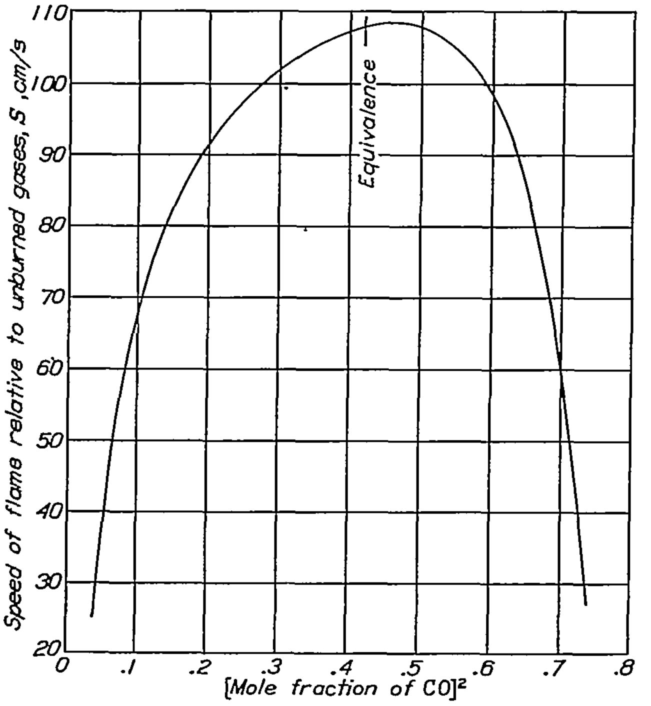

FIGURE 8.—Speed of flame relative to the active gases.

His numerous experiments (reference 1) included several series with CO and O_2, analogous to that reported here. He specified that, in every experiment, the gas mixtures were "saturated with water vapor at the temperature of the room." Although it has been shown in the first part of this paper that this statement cannot be regarded as a sufficiently definite postulation of conditions, it is probable that the large number of experiments made by Stevens over a long interval of time yielded an average result of very much higher accuracy than his individual experiments. Because the average quantity of water vapor within his bubbles cannot be definitely known, a direct comparison of his experimental values of S with those of the present series is impossible. There is, however, an indirect method by which such a comparison can be made.

As a result of all of his work with explosions in gaseous systems, Stevens concluded that the speed of flame relative to the active gases was directly proportional to the mass action product of the concentrations of the active constituents in the original mixture. Applied specifically to the explosive oxidation of CO, this statement means that the relation between S and the initial concentrations of CO and O_2 is expressed by the equation

$$S=k\,[CO]^2\,[O_2],$$

where k is a constant for each value of water-vapor content and the bracketed symbols indicate concentrations of the reactants. Stevens chose the value $k=694$ for the best representation of his data.

If an attempt is made to fit the results of the present measurements by an equation of this type, the best value of k is about 820. That this figure should be much higher than the one found by Stevens is logical since the average temperature at which his experiments were performed was doubtless much lower than that of the present series (29.44° C.).

The deviation of the new results from the equation $S=820\,[CO]^2\,[O_2]$ is shown in figure 9. In the range from 0.5 to 0.8 mole fraction of CO the deviations are relatively small, the maximum being about 4.3 percent. It is obvious that an equation of this type must fit at least approximately in this range, since values of S', R_2, and $[CO]^2\,[O_2]$ show the least variation with concentration here. In other words, curves of S', R_2, and $[CO]^2\,[O_2]$, plotted against the mole fraction of CO, all have relatively flat maxima at or near equivalence.

In the range below a mole fraction of CO of 0.5, where it is likely that the bubble method yields more dependable values of S than in any other range, the deviation between the observed and calculated values of S reaches a maximum of about 20 percent.

In the range for mixtures richer in CO than a mole fraction of 0.8, an equation of the type used by Stevens is totally inadequate to represent the present measurements. Granting that the experimental values of R_2 decrease in precision as the mixtures become very rich, it is inconceivable that there could be sufficient error in the smoothed values of R_2 to account for more than a small fraction of the discrepancy in S between the equation and the data.

