A MOLLIER DIAGRAM FOR THE INTERNAL-COMBUSTION ENGINE

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The limitations of thermodynamics as a tool for studying chemical reactions have been so adequately emphasized in college courses in physical chemistry as to have convinced many automotive engineers that thermodynamic study of the combustion process in an internal-combustion engine can yield no really useful results, that the only way to study knock or combustion mechanism, for example, is to focus attention on experimental studies of rate. The inherent complexity of the thermodynamics of a combustion process carried out at varying total pressure and volume and at such high temperatures as to cause ten different molecular species to be present in appreciable proportions has constituted a further brake on the development of this tool, and the misleading conclusions drawn from over-simplified attacks of the problem have not helped.

Although no claim is made that a thermodynamic study will by itself solve such a problem as engine knock, nevertheless the high temperature level of the combustion process as encountered in engines makes chemical equilibrium more than usually important in relation to rate—and mechanism—studies. Whether a certain combustion process is initiated in a far corner of the chamber ahead of the flame front will depend on the temperature and pressure existing there, which in turn are susceptible of prediction by a thermodynamic treatment of what has occurred in the rest of the chamber. It will be shown that the inherent complexity of a precise thermodynamic treatment of combustion may be reduced to a simple graphical procedure, which will be illustrated by the calculation of the performance of a conventionally "ideal" engine, and by the study of flame movement, temperature, and pressure in an unconventionally "ideal" engine in which combustion occurs during piston movement.

The steam engineer has long been familiar with the use of diagrams representing the thermodynamic properties of steam, and with the advantages of such diagrams for clarifying and simplifying the analysis of the operation of steam power-generating equipment. In the field of internal-combustion engine operation there is the same possibility of use of diagrams. If the quantity and atomic composition of a gaseous mixture are specified, the phase rule tells us that the specification of two properties is sufficient to fix completely all the other thermodynamic properties of the mixture. Consequently all the significant properties can be put on a single plot analogous to the Mollier diagram for steam; and the tedious allowance for variation in specific heat with temperature and for shift in chemical equilibrium can be made *once and for all* during the construction of the chart. The solution of such problems as the determination of the maximum possible efficiency of a particular engine cycle is then as simple as the use of the Mollier diagram by the steam engineer. Important differences exist, however, between the plot for steam and for the working fluid of an internal-combustion engine. In the latter there must be a separate plot for each air–fuel mixture ratio of interest. Furthermore, the mixture prior to combustion is in physical but not chemical equilibrium, and separate charts are necessary for the unburned and the burned mixture. The combustion process itself involves a transfer from one chart to the other.

DIAGRAMMATIC REPRESENTATION OF THE WORKING FLUID

A survey of the literature proved that the idea of representing equilibrium products of combustion on diagrams was not new. In 1932 Pflaum (14) presented such diagrams plotted with enthalpy and entropy as coördinates; the omission of lines of constant internal energy introduced the necessity for trial and error in many calculations of interest. Pflaum also used thermal data which have since been improved enormously in accuracy, and made inadequate allowance for the complexity of the dissociation process. Subsequent to the completion of most of the present calculations Tanaka and Awano (17) and Kühl (10) have published additional diagrams. Tanaka and Awano followed Pflaum's example in the use of old thermal data, in allowance for dissociation, and in presentation of results on the enthalpy–entropy plane. Kühl, however, used modern fundamental data and made allowance for all important molecular species formed due to dissociation. Although diagrams of the types presented by these authors are of enormous assistance in the calculation of an engine cycle, all of them are characterized by the necessity for a considerable amount of algebraic calculation and of trial-and-error methods of solution.

The thermodynamic properties of interest are temperature T, entropy S, enthalpy H, internal energy E, pressure P, and volume V. Since $H = E + PV$ one of these latter four could in theory be omitted, but experience in the solution of various combustion problems indicates that freedom from trial and error necessitates including them all. The calculation of the relations among these six properties requires certain basic thermodynamic data: namely, certain equilibrium constants as functions of the temperature, certain heats of reaction, and the specific heats of the various molecular species as functions of the temperature. The data need not be directly available in just these forms; it is sufficient if these data or certain other data (for example, entropies), related to them by any of a number of thermodynamic expressions, are obtainable.

In recent years the technique of calculating the specific heats of gases over a temperature range extending down to absolute zero has been perfected; the calculations have been carried out for a number of gases, and the results have been published in a series of papers by Johnston and his coworkers (1, 4, 5, 6, 7, 8), and in papers by Kassel (9) and Gordon (2), all of which appeared in the years 1933, 1934, and 1935. Knowledge of the specific heats permits the calculation of entropies; the results of these calculations are given in the papers mentioned. The high precision of the fundamental spectroscopic data used in these calculations and the excellent agreement between these new specific heats and those obtained from recent and refined experimental determinations substantiate the belief that no significant revisions of these values need be expected in the future.

The sources of the internal energy and entropy values for the various molecular species involved in the present work, and the methods used in evaluating changes in internal energy and entropy for the various chemical reactions involved, are summarized in tables 1A and 2A of a previous paper by R. L. Hershey and the present authors (3). The equilibrium constants used are those summarized by Lewis and von Elbe (12).

The fuel chosen as adequately representative of gasoline is octane,[1] C_8H_{18}; its hydrogen–carbon ratio, rather than its molecular weight, is its significant characteristic for the present purpose. The air–fuel ratios chosen for study were three, corresponding to a rich mixture (85 per cent of the theoretical air or 117.6 per cent of the theoretical fuel), a mixture in proportion for perfect combustion, and a lean mixture (110 per cent of theoretical air, or 90.9 per cent of theoretical fuel).

The first problem in the construction of a chart of the burned gases is the determination of the composition of a mixture containing carbon, hydrogen, oxygen, and nitrogen, which is in chemical equilibrium at the conditions specified. Because of the high temperature attained in internal-combustion engines, the number of different kinds of molecules existing in important proportions in the products is much larger than in free-burning flames in furnaces. Preliminary calculations indicated that the products

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[1] It is recognized that the trend in motor fuel quality is towards lower proportions of paraffinic stock; the difference between $(CH_{2.25})_x$ and $(CH_2)_x$ is unknown, but for most thermodynamic calculations it is believed unimportant.

would contain carbon dioxide, water vapor, nitrogen, oxygen, carbon monoxide, hydrogen, OH, H, O, and nitric oxide, the relative importance of the various species depending on the temperature, pressure, and mixture ratio. The method of using data on equilibrium constants to calculate the composition of the products is presented in the reference previously cited (3).

Typical results of such calculations for a total pressure of 800 lb. per square inch on the system are presented in figure 1, showing the effect of temperature on gas composition for each of three mixture ratios (three plots on left). The importance of NO and neutral OH, frequently omitted from consideration in flame-temperature calculations, and even of atomic oxygen and hydrogen at the highest temperatures, is apparent from a study of the figure. The right-hand plot of figure 1 shows how a variation in air–fuel ratio affects the composition of the equilibrium mixtures, when the temperature and pressure are fixed at 5400° Rankine (°F. + 460°) and 800 lb. per square inch.

