REPORT No. 486

INFRARED RADIATION FROM EXPLOSIONS IN A SPARK-IGNITION ENGINE

By Charles F. Marvin, Jr., Frank R. Caldwell, and Sydney Steele

SUMMARY

The variations in intensity and spectral distribution of the radiant energy emitted by the flames during normal and knocking explosions in an engine have been measured at the Bureau of Standards with the financial assistance of the National Advisory Committee for Aeronautics. Radiation extending into the infrared to about 11μ was transmitted by a window of fluorite, placed either near the spark plug or over the "detonation zone" at the opposite end of the combustion chamber. Concave, surface-silvered mirrors focused the beam, first at the slit of a stroboscope which opened for about 2° of crank angle at any desired point in the engine cycle, and then upon the target of a sensitive thermocouple for measuring radiation intensity. Spectral distribution of the radiant energy was determined by placing over the window, one at a time, a series of five filters selected with a view to identifying, as far as possible without the use of a spectrograph, the characteristic emissions of water vapor, carbon dioxide, and incandescent carbon.

Observations through the filters were analyzed to show the relative intensity of the radiation from these 3 substances by 2 independent methods that produced results in satisfactory agreement. In one method, a conventionalized spectrum was made up of geometrical figures having locations and shapes simulating the prominent emissions of the three principal radiators, and the relative amounts of energy required in these regions to account for the readings obtained through the filters were calculated. In the other method, the characteristic spectral distributions for the three principal radiators were determined directly in terms of filter readings by observations through the filters of flames burning separately hydrogen and carbon monoxide, thus producing separately only water vapor and carbon dioxide as radiators; and by similar observations of a black-body furnace simulating radiation from heated carbon particles. The relative extent to which the characteristics of the three principal radiators are exhibited in the observations on composite flames in burners and in the engine are then determined graphically.

The results indicated that nearly all the radiant energy was in the infrared region and was emitted by water vapor and carbon dioxide formed during combustion. During normal combustion, there was evidence that reactions producing water vapor and carbon dioxide continued for 20° or more of engine crank rotation after inflammation of a given element of charge, whereas the reaction period was much shorter in the portion of the charge involved in fuel knock. The full significance of the data is at present obscured by lack of fundamental information regarding the effects of flame depth, density, temperature, and pressure, much of which could be secured by suitable observations of burner and engine flames using as fuels hydrogen and carbon monoxide separately and in known mixtures.

INTRODUCTION

Observations made through transparent windows in the heads of spark-ignition engines (references 1 and 2) have shown that during an explosion a luminous zone originates at the spark plug and spreads rapidly throughout the combustion chamber until the entire charge is inflamed, the whole mass of gas continuing to glow for some time after flame propagation is complete. It has long been known that the color and intensity of the light emitted by the explosion vary with operating conditions, especially with mixture ratio. Flame photographs and stroboscopic observations have demonstrated that there are also variations in actinic value, intensity, and color from point to point in the combustion chamber and from instant to instant during the progress of combustion (reference 3).

In 1922 Midgley and Gilkey (reference 4) pointed out that the significance of these variations might be more readily determined by resolving the radiation into its constituent wave lengths by spectroscopic methods. If this is done for flames burning hydrocarbon fuels, energy is found not only in the visible spectrum but also in the ultraviolet and predominantly in the infrared. Incandescent solids in the flame emit continuous radiation over a large portion of the spectrum; different gases and vapors may be identified by their characteristic banded spectra, the bands appearing bright when the gases are emitting and dark when the gases are absorbing radiation from other sources.

Changes in pressure cause a slight shifting of the bands on the wave-length base; variations in the temper-

ature, depth, and density of the flame alter the total energy and the energy distribution in a complex manner. Thus, much information regarding the obscure combustion processes in an engine might be made available if satisfactory methods of observing and interpreting the radiation could be devised. Some progress has been made toward solving these difficult problems but it is believed that prospects for future achievements far exceed accomplishments to date.

In 1926 and 1927 papers (references 5 and 6) were published describing pioneer spectrographic studies of combustion in an engine at the Massachusetts Institute of Technology. In 1931 investigators at the General Motors Research Laboratories (reference 3) made a distinction between the "flame fronts" and "afterglows" in engine explosions and later spectrographic analyses of the character of the visible (reference 7) and ultraviolet (reference 8) radiation from these different portions of the flame were made for both normal and knocking explosions and interpreted in terms of chemical constituents and reactions. Absorption spectra (references 9 and 10) for a variety of engine conditions and fuels were also photographed, this method permitting examination of the dark unburned gases ahead of the flame front as well as the luminous charge behind.

A major aim in all these investigations was to identify intermediate reaction products, which may be present in very small quantities and have only a transient existence in the flame, in the hope of finding some clue to the mechanism of fuel knock and the action of knock suppressors. For this purpose the photographic method records satisfactorily the ultraviolet, visible, and very short wave infrared radiation. The bulk of the energy radiated from flames, however, appears in the infrared, beyond the reach of the photographic method. This radiation can be measured by its heating effect when focused upon a sufficiently sensitive receiver. Such a receiver responds also to energy in the visible and ultraviolet regions.

Some measurements of the variations during combustion of the total energy transmitted through a quartz window in an engine cylinder were published by Midgley and McCarty in 1924 (reference 11), but no serious attempt to interpret these results was reported. Recently, Hershey (reference 12) used measurements, made through quartz windows, of the total emission and absorption of the gases in an engine combustion chamber as a basis for calculating variations in the charge temperature and obtained good apparent agreement between theoretical and experimental values.

In 1931 the Bureau of Standards became interested in the possibilities of infrared analysis as a sequel to studies (reference 13) of flame travel in an engine cylinder that were being conducted under the sponsorship of the National Advisory Committee for Aeronautics. Mention of a preliminary stage in this work was made by Steele (reference 14) who subsequently described (reference 15) in detail somewhat improved apparatus for measuring the radiation transmitted by fluorite windows in the engine combustion chamber. The present report describes the equipment finally used at the Bureau of Standards and presents typical data with a discussion of their significance.

The authors desire to express their appreciation to W. W. Coblentz of the Bureau's staff for the loan of apparatus and for helpful advice, to A. H. Pfund and D. H. Andrews of Johns Hopkins University for similar assistance, and to A. Wharton and C. H. Roeder who set up the equipment and acted as observers throughout the investigation.

APPARATUS AND PROCEDURE

The engine used is a single-cylinder L-head type equipped with a special head containing 31 small windows symmetrically distributed over the top of the combusion chamber, each window giving a view downward through a small column of charge with its axis essentially parallel to the surface of the spreading flame front. Observations are made through a stroboscope that confines the view to the same selected phase of successive cycles. Thus, by proper choice of window location and stroboscope setting it is possible to isolate for examination a nearly uniform sample of charge ahead of, behind, or within the reaction zone, in any part of the combusion chamber, or at any time in the explosion period.

The stroboscope and the special engine head had been designed for previous measurements of flame travel (reference 13), and a somewhat complicated optical system was devised to adapt this available equipment for the radiation experiments.

Optical system.—Figure 1 shows the apparatus diagrammatically. Radiation passes through the chosen window in the engine head and is brought to a focus, first at the slit of the stroboscope and then on the target of a thermocouple.