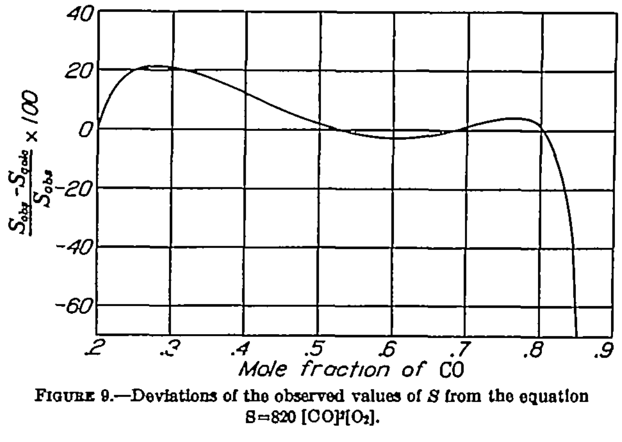

FIGURE 9.—Deviations of the observed values of S from the equation $S=820\,[CO]^2[O_2]$.

Although an equation of the type used by Stevens gives an approximate representation of the data near equivalence, there remains an outstanding discrepancy between the equation and the data even in this range. The equation, regardless of the value of k, gives a maximum value of S at exact equivalence. The observed values of both S' and S, however, show maxima that are very definitely on the rich side of equivalence. It is obviously impossible, therefore, to represent the observed values of S in the range embracing equivalence, within the limit of experimental error, by an equation of this type. It must then be concluded that, although such an equation was satisfactory to represent the results of Stevens within his experimental error, it is inadequate to represent the more exact data.

Actually, according to the present data, values of S' are more closely proportional to $[CO]^2\ [O_2]$ than values of S. If, as shown in figure 10, the observed values of S' are plotted against this product, a curve of peculiar shape results. In this figure the two sets of observed values of S', obtained by the constant-volume and the bubble method, are plotted to show the similarity of the results. For either set an equation of the type $S'-k_2=k_3\ [CO]^2\ [O_2]$, where k_2 and k_3 are constants whose values depend upon the water-vapor concentration, can be made to fit the experimental values of S' to better than 5 percent in the range of concentration from a mole fraction of CO of 0.25 to one of 0.75. For both lean mixtures and rich mixtures the branches of the curves in figure 10 are straight lines, so that an equation of this type could be used to fit the S' data at either end of the concentration range. A single equation of this type is, however, obviously incapable of covering the entire range.

In each of his published reports, Stevens reaffirmed his belief that the speed of flame relative to the active gases in any explosive mixture (whether the combustible gas was a pure compound or a composite fuel) was directly proportional to the mass action product of the concentrations of the active constituents. Close examination reveals that this concept cannot be accepted as more than a rough approximation to the truth, for the following reasons: 1. It demands a maximum value of S at exact equivalence, while the observed maximum is obtained with somewhat richer mixtures; 2. It is not supported by Stevens' own results for rich mixtures of fuels other than CO; 3. It is inadequate to represent the present results for CO and O_2, as shown in figure 9.

It therefore seems necessary to abandon Stevens' concept of the proportionality of S to initial composition, and to continue the search for a relation which will accord with the observed facts.

A brief examination of the consequences of the failure of the simple equation of Stevens to fit the new data may not be amiss. For the sake of simplicity, the reaction between CO and O_2 will be taken as a typical example.

The rate r at which a chemical reaction proceeds in a homogeneous system is defined as the decrease in equivalent concentration of the reacting molecular species in unit time. For the oxidation of CO the law of mass action as applied to reaction rate may be expressed as follows:

$$r=-\frac{d\,[CO]}{dt}=-\frac{d\,[O_2]}{dt}=k_1\ [CO]^2\ [O_2]$$

where r is the reaction rate, t represents time, and k_1 is a constant known as the specific reaction rate. The value of k_1 is constant for any given temperature but varies with the temperature at which the reaction takes place. The rate at which k_1 varies is, in general, great for reactions accompanied by considerable evolution or absorption of heat. For the oxidation of CO large changes in k_1 are to be expected as the mixture ratio is varied, because of the large differences in the temperatures which result from the high heat of reaction.