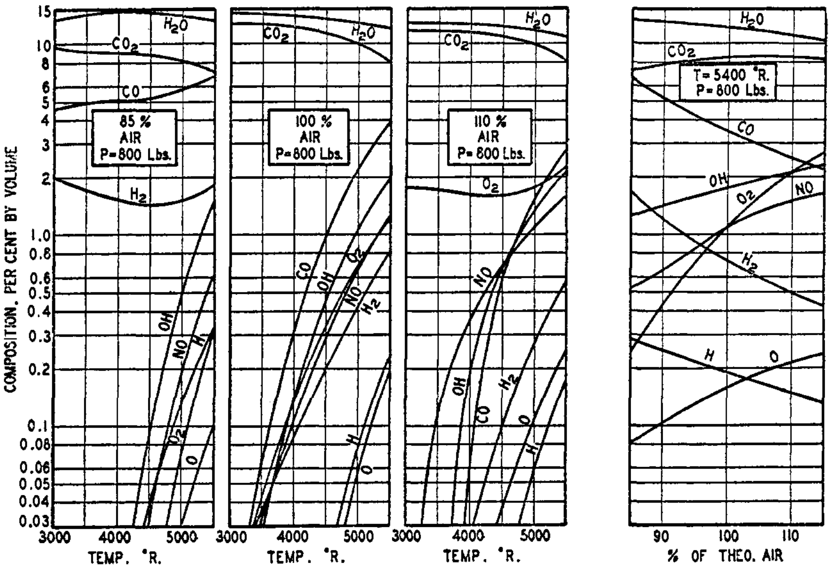


FIG. 1. Effect of air–fuel ratio and temperature on composition of combustion products

With compositions determined for various temperatures and pressures, the next step is the calculation of the various thermodynamic properties fixed by the state of the system, and the presentation of the results on diagrams, one for each mixture ratio under consideration. One such diagram is presented in figure 2, for a rich mixture containing 85 per cent of the required air for complete combustion (not far from the maximum-power mixture ratio). The material basis for the diagram is the quantity of material (C, H, O, N, in the ten molecular arrangements already mentioned) which contains nitrogen and oxygen equivalent to 1 lb. of air. For figure 2 the weight of carbon plus hydrogen associated with the 1 lb. of oxygen plus nitrogen is 0.0782 lb. Other similar diagrams have been constructed for the lean and the "theoretical" mixture (3).

The thermodynamic properties represented on the diagrams, their symbols, units of measurement, and bases, follow: (*1*) Temperature, T, in degrees Rankine or degrees Fahrenheit + 460°; almost horizontal solid lines at 200-degree intervals. (*2*) Volume, V, in cubic feet; diagonal solid lines. (*3*) Pressure, P, in pounds per square inch; diagonal dashed lines of gentler slope than the volume lines.

(*4*) Internal energy, E, in B.t.u., the vertical scale of the diagram. This property is the heat effect attending the conversion, at constant volume and consequently without work, of a mixture from its given condition of composition and temperature to carbon dioxide, water vapor, oxygen, and nitrogen at the base temperature of 60°F. (520° Rankine). Although any path may be chosen in the calculations underlying the construction of the chart, that one simplest to visualize involves cooling the mixture at constant volume to the base temperature, thereby evolving what may be called the sensible internal energy content, E_S, of the mixture, then allowing the mixture to react at constant temperature and volume to produce only carbon dioxide, water (vapor), nitrogen, and oxygen. The heat evolved along this second leg of the path, the internal energy of combustion at the base temperature, is added to the first quantity to give E.

(*5*) Enthalpy or total heat, H, in B.t.u.; almost horizontal dashed lines found only in the upper portion of the diagram. By definition, $H = E + PV\,(144/778)$.

(*6*) Entropy, S, in B.t.u. per degree Rankine, the horizontal scale of the diagram. Calculated by assigning zero entropy to carbon dioxide, water vapor, oxygen, and nitrogen at 14.7 lb. per square inch each and 60°F. (520° Rankine). The entropy of any other gas at the base temperature is then equal to its entropy of formation from the preceding constituents of zero entropy. For further quantitative consideration of the entropy concept, essential to an understanding of the technique of calculating the diagrams but not to their intelligent use, the reader is referred to any standard textbook on thermodynamics.

(*7*) Sensible internal energy, E_S, in B.t.u. This property already has been defined in the discussion of E. In the lower temperature range of figure 2, where the chemical composition of the mixture is fixed by tem-