A disk of polished fluorite 3 to 4 mm (0.118 to 0.157 inch) thick, mounted between rubber-asbestos gaskets near the top of a deep hole in the head as shown at B, provides a window about 3 mm in diameter which receives radiation only from the column of charge directly beneath it. Fluorite was chosen in preference to quartz because of its transparency to longer waves, including prominent bands in the spectra of water vapor and carbon dioxide that previously had not been observed in an engine. Windows free from cleavage planes can be cleaned frequently and used satisfactorily for long periods.

Radiation passes from the window through a small hole in a shield C, which is mounted just above the engine to intercept radiation from the hot metal of the head and from the other windows. Filters for de-

termining spectral distribution are placed successively over the hole, the shield and the filter being cooled by an electric fan. The transmission characteristics of the five filters used are given in figure 2. The filtered radiation is reflected and focused at the stroboscope F by the mirrors E and D.

The stroboscope consists of a fixed eyepiece and two rotating disks driven at different speeds from the

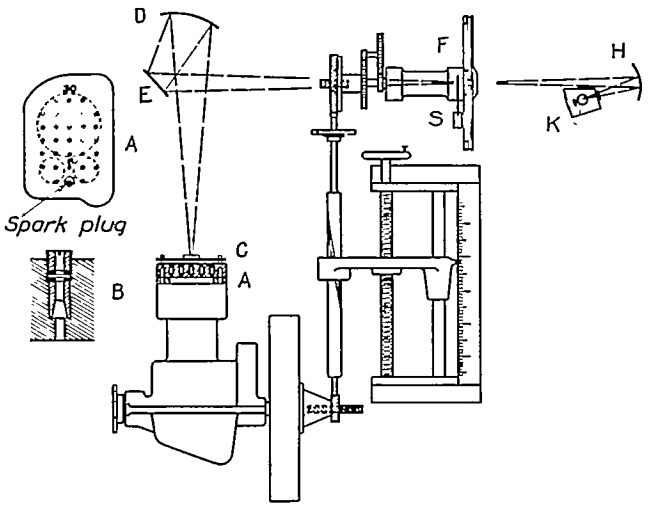

FIGURE 1.—Diagram of apparatus. A, Engine head showing location of windows; B, Detail of fluorite window mounting; C, Radiation shield and filter; D, E, H; Surface silvered mirrors; F Stroboscope; S, Electromagnetically operated shutter, K, Thermocouple.

engine crankshaft through gearing and a phase-changing device. Slots in the disks give an opening once each cycle for a period of about 2° of engine-crank rotation.

The divergent beam of radiation beyond the stroboscope falls upon a third mirror H which focuses it through a rock-salt window upon the target of a single-junction antimony-bismuth vacuum thermo-

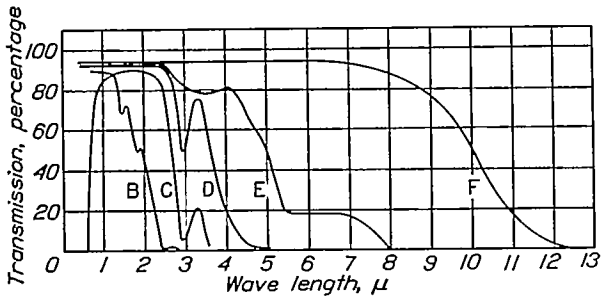

FIGURE 2.—Filter characteristics. B, Pyralin (thickness=2.13 mm); C, Schott's monochromatic red (t=3.18 mm); D, Quartz (t=8.94 mm); E, Microscope cover glass (t=0.15 mm); F, Fluorite (t=3.00 mm).

couple K. Mirrors D, E, and H are silvered on the front surface, and the thermocouple is carefully housed to protect it against drafts and stray radiation.

Electrical system.—The minute e.m.f. produced by the thermocouple under the heating effect of the radiation is determined by balancing it against a controlled and measured e.m.f. using a highly sensitive Thompson galvanometer as a null instrument.

Figure 3 is a diagram of the electrical circuits. The galvanometer G and the thermocouple T are connected in series with the "line control" L and the potentiometer unit E when switch II is closed to the left preparatory to making observations. Switch I is normally open allowing the electromagnetically operated shutter S to close and prevent radiation from reaching the thermocouple, which thereupon assumes the temperature of its immediate surroundings. The line control is adjusted, and readjusted from time to time as necessary, to compensate for any parasitic e m.f. in the thermocouple or galvanometer circuit, thus maintaining the galvanometer mirror in its zero position at all times when the shutter is closed.

When making a reading, switch I is closed. This action opens the shutter, exposing the thermocouple to radiation, and at the same time introduces into the circuit a controlled and measurable e.m.f. from the potentiometer unit, opposing that developed by the

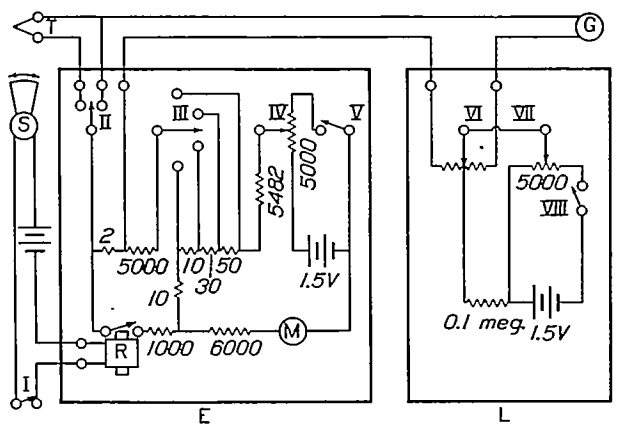

FIGURE 3.—Electrical circuits. T, Thermocouple; G, Galvanometer; S, Shutter; E, Potentiometer unit; M, Milliammeter; R, Relay; L, Line control.

thermocouple The controlled e.m f. is then adjusted to such a value that opening and closing switch I does not throw the galvanometer off zero. The value of the opposing e.m.f. required to balance that developed in the thermocouple is determined from calibration curves for the milliammeter M in the unit E. A choice of four ranges, each covering the full scale of the milliammeter, adds to the convenience and accuracy in making readings. Other advantages of the system, as compared with the method of reading galvanometer deflections used in preliminary work, are that large deflections of the galvanometer are avoided, thus eliminating the errors due to drift of the zero during swings and changes in sensitivity with position on the scale, while speed in reading is greatly increased.

Galvanometer sensitivity can be directly determined by closing switch II to the right and reading the deflection when a known e.m.f. is imposed on the galvanometer from unit E. Precautions were taken to eliminate as far as possible all sources of stray e.m.f. in the system.

Supplementary equipment.—A balanced diaphragm pressure indicator (reference 16) with a timing contact operating in synchronism with the stroboscope disks makes it possible either to measure the instantaneous cylinder pressure corresponding to each radiation reading or to make a complete indicator diagram if desired. Pressure measurements serve as a convenient check on the constancy of engine-operating conditions during a run and as a guide in reproducing conditions when runs are repeated.

The engine, which can be operated on either liquid or gaseous fuels, is also equipped with an ignition system specially designed to give an accurately timed spark and with facilities for accurate measurement of torque, speed, air and fuel consumption, and jacket-water temperature.