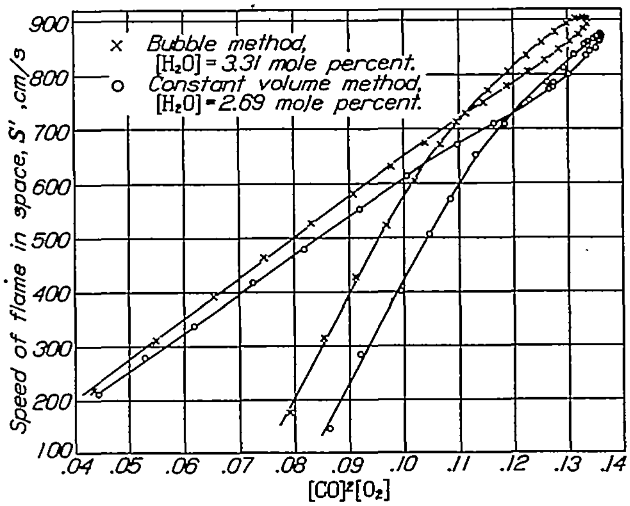

FIGURE 10.—Values of the speed of flame in space plotted against the mass action product.

The equation $S=k\ [CO]^2\ [O_2]$, which fit Stevens' experimental results, is very similar in form to the expression for reaction rate. The important distinction lies in the fact that k_1 is a function of temperature, while a single value of k was considered adequate over the whole range of mixture ratios. For this reason it does not seem proper to consider that S, as defined by the above equation, is a relative measure of reaction rate, and considerable care should be exercised in any attempt to correlate these two quantities, as was done by Stevens in reference 1 (N. A. C. A. T. R. No. 337).

Other work of Stevens included an investigation of the effect of pressure upon the rate of propagation of the reaction zone (reference 1, N. A. C. A. T. R. No. 372). The soap-bubble method was employed, and although no attempt to repeat these measurements has been made, it is of interest to examine his results, giving consideration to the known characteristics of the method. From a large number of records he concluded that his results "would indicate that, over the pressure range examined (100 to 3,000 mm Hg), the rate of propagation S of the reaction zone measured relative to the active gases is independent of pressure."

The present work has shown that the water vapor within the bubble, regardless of its original partial pressure, will assume a partial pressure very close to that in the surrounding air during the time required to blow and fire the bubble. Therefore in the experiments of Stevens the volume percentage of water vapor within the bubbles at the time of firing must have varied inversely as the total pressure. To illustrate, let us assume that the air within which the bubbles were blown was at a temperature at which the vapor pressure of the soap solution was 20 mm and that saturation conditions prevailed. The volume percentages of water vapor within the bubbles at the time of firing would have been as follows: At a total pressure of 100 mm, 20 percent; at atmospheric pressure, 2.8 percent; at 3,000 mm, 0.67 percent. It is at once evident that Stevens' observations upon the effect of pressure were actually observations of the combined effect of simultaneous changes in pressure and water-vapor content. For CO explosions the effect of water vapor is certainly not a negligible factor. For any explosive mixture in which water vapor has a significant effect upon flame speed, the bubble method is inherently unsuited to a study of the effect of pressure.

A series of observations upon the effect of inert gases in explosions of CO and O_2 is now in progress. A comparison of these results with those of Stevens upon the same subject (reference 1, N. A. C. A. T. R. No. 280) will be included in a subsequent report.