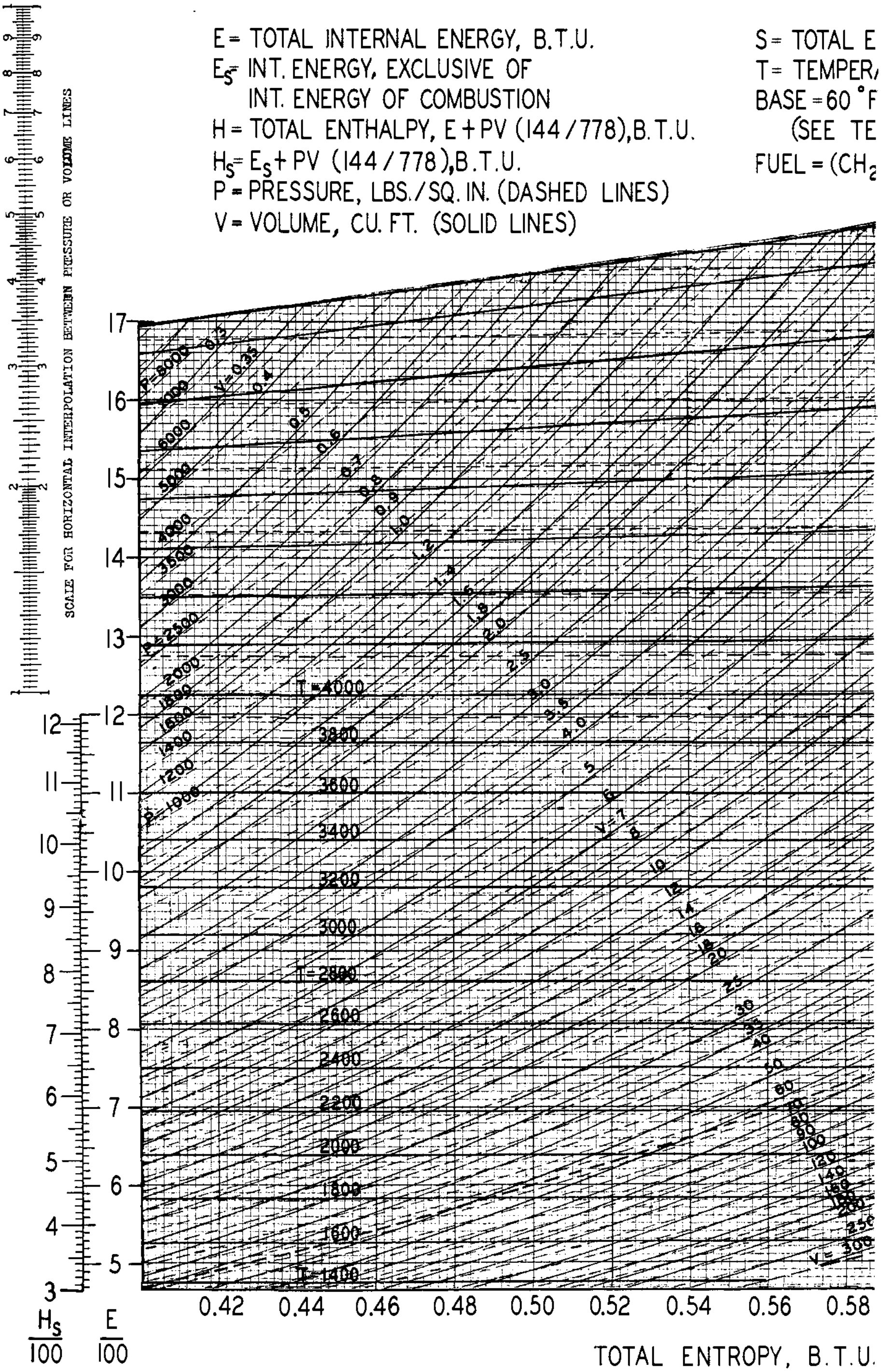
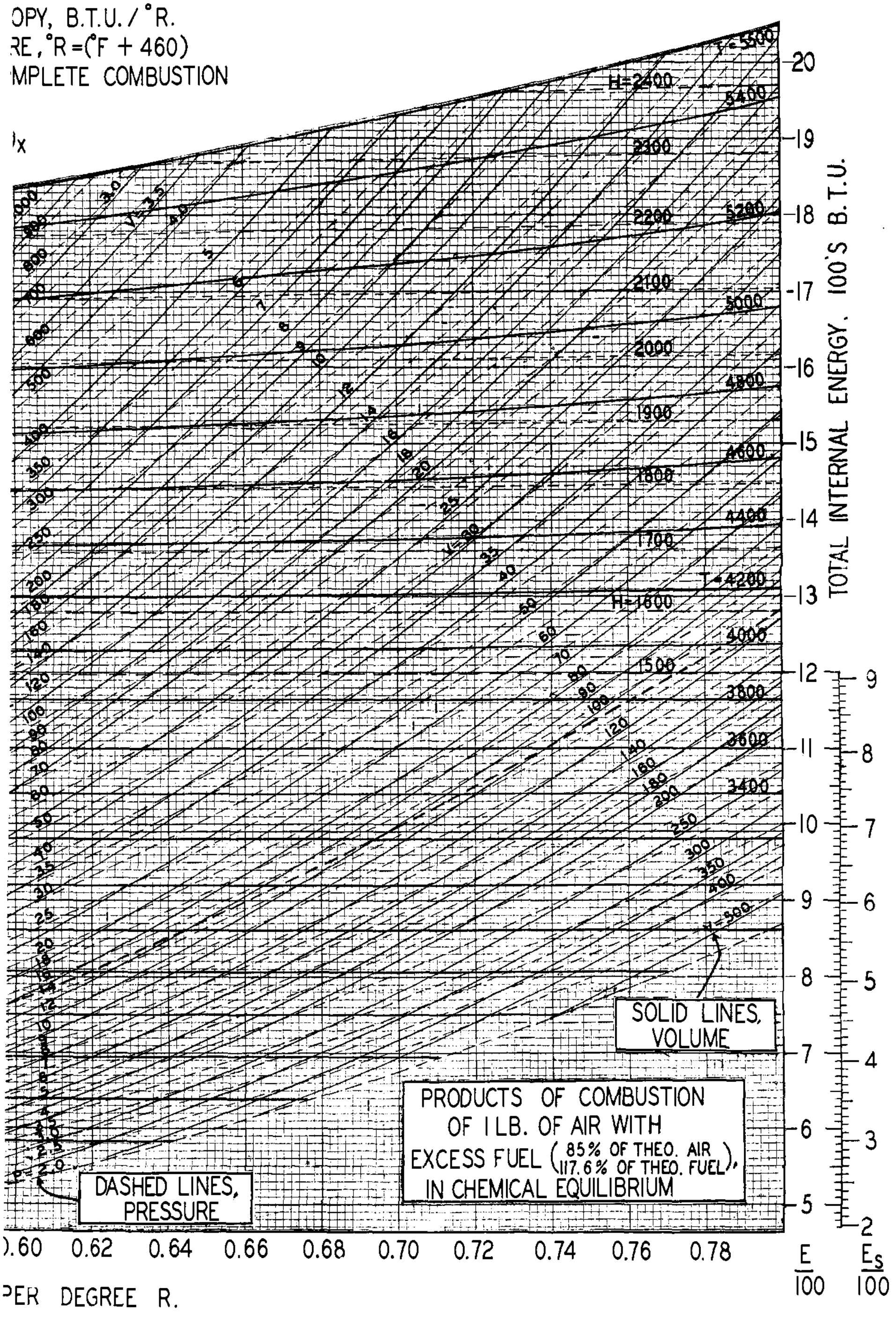


FIG. 2. Thermodynamic properties of the products of com



tion of 1 lb. of air with excess fuel, in chemical equilibrium perature alone,[2] the value of E_S is determined completely by E. Consequently the sensible internal energy is given by the vertical scale on the lower right margin of the diagram, relating E_S and E. The difference between E and E_S is the internal energy of combustion of the carbon monoxide and hydrogen present by virtue of the insufficiency of air.

(*8*) Sensible enthalpy or sensible heat, H_S, in B.t.u. By analogy with H, $H_S = E_S + PV$ (144/778). Like E_S, H_S is a unique function of E at low temperatures and consequently representable by a scale which appears in the lower left margin of the diagram.[3]

The illustration of the uses of figure 2 in the solution of various problems of combustion in engines must await a discussion of the corresponding diagram representative of the unburned mixture. The mixture prior to combustion consists in part of products of combustion of the preceding cycle, and in part of a mixture of fresh fuel vapor and air. The two parts are, of course, identical in weight percentage of C, H, O, and N. In order that the diagram presenting the properties of the unfired gas shall be on the same material basis as that previously discussed, the basis will again be 1 lb. of oxygen plus nitrogen, and 0.0782 lb. of carbon plus hydrogen. Simple stoichiometric calculations show that this would form 0.0392 lb.-mole if present as combustion products (nitrogen, carbon dioxide, water vapor, carbon monoxide, hydrogen) or 0.0354 lb.-mole if present as air and octane vapor. Let the weight fraction of the mixture existing as unpurged combustion products of the previous combustion cycle be represented by f, the weight fraction brought in as fresh air and octane vapor by $(1-f)$. Then the diagram to be constructed representative of the unfired gas must correspond to a number of moles given by $0.0392f + 0.0354\ (1 - f)$, or $0.0354 + 0.004f$. The base temperature is 60°F., as before, and the desired thermodynamic quantities, in general, are the same. However, since the diagram is to be used to calculate adiabatic changes that are physically but not chemically reversible, the entropy basis must be defined to omit chemical contributions to entropy; zero entropy is therefore assigned to each constituent at 60°F. (520° Rankine) and 14.7 lb. per square inch. The total internal energy E is, as before, the sum of two quantities, the sensible internal energy E_S and the internal energy of combustion E_C at the base temperature (fuel and products both as vapor). The former is the heat effect attending the constant-volume cooling to the base

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[2] Because the only chemical reaction possible is the water-gas reaction, $CO_2 + H_2 \rightarrow CO + H_2O$, which is unaffected by pressure.