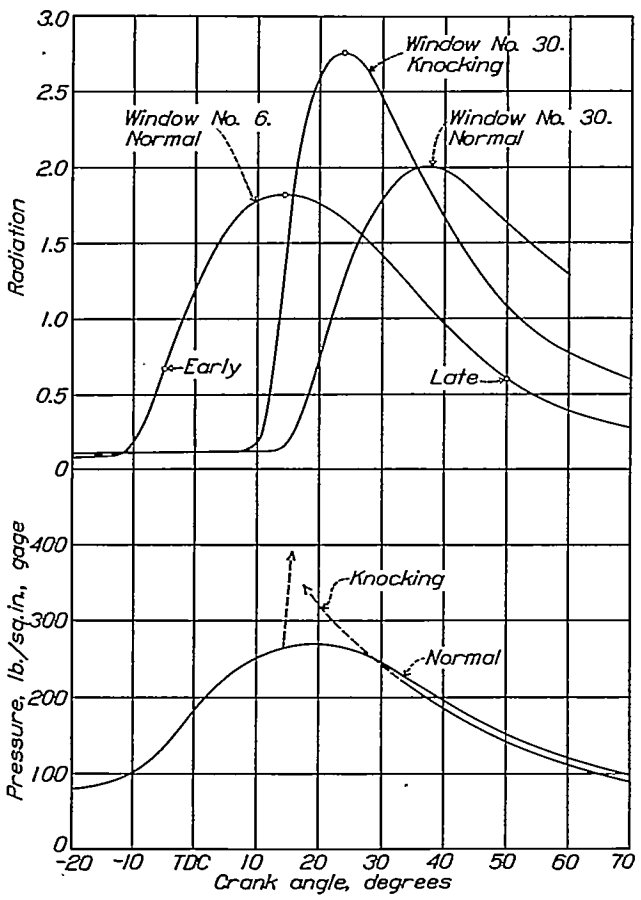

FIGURE 4.—"Total" radiation and pressure diagrams. Circles indicate points for which spectral distributions are given in table I.

Focusing and phasing.—Before starting a run, radiation is carefully focused on the thermocouple target and the over-all sensitivity of the measuring apparatus is checked. The procedure is to insert a miniature electric lamp into the combustion chamber through a hole provided for the purpose and center the filament under the fluorite window. This lamp burning at full brilliance provides a concentrated source of light at the point in the combustion space on which it is desired to focus. When the best possible focus is secured, current through the lamp is reduced to a convenient reference value and radiation from the filament is measured, the reading constituting an over-all check on the accuracy of the focus and the performance of all units in the measuring system.

A high-tension spark, timed by the ignition breaker, is used in making dynamic settings of spark advance, stroboscope, and indicator timer. Light from this spark, which is practically instantaneous and simultaneous with the ignition spark, is first used to illuminate graduations on the periphery of the engine flywheel; the timing is adjusted to give a spark advance of 20°. The stroboscope disks are then viewed by the spark flash and the phase adjusted to give full opening at the instant of illumination. The adjustable brush of the pressure indicator timer is next set to cover the rotating contact when viewed by the spark and, finally, the pointer on the stroboscope phase-changing scale is set to 20°.

EXPERIMENTAL DATA

All runs were made at 20° spark advance, 600 r.p.m., 13:1 air-fuel ratio by weight and with a constant weight of air per cycle equivalent to 75 percent volumetric efficiency at atmospheric conditions of 760 mm Hg and 20° C. The compression ratio was 5.

Considerable difficulty was experienced in obtaining consistent and reproducible observations, due variously to shifting of the focus on the thermocouple target, disturbance of the highly sensitive galvanometer by outside influences, variations in engine-operating conditions, or deposit of "carbon" on the window during the rather extended time required to investigate adequately the combustion period with the five filters. It was therefore necessary to make frequent check readings during runs, one or more check runs under each condition, and some corrections to the observations in order to secure reliable representative data. The typical curves in figure 4 and the spectral distributions for engine flames in table I are the results of careful consideration of a large number of observations. Figure 4 shows the variation with crank position during a normal run in the "total" radiation (transmitted through the fluorite filter) from a region (window 6, fig. 1A) close to the spark plug. Similar data for a window (no. 30, fig. 1A) in the "detonating zone", at the opposite end of the combustion chamber, are also given for two fuels, one burning normally and the other knocking. Circles on the radiation curves indicate the points for which spectral distributions are given in table I.

Ordinates for the radiation curves in figure 4 are thermocouple e.m.f in microvolts. However, absolute values have no particular significance as the e.m.f is dependent not only upon the intensity of the radiation emitted by the flame but also upon the duration of the stroboscope opening and the character of the focus. Inasmuch as the focus could not be exactly reproduced

from day to day, the runs made under otherwise equivalent conditions were corrected to a common scale of ordinates by multiplying all the readings for each run by some constant factor so selected for each run as to bring all runs into optimum agreement. As successive knocking and normal runs in window 30 were made without change of focus, these curves are directly comparable; but as it was necessary to readjust the focus for a change in window, some uncertainty exists concerning the exact equality of the ordinate scales for the different windows.

Runs of about an hour were made without a noticeable accumulation of carbon on the window in position 6, but a brown film collected rapidly in position 30, especially during knocking. When correcting for the scattering and absorption of this film, reference readings through the fluorite filter at a crank angle of 35° after top center were made at timed intervals throughout the runs on window 30. These readings were expressed as fractions of the first reading and plotted against time, the resulting curve being used to correct readings for all crank angles and filters to the original clean-window conditions. There was no evidence of selective absorption in the normal runs but some indication that radiation in the shorter wave lengths was scattered by the film formed during knocking. The spectral distribution at the peak of the knocking radiation curve was therefore determined from subsequent runs in which precautions were taken to keep the window clean and to check readings to assure that there was no effect of deposit on the window.

Using each of the filters, measurements were made of the radiation from transparent flames of hydrogen, carbon monoxide, and city gas burned in a laboratory blowpipe; city gas in a Bunsen burner; benzol and gasoline-benzol blends in a blast torch; and highly luminous flames of gasoline burning on a wick and acetylene in a Von Schwarz burner. Similar observations were made on a small black-body furnace, heated to various temperatures between 800° K. and 1,400° K. Values of black-body radiation above 1,400° K. were obtained from the experimental curves by extrapolation, guided by points calculated from the transmissions of the filters employed and the black-body spectral distributions given in the Smithsonian Physical Tables (reference 17).

In order to compare spectral distributions for the widely different sources of varying total energies, the readings through the several filters for each source were expressed in table I as percentages of the reading with the fluorite filter.

In considering distribution in the engine it is necessary to distinguish between radiation from the flame itself and radiation from the heated combustion chamber, since the latter may constitute a considerable portion of the total radiation early and late in the combustion period. Thus, radiation, probably with essentially black-body distribution, is observed before the flame arrives and some increase in this type of radiation might be expected as the sooted inner surfaces of the combustion chamber are temporarily heated by the explosion. However, the total amount of such radiation probably does not rise above the readings obtained late in the expansion stroke, nor can it be less than the readings early in the compression stroke when the temperatures of gases and walls reach a minimum. Thus, the percentage of combustion chamber radiation in the total for any point on the curves can be estimated within reasonable limits.

The temperature of the gases at the point where the spark occurs (20° advance) was estimated from analysis of the indicator diagram as 650° K. and, since the diagram also shows that the gases lose heat during the latter part of the compression stroke, the temperature of the walls must be below that of the gases, say about 500° K. Increase in temperature of the inner surfaces of the combustion chamber is limited by the rather small increase in radiation attributable to them, and the spectral distribution of the combustion chamber radiation is thus approximately defined.

Since the spectral distribution and percentage of combustion-chamber radiation in the total are known within reasonable limits, it is possible to correct observed spectral distributions for the effects of combustion-chamber radiation and thus obtain distributions representative of the flames alone. The values for the engine given in table I have been corrected for combustion-chamber radiation and are therefore comparable with values for the burner flames.