TEMPERATURES ATTAINED

From the observed values of $\left[\frac{R_1}{R_2}\right]^3$ it is possible to calculate the temperatures prevailing at the time the reaction zone has completed its travel. In addition to the data obtained by the bubble method it is necessary to have equilibrium data and an equation of state for the final gas mixture at the final temperature. Precise values of neither of these quantities is available, but it seems worth while, nevertheless, to find the relation which exists between mixture ratio and temperature attained, on the basis of such equilibrium data as are now at hand.

It is probable that gas mixtures at a pressure of one atmosphere and at both the initial and the final temperature show no greater percentage deviation from the perfect gas law than the percentage experimental error in expansion ratio. If, then, the perfect gas law is used, the initial and final temperatures are related, for the constant-pressure or bubble experiments, by the equation

$$\frac{T_1}{T_2}=\frac{N_2V_1}{N_1V_2}$$

where the subscripts 1 and 2 denote initial and final states, respectively, N is the total number of moles, V is the volume of the gas mixture, and T is the temperature in degrees Kelvin.

Obviously the cube of the radius may be substituted for volume, and the equation becomes

$$T_2=\frac{N_1R_2^3T_1}{N_2R_1^3}$$

The values of N_1, T_1, and of the expansion ratio are known from the bubble experiments. In order to calculate N_2 it is necessary to know what products result from the explosive reaction and the concentration of each at T_2.

For the purpose of the present computation the dissociation of molecular hydrogen and oxygen into their atomic species has been neglected. The dissociation of water vapor has been assumed to take place according to the equation $2\ H_2O \rightleftharpoons 2\ H_2+O_2$. Bonhoeffer and Reichard (reference 3) have shown that the dissociation of water yields not H_2 and O_2, but H and OH, and that the equilibrium data which have previously been considered applicable to the former mechanism actually apply to the dissociation in the manner which they postulated. Since there is thus no problem as to the choice of equilibrium data, and since the amount of water involved in the present experiments is small, it makes but little difference in the calculated values of N_2 (and consequently of T_2) whether the water is assumed to dissociate in the first or second of the above-mentioned ways.

The two reactions

$$2\ CO+O_2 \rightleftharpoons 2\ CO_2$$
$$2\ H_2O \rightleftharpoons 2\ H_2+O_2$$

are involved in the present calculations of N_2. The water gas reaction, $H_2O+CO \rightleftharpoons H_2+CO_2$, does not require independent consideration, since it is merely the resultant or sum of the two reactions given in the preceding sentence. In addition, it does not involve any change in the number of gas molecules present.

The equilibrium equations for the dissociation of CO_2 and H_2O as given by Schüle (reference 4) are based upon such data as were available and are applicable in the range of temperatures involved in the bubble experiments. His values

$$(CO_2)\ \log K_p=8.048-\frac{29800}{T}+0.634\log T-0.000367T,$$

and

$$(H_2O)\ \log K_p=-21-\frac{22746}{T}+8.28\log T-0.001\ T$$

have been used without modification in the calculation of final temperatures.

The method of successive approximations must be used, since it is impossible to calculate N_2 until T_2 is known and vice versa. Since the nature of such calculation is well known and somewhat involved, it is not necessary to include a sample here. Suffice it to state that such computations have been made for numerous values of mixture ratio according to the method outlined above. The results are shown graphically in figure 11. Table II is a summary showing the variation of S', S, expansion ratio, and T_2 with the mole fraction of CO, each initial mixture containing a mole fraction of water vapor of 0.0331.