[3] It is to be noted that $(H - H_S)$ is equal to $(E - E_S)$ and, consequently, to the E of combustion at the base temperature, not to the H of combustion. This is a consequence of the choice of basis of the plots, which makes E_S, not H_S, zero at the base temperature.

temperature without chemical reaction. Since both the number of moles and the specific heat are very insensitive to variations in f, E_S may be evaluated for some mean value of f and used with negligible error even though f varies considerably from the value used.

The internal energy of combustion E_C, on the other hand, changes greatly with f. For the rich mixture under discussion E_C will be $(1 - f)$ times the internal energy of combustion of 0.0782 lb. of octane, plus f times the internal energy of combustion of any hydrogen and carbon monoxide in the products of combustion. Taking the lower heat of combustion of octane at constant volume at 60°F. as 19,270 B.t.u. per pound and of the carbon monoxide and hydrogen associated with the products of combustion of 1 lb. of air as 300 B.t.u. ($E - E_S$ as read from figure 2), the quantity E_C equals $300f + (1 - f)19{,}270 \times 0.0782$. Since E_S, but not E, is substantially independent of the fraction f of unpurged combustion products in the system, the diagram representative of the unfired mixture, figure 3, is made with vertical scales of sensible internal energy E_S. The total value E is obtained by adding to E_S the internal energy of combustion, readily calculated when f is known.

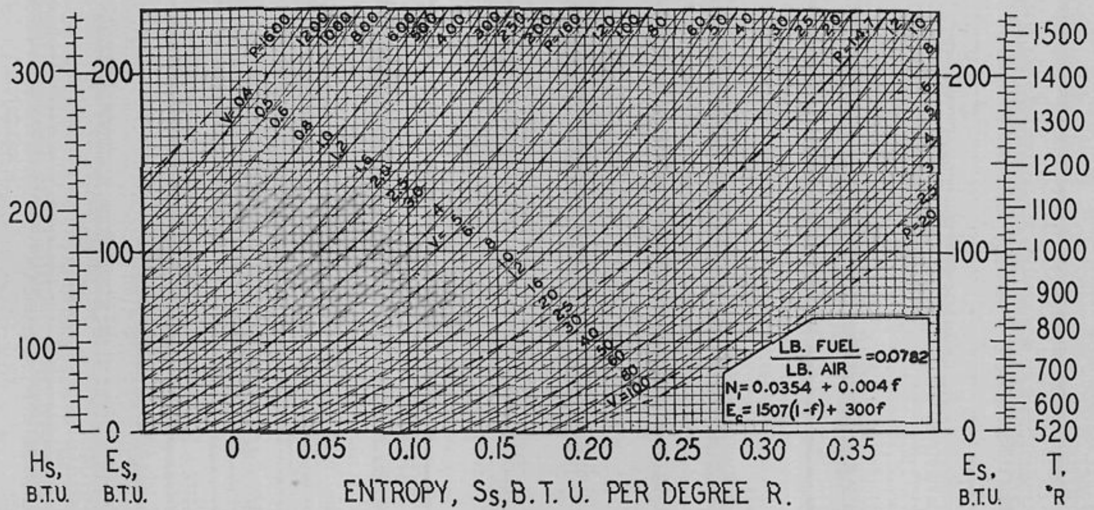

FIG. 3. Thermodynamic properties of a rich mixture of air and octane vapor, plus *unpurged combustion products, before firing.* E_S = internal energy exclusive of internal energy of combustion, in B.t.u.; H_S = enthalpy = $E_S + PV$ (144/778) in B.t.u.; S^S = entropy exclusive of entropy of combustion; P = pressure in pounds per square inch (dashed lines); V = volume in cubic feet (solid lines); T = temperature in degrees Rankine (= °F. + 460°); base = 60°F. (see text); fuel = octane, C_8H_{18}; f = weight fraction of charge left in clearance volume (see text).

Since in the unfired mixture no chemical changes are occurring, the internal energy E_S is a unique function of T. Accordingly a scale on the right of the diagram relates these quantities. Similarly a scale on the left relates H_S (= $E_S + PV$ (144/778)) and E_S.

The method of using figure 3 representing the unfired gas, referred to hereafter as the "unburned" chart, and figure 2, referred to as the "burned" chart, will now be illustrated by examples.

EFFICIENCY AND M.E.P. OF IDEAL OTTO CYCLES

Let it be desired to study the thermodynamic limitations on power output and mean effective pressure when an Otto cycle engine is operated using octane with 85 per cent of theoretical air, with a compression ratio of 6, the intake and exhaust manifold pressures atmospheric, and the fuel–air mixture leaving the carburetor completely vaporized and at 90°F. Figure 4 represents an indicator diagram for the ideal cycle. Reference to the successive states of the system will be made by appending subscripts corresponding to the numbered points on the diagram. Because of the relation of a cycle to that preceding it, it will be necessary temporarily to assume knowledge of two quantities, and these are most conveniently T_1, the temperature of the mixture of fresh and unpurged gas prior to compression, and f, the fraction of the gas from the preceding cycle left in the cylinder prior to the intake stroke. These will be assumed to be 650° Rankine (190°F.) and 0.05, respectively; they may be checked readily later.

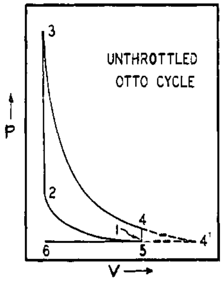

FIG. 4. Ideal indicator diagram for unthrottled Otto cycle

Step 1-2, compression of the charge. On figure 3 the right-hand scale indicates that, when $T_1 = 650°$ Rankine, E_{S1} equals 26 B.t.u. On the diagram locate the condition 1, corresponding to $E_{S1} = 26$ and $P_1 = 14.7$ lb. per square inch (heavy dashed line). From the diagram read $V_1 = 16.8$ cu. ft. Since step 1-2 is an adiabatic reversible compression and consequently isentropic, move vertically on the diagram from V_1 to V_2 ($= 16.8/6 = 2.8$ cu. ft.). From the diagram, read $E_{S2} = 138$ B.t.u.

Step 2-3, adiabatic combustion at constant volume, $V_3 = V_2 = 2.8$. At point 2 the total internal energy E_2 equals the sum of the sensible value E_{S2} and the chemical value of E_{C2}, which latter value is $1507\ (1 - f) + 300f = 1507 \times 0.95 + 300 \times 0.05 = 1447$. Then the total $E_2 = 138 + 1447 = 1585$ B.t.u. Since combustion occurs at constant volume and is adiabatic, there is no change in internal energy. Therefore, $E_3 = 1585$ and $V_3 = 2.8$, permitting the location of a point on the diagram representing the combustion products in chemical equilibrium, figure 2. For convenience in subsequent use of figure 2, the entropy S_3 will be recorded; it is 0.576.