A water cell, practically opaque to radiation in the infrared, was used in preliminary engine runs but no appreciable readings were obtained with this filter and its use was discontinued. It demonstrated, however, that energy radiated by the explosion in the visible region is negligible as compared with that emitted in the infrared.

DISCUSSION

SPECTRAL DISTRIBUTION

Spectrum analyses have shown that the principal emitters of radiant energy in nonluminous hydrocarbon flames are the final reaction products H_2O and CO_2. Thus, according to Garner (reference 18), "The hydrocarbon flame spectrum is in fact composite in character, consisting of two superposed spectra, the one identical with the spectrum of the carbon monoxide and the other with that of the hydrogen flame. . . . Paschen made the discovery that water vapor and carbon dioxide, when heated to a high temperature gave out radiation with band maxima at the same wave lengths as the maxima for the hydrocarbon, carbon monoxide, and hydrogen flames. . . . Paschen also drew attention to the fact that the band maxima occurred at very nearly the same positions as the absorption maxima

previously observed by Ångström for carbon dioxide. These observations admit of only one interpretation, they prove that the oscillators emitting the radiation from hydrocarbon flames are molecules of carbon dioxide and water." For luminous flames appreciable quantities of energy are also emitted by incandescent carbon particles.

Two independent methods have been devised for analyzing the readings through the filters with the

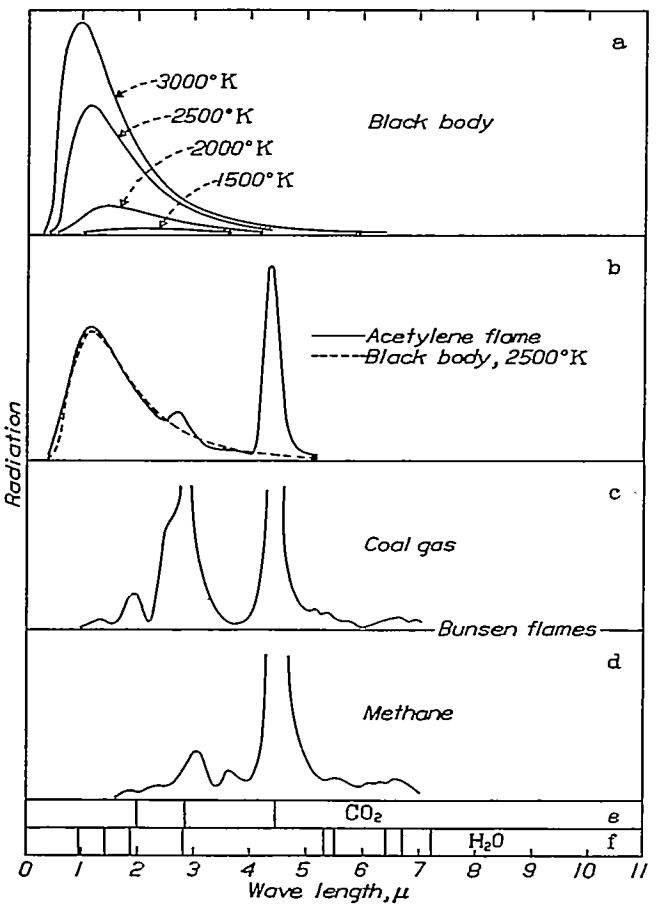

FIGURE 5.—Typical spectra.

object of identifying these three principal radiators, determining their relative potency in the flames examined, and following their development during combustion in the engine.

Derivation of spectra.—The use of 5 filters of known transmission characteristics permits the separation of the radiation into 5 spectral regions. Since the filters do not cut off sharply, but overlap, distinct spectral regions are not isolated by taking differences between readings with successive filters in the series; and because the filters vary in spectral transmission, observed energies in these different regions are not proportional to emitted energies. One method of interpreting the observations is to assume more significant spectral regions, selected to represent approximately the prominent emissions typical of the spectra of the principal radiators, and to calculate the relative amounts of energy that must be emitted in these chosen regions to account for the readings obtained through the filters.

Available spectra, including those shown in figure 5, were used as a guide in erecting the five geometrical figures comprising the conventionalized composite spectrum a (figs. 6 and 7). The unknown areas of the five figures, representing the relative energies emitted in the corresponding spectral regions are designated "J_1", "J_2", "J_3", "J_4", and "J_5".

The triangle J_1 was set up to represent roughly the distribution of energy according to wave length in the spectrum of incandescent carbon, which approximates that for a black body or perfect radiator. Spectra for black bodies at different temperatures are plotted in

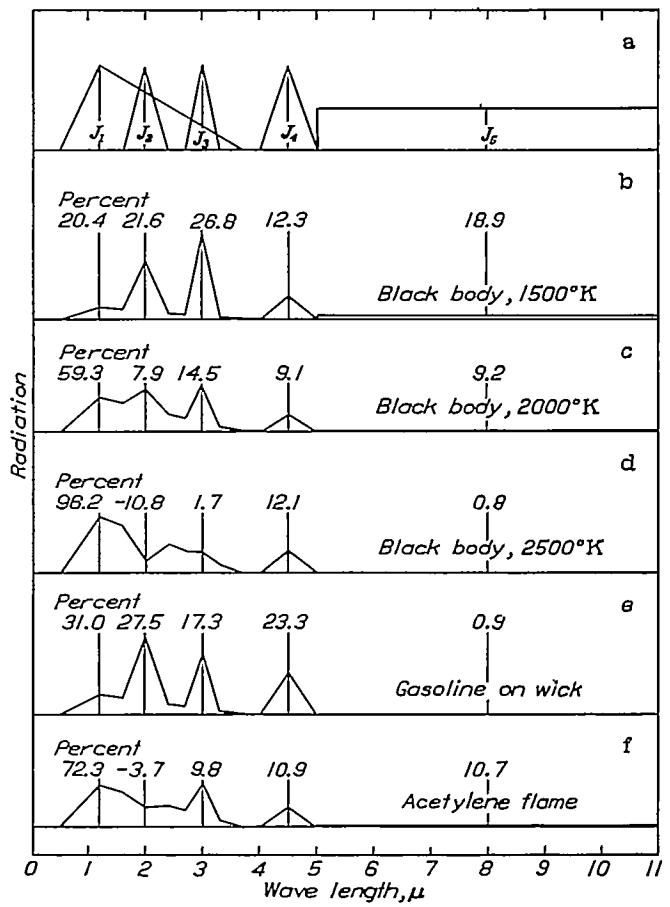

FIGURE 6.—Conventionalized spectra. Black-body and highly luminous flames

figure 5a from data in the Smithsonian Physical Tables and the distribution for 2,500° K. is reproduced in figure 5b to show its close similarity to the radiation from incandescent carbon particles in the spectrum (reference 19) of a highly luminous acetylene flame.

Carbon dioxide and water vapor are characterized by banded spectra. The location of the maxima (reference 20) for the more prominent bands are shown on the scales e and f (fig. 5) and the character of the energy distribution in these bands is indicated by the typical spectra b (reference 19), c and d (reference 21). The triangles J_2 and J_3 were set up to simulate the com-

bined bands of CO_2 and H_2O near 2μ and 3μ, respectively; J_4 represents the very intense band of CO_2 between 4μ and 5μ, and J_5 the numerous bands of H_2O scattered beyond 5μ.