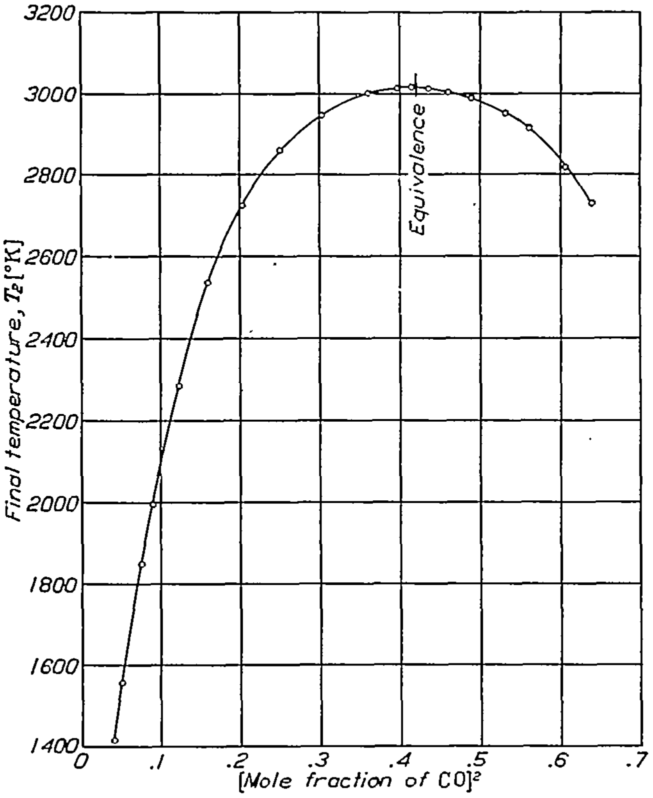

FIGURE 11.—Variation in the temperature attained with mixture ratio.

If a comparison is made between the percentage conversion of CO and CO_2 for mixtures of CO and O_2 in the wet and dry state, it is found that in a narrow range of concentration embracing equivalence, the conversion is more complete in the wet mixtures. The conversion is likewise greater on the rich (in CO) side than on the lean. It is possible that there may be some connection between this fact and the fact that the flame speed is greater in slightly rich than in equivalent mixtures.

The calculated values of temperature show a maximum at equivalence. This fact is to be expected because the formulated values of R_2 show a maximum at this point. It is well to point out that the observed values of R_2 show sufficient spread to make it impossible to tell from the results just where the maximum actually occurs. Such is not the case for values of S', which have been shown by both the constant-volume and constant-pressure method to have maxima slightly on the rich side of equivalence. Even though the calculated values of temperature are not sufficiently precise to locate the true peak, this fact does not mean that errors in them are large, because the curve is comparatively flat in the region of equivalence.

The present results yield a maximum temperature of 3,016° K for an equivalent mixture of CO and O_2 containing 3.31 mole percent of H_2O at a total pressure of 750 mm. Schüle (reference 4) gives 3,028° K as the maximum attainable temperature in equivalent

TABLE II

Summary of results by the bubble method (H_2O *assumed to dissociate into* H_2 *and* O_2)