Step 3-4, adiabatic reversible expansion, therefore isentropic, to $V_4 = V_1 = 16.8$. Move vertically downward along the entropy line $S = 0.576$ of figure 2 from $V_3 = 2.8$ to $V_4 = 16.8$, and read $E_4 = 1010$.

Step 4-5, opening of exhaust valve and release of pressure to atmospheric. Although this step is irreversible, if all pressure drop is assumed localized at the exhaust port, then that portion of the charge remaining in the cylinder may be considered to have undergone an adiabatic reversible expansion, doing work on the gas flowing through the port. The condition of the mixture at point 5 then corresponds to point 4′ on the dotted portion of the diagram, figure 4. Move down vertically on $S = 0.576$ of figure 2 to $P_{4'} = 14.7$ lb. per square inch, the heavy dashed line, and read $E_{4'} = 723$ and $V_{4'} = 66$, and from the scale on the left, $H_{S4'} = 610$. These quantities correspond to an amount of material equal to the whole charge, whereas only the fraction $V_5/V_{4'} = 16.8/66$ or 0.255 of it is left in the chamber.

Step 5-6, expulsion of all but the fraction V_6/V_5 of the remaining gas at constant pressure. This step leaves $V_6/V_{4'}$ or 2.8/66 or 0.0424 of the original charge in the cylinder. This is the fraction f, assumed to be 0.05 at the beginning of the calculation.

Step 6-1, mixing of the unpurged gas f with $(1 - f)$ of fresh fuel–air mixture as the piston moves to bottom dead center. Since this step occurs at constant pressure the total H is constant, and since no chemical reaction is occurring, H_S is constant. Therefore the sensible heat of the unpurged residue (which still corresponds in condition to that at point 4′ where H_S equalled 610) plus that of the entering fresh charge must equal that of the mixture at point 1. From figure 3 a fresh charge at 90°F. (550° Rankine) has an E_S of 6 (right-hand marginal scale) and an H_S of 43 (left-hand marginal scale).

Then

$$H_{S1} = 0.0424 \times 610 + 0.9576 \times 43 = 68 \text{ B.t.u.}$$

From figure 3, when $H_S = 68$, $E_S = 23$, and $T = 640°$ Rankine.

This constitutes a check on the value originally assumed for T_1, namely, 650° Rankine. Although this whole calculation could now be repeated with the better values for T_1 and f, the changes resulting therefrom would be found small; they will be ignored in the present example. The next step is the calculation of thermal efficiency. The work of the cycle is $(E_3 - E_4)$

$-(E_2 - E_1)$ and, since no chemical change occurred between 1 and 2, $E_2 - E_1 = E_{S2} - E_{S1}$. The work is, therefore, $(1585 - 1010) - (138 - 26) = 463$ B.t.u. This work is accomplished by the introduction of $(1 - 0.0424)$ lb. of fresh air and $(1 - 0.0424)\ 0.0782$ or 0.0749 lb. of fresh fuel. Adopting the conventional H of combustion of fuel as the denominator in the expression giving efficiency and using the value 19,240 as the net heat of combustion of octane vapor at constant pressure, one obtains for thermal efficiency,

$$\frac{463}{0.0749 \times 19{,}240} \times 100 = 32.1 \text{ per cent}$$

The mean effective pressure in pounds per square foot is equal to the net work of the cycle in foot-pounds, divided by the displacement volume in cubic feet:

$$\text{M.e.p., in pounds per square inch} = \frac{463 \times 778}{(16.8 - 2.8) \times 144} = 178$$

For more precise calculation of mean effective pressure or volumetric efficiency it is recommended that V_1 be determined by use of the perfect gas law from the known values of T_1, P_1, and N_1 (the number of moles of charge for compression, obtained from f):

$$V_1 = 0.729 N_1 T_1 (14.7/P_1) \tag{A}$$

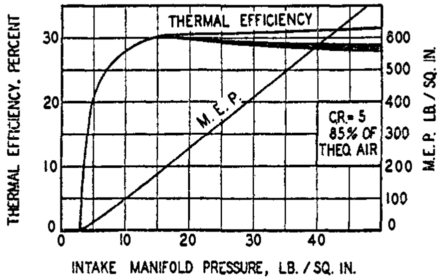

FIG. 5. Effect of intake manifold pressure on the efficiency and mean effective pressure of an Otto-cycle engine

The temperature and pressure at various points in the cycle may, of course, be determined from the charts during the calculation of the efficiency.

The application of thermodynamic-property charts such as figures 2 and 3 has been illustrated elsewhere (3) with numerical examples of the calculation of the performance of various other ideal engine cycles, including throttled, supercharged, variable-cutoff, compression-ignition, and gas turbines. Figure 5, summarizing some of that work, shows the calculated effect of intake manifold pressure, varied by throttling or supercharging, on the thermal efficiency. The efficiency increases rapidly from zero at 3 lb. per square inch where the pumping loop and work-output loop exactly counterbalance. Above atmospheric intake pressure, the efficiency increases slightly with increased supercharging if the cycle is not charged with the work of supercharging. If the latter work is included, the efficiency drops off slightly at high supercharge pressures, the magnitude of the effect depending on the characteristics of the supercharger. (Isothermal and adiabatic supercharger operation, representing the limiting values, are indicated by two lines connected by a shaded area.) The mean effective pressure, on the same basis as the top curve of thermal efficiency, is shown in the same figure. The mean effective pressure is seen to increase substantially linearly with intake manifold pressure.

EFFECT OF FLAME TRAVEL ACROSS THE COMBUSTION CHAMBER

The problem previously considered was simplified to the extent of assuming that combustion took place instantaneously, yielding homogeneous combustion products. Use of the charts will now be made to illustrate the effect, on the pressure–temperature–space–time relations, of the travel of the flame across the combustion chamber. The first example to be considered will be that of combustion occurring at constant total volume (e.g., in a bomb or at top dead center in an engine). Later examples will illustrate the effect of the motion of the piston.

As a flame passes through a confined mass of gas–air mixture the pressure rises continually, the burning of an infinitesimal amount being accompanied by an infinitesimal rise in pressure. Any given element of the gas–air mixture, then, burns at constant pressure or constant enthalpy. As the combustion progresses, both the burned gas behind the flame front and the unburned gas ahead of it are compressed isentropically if no heat is lost. Since flame velocities are low compared to the velocity of sound, the pressure may be assumed uniform throughout the mass. Flame velocities are high, however, relative to the velocities of any eddy currents set up by the passage of the flame, so that mixing should be relatively slight. Furthermore, heat transfer by conduction alone is negligible in the time of passage of flame through a charge. In the limit, then, each element of gas may be assumed to undergo an isentropic compression from its original state as the flame moves towards it, a combustion at constant pressure when the flame reaches it, and a further isentropic compression as the flame moves on into the unburned part of the charge.