Having thus assumed the spectral regions in which the bulk of the radiation is expected for the flames examined, the next step is to determine from the observations through the filters the relative amounts of energy in these regions for the different flames.

The fraction of the energy emitted in any J region that will pass a given filter can be calculated from the transmission curve for the filter in that region. The total reading for a given filter will be the sum of all such fractions for the filter, thus:

$$p=0.575J_1+0.410J_2$$
$$r=0.759J_1+0.891J_2+0.101J_3$$
$$q=0.890J_1+0.922J_2+0.628J_3+0.046J_4$$
$$m=0.912J_1+0.929J_2+0.840J_3+0.696J_4+0.088J_5$$
$$f=0.940J_1+0.940J_2+0.940J_3+0.940J_4+0.768J_5$$

where p, r, q, m, and f are the readings obtained from any source through pyralin, red, quartz, microscope cover glass, and fluorite filters, respectively. These 5 simultaneous equations were solved for the 5 values of J in terms of the radiation readings, thus:

$$J_1=4.252p-2.358r+0.417q-0.033m+0.004f$$
$$J_2=-3.524p+3.307r-0.585q+0.046m-0.005f$$
$$J_3=-0.866p-1.553r+2.027q-0.158m+0.018f$$
$$J_4=0.184p+0.540r-2.277q+1.878m-0.215f$$
$$J_5=-0.057p+0.078r+0.511q-2.120m+1.545f$$

In comparing radiation from different sources and under different conditions, J_1 to J_5 are expressed as percentages of the total radiation, ΣJ. This basis was used in presenting the conventionalized spectra in figures 6 and 7.

Figure 6 shows the application of the analysis to black-body radiation and to the highly luminous flames. For such flames J_1 has a positive value of considerable magnitude, the highest occurring for the black-body at 2,500° K. where 96 percent of the energy is in J_1. This is the condition which J_1 was originally set up to simulate, as temperatures of the order of 2,500° K. were anticipated in the engine. However, even here a single triangle can only roughly represent black-body energy distribution and as the temperature changes it becomes more and more inadequate. At lower temperatures, emission in the longer wave lengths is relatively stronger and appears more prominently in the other conventionalized regions, giving very distorted spectra. It is evident, however, that flames strongly incandescent with carbon yield fairly high values of J_1.

In all the transparent flames of figure 7, J_1 is small and negative, which indicates that incandescent carbon is unimportant as a source of energy in these flames. The consistently negative values (physically impossible) are probably caused by failure of the conventionalized bands to represent accurately the actual flame spectra in the shorter wave lengths.

Regions J_2 and J_3 were set up to represent combined radiation from H_2O and CO_2 but comparison of spectra b and c (fig. 7) indicates that they are very largely characteristic of H_2O radiation, CO_2 contributing only slightly in these regions.

It will be noted that the spectrum (fig. 7b) of the hydrogen flame, which yields only water vapor as a final combustion product, shows a very considerable amount of energy in the region J_5, which was set up

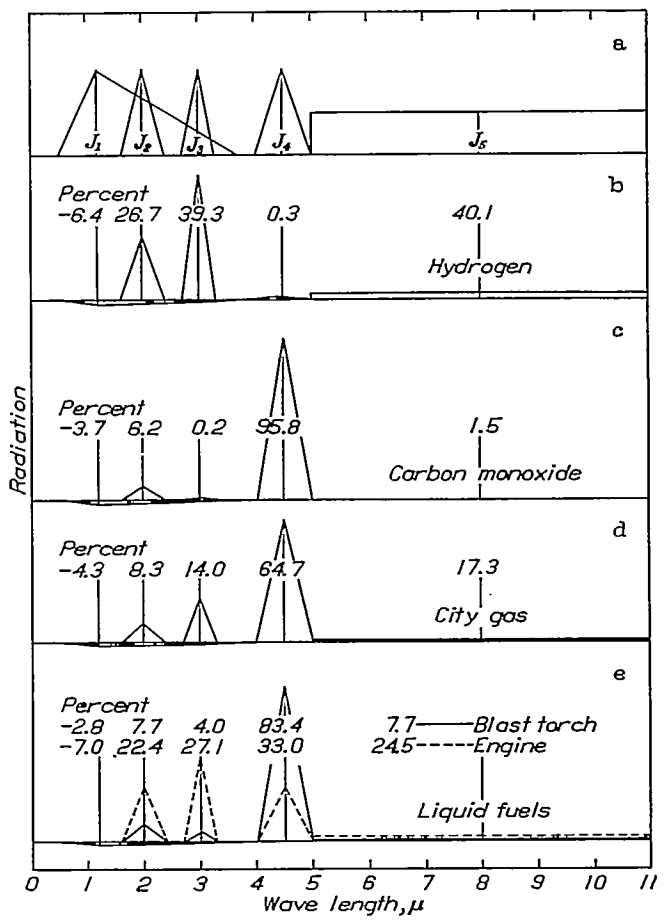

FIGURE 7.—Conventionalized spectra. Nonluminous and engine flames.

to simulate the numerous bands due to water vapor beyond 5μ; the amount of energy in J_4, however, is negligible. Conversely, the spectrum (fig. 7c) of the CO flame, which yields only CO_2 as a final product, shows a high value of J_4, which was erected to simulate the intense CO_2 band between $4\ \mu$ and $5\ \mu$, while J_5 is negligible. Apparently these two spectral regions distinguish sharply between radiation from H_2O and CO_2 as was anticipated. The fact that energy disappears almost completely in one region or the other when the substance radiating in that region is absent from the flame indicates that the choice of shapes and locations for J_4 and J_5 was particularly fortunate.

As would be expected, the spectra d and e (fig. 7) for complex fuels, producing both H_2O and CO_2 as combustion products, show values of J_2 to J_5 intermediate between those for the simple fuels. Thus, the liquid fuels burned in the torch produce a spectrum very much like that for the CO flame but showing slightly more energy in the J_2, J_3, and J_5 regions characteristic of water vapor, and slightly less in the CO_2 region J_4. The flame of city gas shows a further rise in energy in the water-vapor regions at the expense of the J_4 band of CO_2, while radiation from water vapor becomes

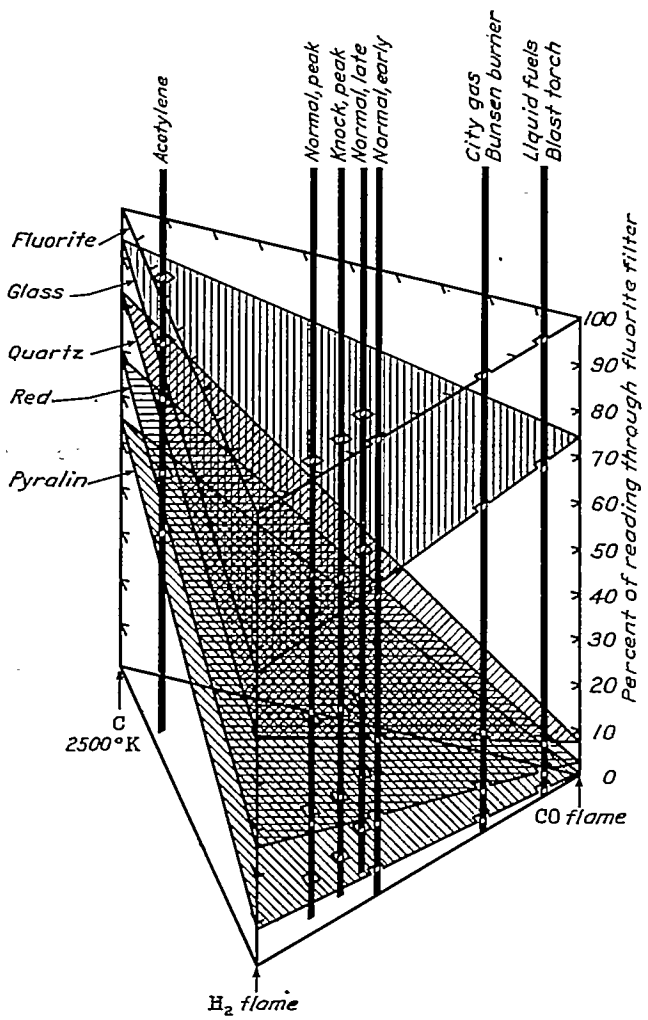

FIGURE 8.—Diagram for analyzing spectral distributions.