Initial composition at T_1			Flame speed		Expansion ratio $\left(\frac{R_2}{R_1}\right)^3$	Final temperature, T_2	Dissociation		Final composition at T_2				
CO	O_2	H_2O	In space S'	Relative to active gases S			CO_2	H_2O	CO	O_2	H_2O	H_2	CO_2
Mole fraction			cm/s.			°K	Percent		Mole fraction				
0.2000	0.7669	0.0331	106.0	25.20	4.207	1,414	0.0	0.0	0.0000	0.7410	0.0368	0.0000	0.2222
.2250	.7419	.0331	164.0	35.92	4.566	1,557	.0	.0	.0000	.7092	.0373	.0000	.2535
.2750	.6919	.0331	289.0	54.85	5.269	1,848	.0	.0	.0000	.6428	.0384	.0000	.3188
.3000	.6669	.0331	350.5	62.49	5.608	1,996	.2	.0	.0008	.6083	.0389	.0000	.3520
.3500	.6169	.0331	472.0	75.47	6.254	2,285	1.9	.3	.0081	.5376	.0398	.0001	.4144
.4000	.5669	.0331	581.0	84.94	6.840	2,537	7.9	1.0	.0388	.4692	.0402	.0004	.4514
.4500	.5169	.0331	675.5	91.87	7.353	2,726	18.1	2.4	.0998	.4080	.0396	.0010	.4516
.5000	.4669	.0331	758.0	97.40	7.782	2,860	29.2	3.9	.1774	.3528	.0386	.0015	.4297
.5500	.4169	.0331	827.5	102.2	8.097	2,947	38.3	5.9	.2533	.2985	.0375	.0023	.4084
.6000	.3669	.0331	877.5	105.7	8.299	3,000	45.3	7.6	.3248	.2438	.0365	.0030	.3919
.6300	.3369	.0331	896.5	107.3	8.354	3,014	48.5	8.5	.3640	.2098	.0361	.0034	.3867
.6446	.3223	.0331	900.5	107.7	8.361	3,016	49.6	8.8	.3812	.1928	.0360	.0035	.3870
.6600	.3069	.0331	905.0	108.3	8.354	3,013	47.1	9.2	.3993	.1739	.0358	.0036	.3874
.6800	.2869	.0331	904.5	108.7	8.319	3,005	42.9	9.6	.4206	.1488	.0357	.0038	.3911
.7000	.2669	.0331	895.5	108.4	8.264	2,989	38.1	10.0	.4420	.1236	.0356	.0040	.3948
.7300	.2369	.0331	867.0	106.6	8.137	2,951	29.2	10.6	.4729	.0850	.0355	.0042	.4024
.7500	.2169	.0331	835.0	104.2	8.013	2,912	22.1	11.1	.4950	.0599	.0353	.0044	.4054
.7800	.1869	.0331	755.0	97.1	7.78	2,816	10.7	12.4	.5343	.0284	.0347	.0049	.3997
.8000	.1669	.0331	674.5	89.0	7.58	2,728	3.3	14.0	.5674	.0092	.0339	.0055	.3840
.8300	.1369	.0331	480	----------	----------	----------	----------	----------	----------	----------	----------	----------	----------
.8500	.1169	.0331	291	----------	----------	----------	----------	----------	----------	----------	----------	----------	----------
.8650	.1069	.0331	120	----------	----------	----------	----------	----------	----------	----------	----------	----------	----------

mixtures at atmospheric pressure. The quantity of water is not stated. This agreement lends added confidence to the results by the bubble method, especially as to its merit for measuring expansion ratios.

CONCLUSIONS

As a consequence of the results of the various experiments which have been described, the following conclusions as to the bubble method of investigating gaseous explosive reactions have been drawn.

1. The method can be used for precise determination of the speed of flame in space when and only when—

A. Sufficient light is emitted by the explosion for photographic purposes.

B. The initial concentration of the explosive mixture is adequately controlled, a requirement which, for mixtures of CO and O_2, demands precise control of—

  a. The composition of the mixtures from which the bubbles are blown.

  b. The temperature and water-vapor concentration of the atmosphere in which the bubbles are blown.

C. No constituent of the mixture dissolves rapidly in the soap solution, and

D. For the particular apparatus used in these tests, the actual values of the speed of flame in space lie between 150 and 1,500 centimeters per second.

2. The method can be used to determine expansion ratio (and hence also the speed of flame relative to the active gases) in all mixtures for which it is suitable for determinations of spatial flame speed, except for those very rich in combustibles.

3. The method is not applicable to a study of the effect of water vapor, but can be used to study the effect of varying the proportions of the other constituents while the water-vapor concentration is held constant.

4. The use of the method may be profitably extended to include other combustible gases and a study of the effects of diluents, both active and inert.

The agreement between the results of the bubble method and the constant-volume method is satisfactory. The calculated value of the maximum temperature attained is in satisfactory agreement with a value obtained by independent methods. The bubble method is therefore believed to be satisfactory for measuring expansion ratios, within a restricted range of concentration.

The results of the present series of bubble experiments are more accurate than the earlier values obtained by Stevens using the same method. The new results cannot be adequately represented by the simple relations which were satisfactory for the less accurate data. A number of the conclusions drawn by Stevens are therefore open to serious question. It is hoped that the results which have been presented, together with those which are planned for the future, will lead to a more exact interpretation than was possible with the less accurate data.

National Bureau of Standards,
Washington, D. C., *January 10, 1935.*

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