A statement of the problem and of the basic assumptions follows: A confined gas–air mixture is ignited and, as the flame is propagated, the total volume is held at a constant value and there is no external heat loss, no mixing, and no heat flow between adjacent elements of gas. Pressure gradients throughout the mass are negligible. The relations to be found are: (*a*) the relation between the mass-fraction burned and the pressure, and (*b*) the temperature distribution through the mass at any time.

NOMENCLATURE

The numerical values of all extensive properties are to be those corresponding to the basis of the property charts.

E_{p_0}, in B.t.u. = initial internal energy of unburned gas–air mixture at the original pressure p_0.

c = mass fraction of the charge burned when the pressure has reached the value p_c.

E_{p_c}, in B.t.u. = internal energy of the unburned gas–air mixture after isentropic compression from the initial pressure p_0 to the pressure p_c.

x = mass-fraction position of the element which burned when the pressure was p_x.

$E_{p_xp_c}$, in B.t.u. = internal energy of that element of the burned gas at the pressure p_c which has a mass-fraction position x, or which has reached pressure p_c along the path: isentropic compression of the unburned gas–air mixture from the initial p_0 to p_x, combustion at the constant pressure p_x, isentropic compression of the burned gas from p_x to p_c.[4]

The initial internal energy of the system is E_{p_0} and, since the combustion is to take place at constant total volume, the internal energy of the entire system must remain constant at this value, although it will be composed of elements having different energies. When the fraction c of the charge has burned the pressure has risen to the value p_c, and the internal energy of that portion of the charge as yet unburned will be

$$E_{p_c}(1 - c) \tag{1}$$

The energy of the burned portion of the charge is more difficult to evaluate, since there is a continuous variation in energy throughout it. By the definition of $E_{p_xp_c}$ the energy of the burned portion is:

$$\int_0^c E_{p_xp_c}\,\mathrm{d}x \tag{2}$$

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[4] Note that the single pressure subscript on E denotes unburned gas and the double pressure subscript denotes burned gas.

The sum of this integral giving the energy of the burned portion and the energy of the unburned portion must equal the constant energy of the system, or

$$E_{p_c}(1 - c) + \int_0^c E_{p_x p_c}\,dx = E_{p_0} \tag{3}$$

The solution of equation 3 would be extremely difficult without the thermodynamic property charts except by the use of unwarranted simplifying assumptions. Even with the charts its use is difficult without certain working plots which will now be described.

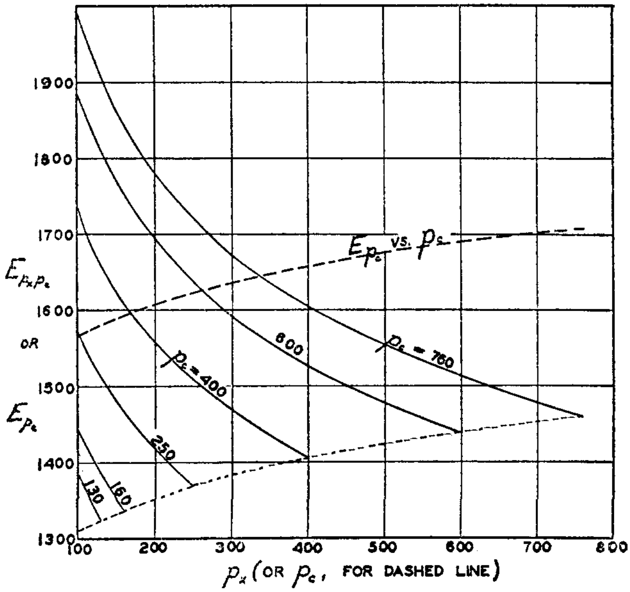

FIG. 6. Relation between E_{p_c} and p_c (single dashed line) and between $E_{p_x p_c}$ and p_x for different constant values of p_c (solid lines). (See table of nomenclature.)

Figure 6 presents (single dashed line) the relation between E_{p_c} and p_c. The construction of this curve follows simply from the "unburned" chart (figure 3). Since, by definition, E_{p_c} is the internal energy of the unburned mixture after isentropic compression from its initial state, the intersections of the pressure and energy lines at the entropy of the initial gas–air mixture determine the curve of E_{p_c} versus p_c. The "sensible" energy will be read from the chart, and E_{p_c} is the sum of this value and the energy of combustion.

The family of curves in figure 6 represents $E_{p_x p_c}$ versus p_x for various constant values of p_c. These curves must be obtained from the "burned" chart, figure 2. The evaluation of any point on these curves must be carried out as described in the definition of $E_{p_x p_c}$. At a given pressure p_x, the properties of the unburned gas are read from the "unburned" chart, figure 3, at the initial entropy. In this case H_S is the only property of interest. The energy of combustion is to be added to the value of H_S as read from the chart, giving H. Since by definition of $E_{p_x p_c}$ the gas must be burned at the constant pressure p_x, or the constant value of H just found, a point may be located on the "burned" chart, figure 2, at these values of p and H and the corresponding value of internal energy read. This value is $E_{p_x p_c}$ for $p_x = p_c$. Values of $E_{p_x p_c}$ for the same value of p_x and for other values of p_c may be located by moving along a line of constant entropy from the value just found.

The technique of using equation 3 involves a stepwise calculation with the pressure p_c chosen as the independent variable. For the first step, if the value of p_c is chosen not greatly different from the initial pressure p_0, the value of c to be found will be small and will be denoted by $\Delta' c$. Equation 3 may then be written:

$$E_{p_c}(1 - \Delta' c) + (E_{p_x p_c})'_{\text{av.}} \Delta' c = E_{p_0} \tag{4}$$

in which $(E_{p_x p_c})'_{\text{av.}}$ indicates the average energy of burned gas at the pressure p_c which burned at pressures varying from p_0 to p_c. If the step is small and/or if the relation connecting c and p_c is substantially linear, $(E_{p_x p_c})'_{\text{av.}}$ is the average value of $E_{p_x p_c}$ as obtained from figure 6 between $p_x = p_0$ and $p_x = p_c$ along the curve for the value of p_c chosen.

For illustration by means of a particular example, consider an engine with a compression ratio of 6.0 operating with a mixture ratio corresponding to 85 per cent of theoretical air and with $f = 0.042$, $p_1 = 14.7$, and $T_1 = 643°$ (from which $V_1 = 16.5$) at the end of the compression stroke ($V_2 = 2.75$); one finds from figure 3 that $E_{S2} = 138$, $T_2 = 1155$, $p_2 = 160$, $H_{S2} = 220$, $E_2 = 138 + 1507(1 - 0.042) + 300(0.042) = 1594$, and similarly $H_2 = 1676$. Now let the charge be ignited at the conditions just specified, with the piston held at top dead center (volume constant at 2.75) while the flame sweeps through the combustion chamber. The relation between the mass-fraction burned and the pressure, and the temperature distribution through the mass are now to be calculated.