relatively even more prominent in the typical spectrum for the engine flame. The changes in energy are so consistent for all of the flames and spectral regions involved as to suggest that, quantitatively as well as qualitatively, differences between these composite flames might be explained solely by differences in the relative intensity of the radiation from H_2O and CO_2, each substance emitting with its characteristic spectral distribution as exhibited in the flames of the simple fuels, H_2 and CO.

If this is the case, then a similar consistency must exist for the relative filter readings from which the values of J for the several flames were derived. Although the filter readings are less sensitive than the J values to shifts in the relative potency of H_2O and CO_2 as radiators, their use would eliminate errors due to inaccuracies in determining filter transmissions and in setting up a conventionalized spectrum.

Graphical analysis.—The diagram in figure 8 was devised as a means of interpreting relative filter readings directly in terms of the relative intensity of the radiation from the three primary sources—incandescent carbon, carbon dioxide, and water vapor.

If a flame burning CO, and thus producing only CO_2 as a combustion product, is observed through each of the filters in turn; and if the energies transmitted by filters B, C, D, and E are each expressed as percentages of the energy transmitted by F, the result will be a set of values, arbitrary to be sure, but nevertheless characteristic of the spectral distribution of radiation from CO_2. With appropriately chosen filters, quite a different set of values will be obtained if a hydrogen flame, producing only H_2O as a product, is observed; and a still different set will be secured from observations on incandescent carbon. Three such sets of values have been taken from table I and plotted on the three vertical edges of the equilateral triangular prism in figure 8. On each edge there is thus a value for each filter, the three points for any given filter defining a plane which cuts through the prism and constitutes a locus for all values that would be obtained with that filter in observing composite flames meeting the conditions required for exact analysis by this method, namely, (1) that the three principal radiators emit in the composite flame with the spectral distributions assigned to them on the axes, and (2) that radiation from other sources and selective absorption be negligible in amount. Thus, each vertical line piercing the prism will represent such a composite flame, its spectral distribution being defined in terms of relative filter readings by the intercepts of the several planes on the line, and the relative intensity of the radiation from its three constituent radiators will be shown by the proximity of the line to their respective axes on the edges of the prism, i.e., the top and bottom surfaces of the prism are plots on triangular coordinates of the relative intensity of the radiation from incandescent carbon, H_2O and CO_2. In the figure, several strips, on which filter readings for different flames are plotted, have been located where the readings show the minimum total deviation from the corresponding planes. Only one reading on these strips, that for the glass filter on "Normal, Peak", departs from the diagram by more than 2 percent.

The application of this type of analysis to radically different flames demands either that the spectral distributions for the primary radiators remain fixed over a wide range of flame temperatures, depths, densities,

and pressures or that the effects of these factors upon spectral distributions be known so that values used on the axes may be selected to suit conditions in the flames analyzed.

For example, the spectrum of incandescent carbon is practically independent of the concentration of the carbon particles but varies with temperature like that for a black-body. The distribution on the carbon axis should therefore be that for a black-body at the temperature of the carbon particles in the particular flame examined. For flames high in carbon radiation, readings on the flame may serve to indicate the appropriate distribution for the axis, hence the carbon temperature. Thus, the readings for the acetylene flame fit the diagram best when a black-body distribution for about 2,500° K. is plotted on the carbon axis.

Apparently only a small percentage of the radiation from the engine flames is attributable to incandescent carbon—not enough to permit even an approximate estimate of the temperature of the carbon particles by this method. However, the positions of such flames on the diagram are not greatly affected by the distribution on the carbon axis and high accuracy in determining this distribution is therefore not essential.

The fact that 6 of the 9 distributions listed in table I for flames of complex fuels in the engine and burners can be located on the diagram with maximum deviations for any filter of 2 percent (within the limits of error of observation), while 2 of the remaining 3 show maximum deviations of only 4 and 7 percent for a single filter, is circumstantial evidence that spectral distribution of H_2O and CO_2 remain essentially constant in these widely different flames. However, there is a possibility that shifts in distributions of the primary radiators might so compensate or perhaps combine with radiation from other sources or with selective absorption, to produce a distribution that would still fit the diagram although the emitting flame did not meet the two previously mentioned requirements for analysis by this method. More rapid increase in energy in the shorter wave bands as flame temperature rises, and more rapid development of the weaker wave bands as depth or density increase, are possible sources of shifts in the spectral distributions of H_2O and CO_2.

A careful survey through the filters of the radiation from burner flames of different depths burning separately H_2 and CO with O_2 and with air, and similar observations for these simple fuels with air in the engine, would indicate the extent and character of possible variations in the spectral distributions for H_2O and CO_2 over the range of operating conditions of interest. If operating factors are found to produce characteristic effects, there is a possibility that these effects, once evaluated, might be recognized in the spectra of composite fuels, thus yielding indications regarding temperature or concentration of H_2O and CO_2 in the engine. If operating conditions have a negligible effect, then failure of composite flames to fit the diagram must be due to radiation from other sources or to selective absorption, and the chance that flames fitting the diagram do not also meet the conditions for analysis becomes very remote.

The relative intensity of the radiation from water vapor, carbon dioxide, and incandescent carbon in flames, hence the location on figure 8 of flames meeting the requirements for analysis by this method, will be fixed by: (*a*) The relative degree to which radiation from each substance in the flame approaches saturation; (*b*) the relative number of molecules of each substance emitting to the receiver; and (*c*) the relative mean activities of these molecules as radiators.

(*a*) If the depth or density of a flame is increased, its other characteristics remaining unchanged, for example, by adding successive identical burners one behind another, radiation will increase at a decreasing rate until finally, adding another burner will produce no appreciable change. At this point the radiation is said to be saturated. Different depths or densities of flame are required to saturate the radiation from different substances. Thus, if radiation from CO_2 is more nearly saturated than radiation from H_2O in the blast torch flame burning liquid fuels, the greater concentration of both substances when these fuels burn in the engine would result in a relative increase in the radiation from H_2O. This reasoning offers a possible explanation for the relative positions of engine and torch flames on figure 8, but it fails to explain why the Bunsen flame, which has less depth than the torch flame, should also show relatively stronger radiation from H_2O.

(*b*) Relatively numerous incandescent carbon particles undoubtedly account for the strong radiation from carbon in the acetylene flame. What little evidence there is for the presence of incandescent carbon in the engine appears late in the combustion process. The fact that H_2O and CO_2 radiate with about the same relative intensities early and late in the radiating period, might indicate that these two substances are developed simultaneously and in approximately fixed proportions rather than successively, or preferentially, during burning in the engine. Since the proportions of H_2O and CO_2 in the final exhaust products for the engine and for the Bunsen and torch flames are about the same, there seems to be little likelihood that (*b*) could be very influential in causing the different locations of these flames on the diagram.

(*c*) It is possible that an increase in the general level of flame temperature, accomplished, for example, by preheating the charge as occurs during compression in an engine, might increase the radiant activity of one substance in the flame more than that of another, and thus produce a shift in the position of the flame on the diagram. However, there is some uncertainty as

to whether the activity of newly formed molecules in flames is dependent only upon temperature or also upon their condition during the process of formation. One theory (reference 22) attributes the radiation from a flame (burning hydrogen, for example) to the formation at the instant of combustion of "an intensely vibrational system of hydrogen and oxygen"; which, after an indefinitely short period, gives rise to steam, at first in a highly vibrating condition, but finally settling down to a state of "equilibrium" in which molecular activity corresponds with the temperature of the environment. During their transient existence, the intensely vibrational systems may emit a considerable amount of radiant energy which would not, therefore, appear as sensible heat in the steam.

However, whether the radiation in the infrared is purely thermal or partly thermal and partly "chemical", the activity of newly formed molecules of H_2O and CO_2 will probably vary, depending upon the character of the reaction by which they are produced. Thus, CO_2 and H_2O formed by decomposition of primary oxidation products, which have dissipated to their surroundings more or less of their heat of formation, would be expected to contain less thermal energy and probably less "vibrational" energy than CO_2 and H_2O produced by direct oxidation of hydrogen and carbon monoxide molecules.

It seems probable that the relative positions of the engine, the Bunsen, and the torch flames on the diagram might be strongly influenced by (*c*) the varying relative activities of the H_2O and CO_2 molecules in these flames due to their production by different types of reaction. The possibility of obtaining from measurements of infrared radiation some clue to the character of the final reactions producing H_2O and CO_2 in the engine is an interesting one worthy of further study.

Observations through the filters of burner and engine flames extended to include mixtures of the simple fuels, hydrogen and carbon monoxide, would yield information regarding the effects of degree of saturation and general temperature level on the relative potency of H_2O and CO_2 as radiators. With these factors accounted for, conclusions regarding preferential burning and the types of reactions finally producing CO_2 and H_2O could be stated with more confidence.

In view of the large differences in spectral distribution between burner and engine flames and the numerous factors that might be expected to affect spectral distribution, it is rather surprising that distributions remain so nearly constant under widely varying conditions in the engine. Thus, shortly after the flame arrives under a window the relatively small amount of radiation is presumably due to a relatively small number of very newly formed, therefore highly active, molecules. Late in the stroke, radiation with a similarly low total value would presumably be due to relatively numerous molecules that had lost much of their activity through cooling processes. At the peak of the knocking run where the highest values of total radiation were found, both high activity and high concentration would be expected. And yet, for all three of these widely different conditions, spectral distributions are nearly the same. This fact might be taken as further circumstantial evidence that activity and degree of saturation do not greatly affect spectral distributions of H_2O and CO_2; and also that degree of saturation and general temperature level do not materially affect the relative potency of H_2O and CO_2 as radiators.

TOTAL RADIATION

Since energy radiated by the flame in the engine appears to orginate almost exclusviely from molecules of H_2O and CO_2 formed by the combustion process, the "total" radiation (through the fluorite filter) after the flame arrives inder a given window can increase only through an increase in (*a*) the number of such molecules under the window or (*b*) their mean activity as radiators.

Although the number of molecules of H_2O and CO_2 would be expected to increase continuously during combustion in a given element of charge, the number under a given window will be affected also by local variations in the density and depth of the charge under that window. Thus, when the zone of intense reaction which follows the flame front in a normal explosion arrives under window number 30, the rapid liberation of heat causes local expansion which forces some of the products newly formed under the window out into surrounding regions. Since the piston is moving downward during burning there will be a further general expansion which, however, is more than offset, so far as its effect on radiation is concerned, by the accompanying increase in the depth of charge under window 30. It is obvious from the steep descent of the radiation curves beyond their peaks that the gradual increase in the number of molecules due to the downward movement of the piston is far from sufficient to offset the effect of cooling on radiation. In order to reach or maintain the maximum value of radiation, it is therefore necessary that new molecules be formed at a rapid rate under the window.

It seems reasonable to suppose that the maximum activity of a molecule as manifested in the infrared region is attained during, or immediately after its formation, and that thereafter it will rapidly lose activity through radiation and collision with neighboring inert or uncombined molecules until it reaches a condition compatible with the temperature level of the surrounding charge. Unless there is a very marked, and hardly to be expected, increase in the activity of newly formed molecules as combustion progresses—

enough to compensate for the decreasing activity of the growing number previously formed—the mean activity (*b*) will decrease in spite of continued formation of new molecules.

In this connection, it is possible that radiation from the last molecules to form is predominant. If this be so, total radiation at any time in the cycle would depend very largely upon the rate of formation and upon the activity at formation.

In any case, the fact that total radiation for a normal explosion increases in window 30 for about 20° of crank travel after the arrival of the flame can only mean that reactions producing H_2O and CO_2 are continuing for at least this period, and probably longer, after inflammation. This prolonged afterburning would account for previous observations (reference 13) that pressure may continue to rise for a considerable time after inflammation is complete, with evidence of some heat liberation after the pressure has reached a maximum. In this connection it is of interest to note that the exponent of expansion, as determined from the indicator diagram for the normal run, increases rapidly, indicating continued liberation of heat at a decreasing rate until about 35° after top center, when the exponent becomes approximately constant. At about the same time the total radiation in window 30 reaches a maximum, i.e., definite evidence of reaction in the last portion of the charge to burn disappears.

The continuation of reaction at a given point in the cylinder for 20° or so after inflammation does not necessarily require that heat liberation be as rapid near the end as near the beginning of this period; nor does it necessarily conflict with the somewhat shorter period required for the disappearance of oxygen as reported (reference 23) by Withrow, Lovell, and Boyd, but in connection with their data, might indicate that all free oxygen is first combined in intermediate products which are later converted to H_2O and CO_2. It does, however, throw doubt upon the accuracy, for explosions in the engine, of calculations of flame movement or pressure rise based on the assumption that combustion is completed in a narrow flame front.

Variations in total radiation for the knocking condition are in accord with the generally accepted view that fuel knock is characterized by practically simultaneous inflammation throughout the last portion of the charge to burn, accompanied by a rapid rise of pressure to such a height as could exist only locally in the engine cylinder.

During fuel knock, flame arrives in window 30 earlier and radiation reaches a peak sooner after the appearance of flame, indicating not only earlier ignition of the last portion of the charge to burn but also more rapid reaction following inflammation than in the normal explosion. It is obvious that radiation for a single knocking explosion would show a steeper rise and a higher and sharper peak than the experimental curve, which is a composite of many explosions in which variation occurred in the timing of the knock. As would be expected, the rapid rise in radiation is followed by a rapid fall as the gas under the window expands to relieve the local high pressure in the detonation zone. After uniformity in pressure has been reestablished in the cylinder, both radiation and pressure curves for the knocking run are found below those for the normal run, indicating a greater loss of energy from the highly active and concentrated charge involved in the knock. This loss doubtless accounts for the higher cylinder temperatures and lower power which are known to accompany severe fuel knock.