As outlined above, the first step involves the choice of p_c which, for the present example, will be chosen as 250. From the dashed curve of figure 6, E_{p_c} (for $p_c = 250$) $= 1624$. The average value of $E_{p_x p_c}$ between $p_x = 160$ and $p_x = 250$ along the curve labeled $p_c = 250$ is 1414, which equals $(E_{p_x p_c})'_{\text{av.}} \cdot E_{p_0} = 1594$. Substitution of these values into equation 4 yields $\Delta' c = 0.143$, i.e., by the time the pressure has risen from 160 to 250, 14.3 per cent of the charge has been swept by flame.

For the second step equation 4 must be modified to:

$$E_{p_c}(1 - \Delta'c - \Delta''c) + (E_{p_xp_c})'_{\text{av}}.\Delta'c + (E_{p_xp_c})''_{\text{av}}.\Delta''c = E_{p_0} \qquad (5)$$

in which $(E_{p_xp_c})'_{\text{av}}$. is now to be evaluated between the same values of p_x but along the curve for the second chosen value of p_c. $(E_{p_xp_c})''_{\text{av}}$. is then the average $E_{p_xp_c}$ between p_x = the first chosen value of p_c and p_x = the second chosen value of p_c, along the curve for the second chosen value of p_c. Since $\Delta''c$ is now the only unknown in equation 5, its value can be determined and added to $\Delta'c$ to give the total c up to this point.

For each successive step, corresponding new terms in Δc and $(E_{p_xp_c})_{\text{av}}.\Delta c$ must be added. It will be noted that each of the terms $(E_{p_xp_c})_{\text{av}}$. will be obtainable from figure 6 by averaging along the p_c-curve over the pressure interval within which the corresponding increment burned.

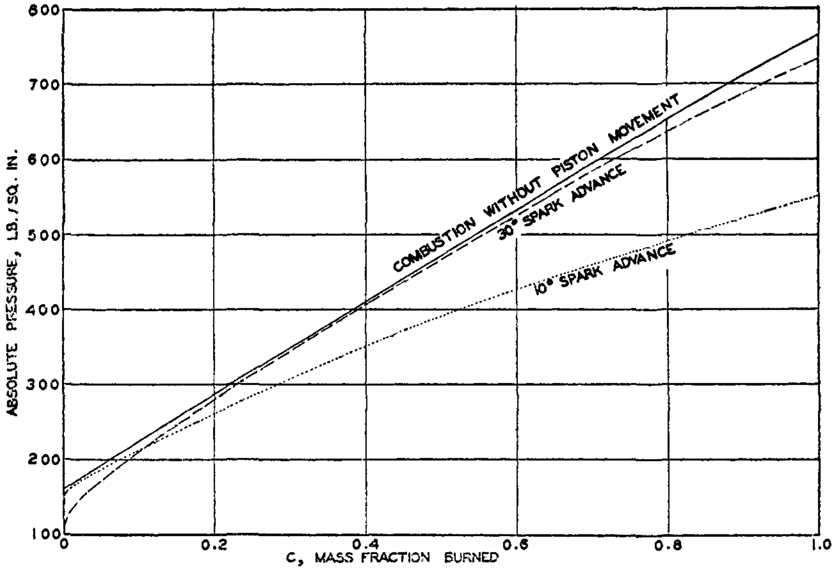

FIG. 7. Change of pressure with progress of combustion for three conditions of firing

The final results of this stepwise calculation are presented in figure 7 (solid line labelled "combustion without piston movement") as p_c versus c. It will be noted that the relation is found to be substantially linear throughout, so that somewhat larger steps could have been taken without appreciable loss in precision. (The literature contains examples of studies of flame propagation based on this simplifying assumption of linearity between p_c and c.)

The final pressure is 765 lb. per square inch, a value to be compared with the pressure 775 reached at point 3 in the previously discussed unthrottled Otto cycle where perfect mixing was assumed at all points. Obviously, if the products of combustion in the present example were thoroughly mixed, at constant volume, conditions would be identical with those at point 3 in the unthrottled Otto cycle example. This mixing would be accompanied by a slight rise in pressure because of the higher specific heat (including dissociation) at the higher temperatures. The phenomenon has been investigated by Mache (13) and by Lewis and von Elbe (11), the latter reporting changes in pressure up to 0.8 per cent for hydrogen–oxygen explosions. The small difference in the pressures indicates that calculations of the type just discussed should be predicated on interest in the temperature distribution through the mass rather than interest in the pressure after combustion. The calculation of the temperature distribution will now be discussed.

The temperature distribution for the present example is presented in the left half of figure 9 as temperature versus mass fraction measured from ignition point. The lowermost curve presents the temperature of the unburned gas ahead of the flame front. The points for this curve were obtained from the "unburned" chart, figure 3, by reading the temperature along the isentropic path as a function of the pressure and obtaining the corresponding mass fraction from the p_c versus c plot just discussed. The middle solid curve represents the temperature attained at the instant of combustion of any given layer. Combustion at constant pressure or constant H provides a means of calculating these points from the corresponding points on the lower curve. The upper curve presents the temperature distribution at the end of combustion. Points for this curve are calculated from the corresponding points on the middle curve by isentropic compression to the final pressure, using figure 2. These curves will be discussed later in comparison with other results. The temperature distributions throughout the charge at various times during the combustion are shown by the dotted lines, the vertical portions showing the position of the flame front.[5]

Part of the technique of making the calculations with allowance for piston movement is the same as that outlined above. Equation 3 (or 4 or 5) is modified only to the extent of correcting the right-hand side for the change in the total energy of the system caused by the work done by the piston. This is simply the average pressure during one of the small steps, multiplied by the change in volume (with the proper sign). Care must be exercised if the piston goes through top dead center in one of the steps. However, equation 4 or equation 5, with the work correction, is not sufficient in this case because the pressure–volume relation is not known in

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[5] These results on flame propagation replace those given in figure 7 of reference 3, which were obtained by a method there labelled an approximation.

advance, and hence the work term is not fixed by the technique of choosing p_c. Additional information related to flame speed—information which no purely thermodynamic analysis can hope to yield—is necessary. The most convenient form that this information can take is relation between c, the mass fraction burned, and crank angle, readily converted to the relation between c and chamber volume, V. With this latter relation given, the calculation for a single step of the combustion process involves trial and error in finding those values of Δc and ΔV which will satisfy both equation 4 (or 5), with the work term included, and the c–V relation.

For illustrative purposes two examples have been calculated, with ignition 30° and 10°, respectively, before top dead center. In both cases combustion was assumed to have been completed in 40° of crank revolution. As a fair approximation the fraction burned was assumed proportional to the cube of the time after ignition, or to the cube of the crank travel after ignition. This approximation was combined with the known relation of volume to crank angle to produce the curves of figure 8, giving the c–V relation for the two cases in question. Admittedly the relations presented in figure 8 represent an assumption, although data presented by Rassweiler and Withrow (15) indicate that pressure is nearly cubic in time. The assumptions do not detract from the value of the examples as illustrations of a method.