Under window 6 the expansion accompanying the arrival of the zone of most rapid reaction is followed by recompression as the zone proceeds through the remainder of the charge. This recompression is accompanied by a movement under the window of charge driven back toward the spark plug by the continued expansion in the advancing zone. Thus, the element of charge observed when radiation is a maximum is not the same element that was observed at inflammation but one reached by the flame later in its travel. These conditions probably account for the somewhat longer period of increasing total radiation in window 6, 25° as compared to 20° for window 30 where there is no recompression and little or no gas movement.

CONCLUSIONS

Nearly all the energy radiated by the flame in an engine is in the infrared portion of the spectrum and is apparently emitted almost exclusively by water vapor and carbon dioxide formed in the combustion process, radiation from incandescent carbon being relatively very weak.

In a normal explosion, radiation from a given element of charge begins to increase upon arrival of the visible flame and continues to rise for about 20° of crank travel thereafter, indicating that reactions producing water vapor and carbon dioxide persist for at least this period and probably longer after inflammation.

When fuel-knock occurs, flame appears earlier in the region remote from the spark plug and radiation reaches a maximum much sooner after the appearance of flame. This phenomenon indicates not only earlier ignition of the last portion of the charge to burn but more rapid reaction following inflammation than in the normal type of burning.

Measurements of total radiation thus provide a convenient means of determining the effect of engine-operating conditions on the depth of the reaction zone behind the flame front and the duration of combustion in a given element of charge.

Although total radiation varies greatly during the engine cycle and considerably for different engine-operating conditions, spectral distribution shows only

small changes over a wide range of operating conditions. The significance of these small changes is obscured by lack of fundamental data regarding the effects of flame depth, density, temperature, and pressure on the spectral distributions of H_2O and CO_2 and upon the relative potency of these substances as radiators. It is believed that observations through filters of burner and engine flames using as fuels H_2 and CO separately and in known mixtures would provide the basic data required for a more adequate interpretation.

BUREAU OF STANDARDS,
WASHINGTON, D.C., *February 27, 1934.*

REFERENCES

1. Ricardo, H. R.: Some Notes on Petrol-Engine Development. The Automobile Engineer, vol. 17, April 1927. p. 149. Also T.M. No. 420, N.A.C.A., 1927.
2. Glyde, H. S.: Experiments to Determne Velocities of Flame Propagation in a Side Valve Petrol Engine. Jour. Instn. Petroleum Technologists, vol. 16, November 1930, p. 756.
3. Withrow, Lloyd, and Boyd, T. A.: Photographic Flame Studies in the Gasoline Engine. Ind. & Eng. Chem., vol. 23, May 1931, p. 539.
4. Midgley, Thos., Jr., and Gilkey, W. K.: Spectroscopic Investigation of Internal Combustion. Jour. S.A.E., vol. 10, March, 1922, p. 218.
5. Clark, G. L., and Thee, W. G.: Ultraviolet Spectroscopy of Flames of Motor Fuels. Ind. & Eng. Chem., vol. 18, May 1926, p. 528.
6. Clark, G. L., and Henne, A. L.: Ultraviolet Spectroscopy of Engine-Fuel Flames. Jour. S.A.E., vol. 20, February 1927, p. 264.
7. Withrow, Lloyd, and Rassweiler, G. M.: Spectroscopic Studies of Engine Combustion. Ind. & Eng. Chem., vol. 23, July 1931, p. 769.
8. Rassweiler, G. M., and Withrow, Lloyd; Emission Spectra of Engine Flames. Ind. & Eng. Chem., vol. 24, May 1932, p. 528.
9. Withrow, Lloyd, and Rassweiler, G. M.: Absorption Spectra of Gaseous Charges in a Gasoline Engine. Ind. & Eng. Chem., vol. 25, August 1933, p. 923.
10. Rassweiler, G. M., and Withrow, Lloyd: Spectrographic Detection of Formaldehyde in an Engine Prior to Knock. Ind. & Eng. Chem., vol. 25, December 1933, p. 1359.
11. Midgley, Thos., Jr., and McCarty, H. H.: Radiation Characteristics of the Internal-Combustion Engine. Jour. S.A.E., vol. 14, February 1924, p. 182.
12. Hershey, A. E.: Flame Radiation and Temperature Measurements on an Internal-Combustion Engine. Ind. & Eng. Chem., vol. 24, August 1932, p. 867.
13. Marvin, C. F., Jr., and Best, R. D.: Flame Movement and Pressure Development in an Engine Cylinder. T.R. No. 399, N.A.C.A., 1931.
14. Steele, Sydney: An Investigation of Infra-Red Radiation from an Engine. Nature, vol. 128, August 1, 1931, p. 185.
15. Steele, Sydney: Infra-Red Radiation from an Otto-Cycle Engine. Ind. & Eng. Chem., vol. 25, April 1933, p. 388.
16. Dickinson, H. C., and Newell, F. B.: A High-Speed Engine Pressure Indicator of the Balanced Diaphragm Type. T.R. No. 107, N.A.C.A., 1921.
17. Fowle, F. E.: Smithsonian Physical Tables (7th edition), 1927, p. 248.
18. Garner, W. E.: Radiant Energy from Flames. Ind. & Eng. Chem., vol. 20, October 1928, p. 1009.
19. Coblentz, W. W.: Selective Radiation from Various Substances IV. Bulletin of the Bureau of Standards, vol. 9, 1913, p. 99.
20. Bailey, C. R., and Kun-Hou Lih: The Infra-Red Emission Spectra of the Bunsen and Allied Flames. Trans., Faraday Soc., vol. 25, 1929, p. 31.
21. Bailey, C. R., and Kun-Hou Lih: The Infra-Red Emission Spectra of the Separated Cones in the Methane and Bunsen Flames. Trans., Faraday Soc., vol. 25, 1929, pp. 34, 35.
22. Bone, W. A., and Townend, D. T. A.: Flame and Combustion in Gases. Longmans, Green & Co., Ltd., 1927, p. 207.
23. Withrow, Lloyd, Lovell, W. G., and Boyd, T. A.: Following Combustion in the Gasoline Engine by Chemical Means. Ind. & Eng. Chem., vol. 22, September 1930, p. 945.

TABLE I.—RELATIVE ENERGY TRANSMITTED BY FILTERS FROM VARIOUS SOURCES

Source	Energy through filters, percent of energy through fluorite				
	Fluorite	Glass	Quartz	Red	Pyralin
Engine, normal, early	100.0	60.5	34.5	10.0	0.0
Engine, normal, peak	100.0	75.0	45.0	21.0	7.5
Engine, normal, late	100.0	70.5	39.0	20.5	9.0
Engine, knock, peak	100.0	69.5	41.0	21.5	8.5
Hydrogen in laboratory blowpipe	100.0	64.5	50.5	20.0	8.0
Carbon monoxide in laboratory blowpipe	100.0	74.0	7.5	3.0	.5
City gas in laboratory blowpipe	100.0	68.0	17.0	0.0	1.0
City gas in Bunsen burner	100.0	71.0	21.5	9.0	2.5
Liquid fuels [1] in blast torch	100.0	72.0	12.0	5.5	2.0
Gasoline on wick	100.0	90.0	69.0	53.0	31.0
Acetylene in von Schwarz burner	100.0	86.0	73.5	57.0	43.5
Black-body at 1,500° K	100.0	79.0	61.0	41.5	22.5
Black-body at 2,000° K	100.0	87.5	75.5	58.0	40.5
Black-body at 2,500° K	100.0	93.5	82.0	67.5	54.0

[1] Benzol and blends with gasoline.