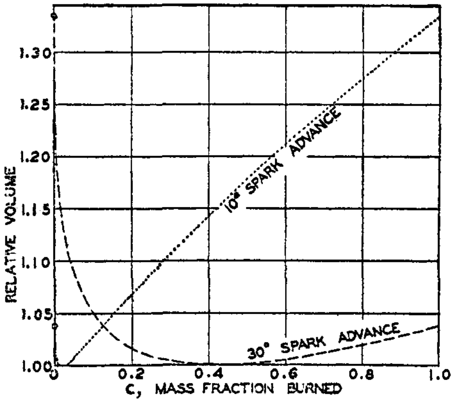

FIG. 8. Progress of flame in relation to piston movement

The stepwise-calculated relations of pressure to fraction burned are presented in figure 7 as the dashed and dotted lines. Since ignition occurs before top dead center has been reached, combustion starts at a lower pressure than in the previous example. During the early stages of combustion the pressure rise is more rapid than in the previous example, by virtue of the combined effects of combustion and compression by the piston. Beyond top dead center, however, the expansion resulting from piston movement causes a decrease in the slope of the curves. This latter effect is particularly pronounced in the example with 10° spark advance, since nearly all the combustion occurs during the expansion stroke.

With the relation of pressure to fraction burned known, the calculation of the temperature distribution curves presented in the right half of figure 9 is as described in the first example. These curves show clearly the increase in temperature caused by advancing the spark. Of particular interest are the two lowermost curves, which represent the temperature in the unburned portion into which the flame is advancing. Near the end of combustion the temperature of the unburned gas is about 100° higher when the spark advance is 30° than when it is 10°. This temperature difference, alone or in conjunction with the large pressure difference occurring simultaneously, undoubtedly affects the nature of the reactions ahead of the flame front where "knock" probably starts. It is to be noted

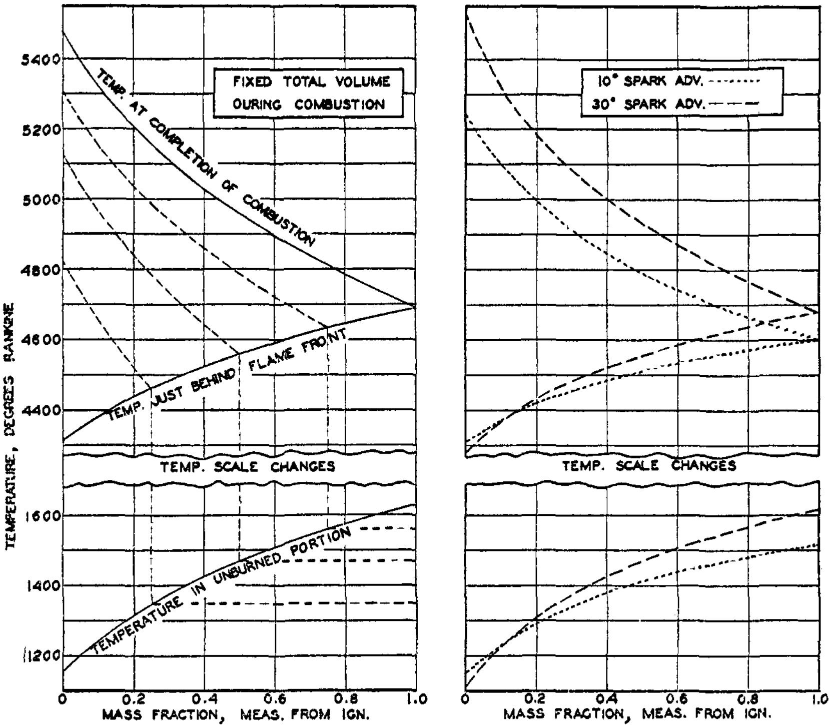

FIG. 9. Effect of flame travel on temperature in a combustion chamber. Left—chamber of fixed volume; right—30° and 10° spark advance, with flame travel occupying 40° of crank revolution.

also that the usually calculated compression temperature is that at $c = 0$, which is several hundred degrees lower than the actual temperature in the later stages of combustion.

Experimental studies of the variation in flame temperature across an engine head confirm the general character of the upper curves of figure 9. Rassweiler and Withrow (16), using the sodium D line reversal method to measure temperatures in an engine operating with open throttle with 80 per cent of theoretical air and a compression ratio of 4.4, found the temperature at the firing end to rise from 4200°R. (at 10° of crank revolution after firing) to a peak of 4800°R., under non-knocking conditions.

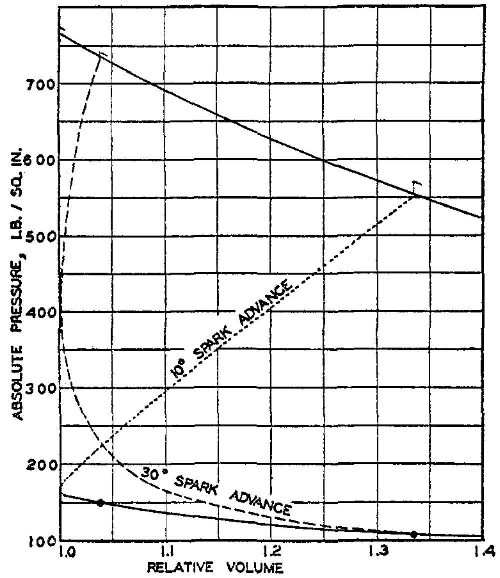

FIG. 10. High-pressure end of indicator card for conditions of figure 9. (Note: zero of P and maximum V not shown.)

Calculations following the method of the present paper, with the simplifying assumption of all combustion occurring at top dead center, indicated temperatures at the spark plug of 4220°R. and 5250°R. at the start and completion of combustion, respectively. That the latter value is considerably in excess of that obtained by experiment is to be expected, since the time of combustion was not zero, but approximately 40° of crank revolution.

The relation of pressure to total chamber volume, for the three examples considered, was obtained by combining the V–c and p–c relations of figures 7 and 8. The results are presented in figure 10, which represents an enlargement of the upper corner of the calculated indicator cards for the three cases. The solid curve, part of which is the left edge, corresponds to combustion at top dead center. It is to be noted that the area of the card for 30° spark advance is only slightly less (about 2 per cent) than that of the conventionally "ideal" cycle; an important conclusion is that the simplification of calculations of the efficiency of various engine cycles by assuming combustion at top dead center, does not lead to any great error. The area of the indicator card for 10° spark advance, however, is much less than that of the others. According to figure 10 it is approximately 40,000 ft.-lb. or 51 B.t.u. less than the "ideal" cycle. The latter cycle, according to the first example discussed, yields a work output of 463 B.t.u., from which one concludes that retarding the spark advance from 30° to 10° is accompanied by approximately 10 per cent loss in efficiency.

SUMMARY

Quantitative calculations of the effects of flame propagation and of piston movement on the temperatures attained in the various parts of on Otto-cycle engine charge during combustion are made relatively simple by the use of a Mollier diagram of the properties of the conbustion products of octane and air. The method is applied to a consideration of the effect of spark advance on the temperature attained ahead of the flame front, and it is concluded that the results are significant in studies of engine knock.

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