NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL NOTE

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CHARTS OF THERMODYNAMIC PROPERTIES OF FLUIDS ENCOUNTERED IN CALCULATIONS OF INTERNAL COMBUSTION ENGINE CYCLES

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SUMMARY

A single chart has been prepared that simplifies the calculation of the thermodynamic properties of air, various octene-air mixtures, and mixtures of those with their products of combustion at all temperatures below which chemical dissociation becomes unimportant. The chart is based on the use of 1 pound mol of mixture, and examples of its use are given in the form of the calculation of a turbocompressor power plant and a supercharged Otto engine cycle.

INTRODUCTION

Reference 1 presented thermodynamic property charts for the products of combustion of octene and air in different ratios. For the calculation of various engine cycles, there is necessary in addition a chart or set of charts giving the thermodynamic properties of unburned air-fuel mixtures. Such an unburned-fuel-air mixture chart has been calculated, and so plotted that it applies to various air-fuel ratios and various ratios of burned to unburned gases, and includes pure air as the basic chart.

This investigation, conducted at the Massachusetts Institute of Technology, was sponsored by and conducted with the financial assistance of the National Advisory Committee for Aeronautics.

The completion of this project would not have been possible without the conscientious and efficient assistance of Mrs. Edward Addelson, who made all the calculations and did all the drafting and lettering on the final charts.

FUNDAMENTAL DATA

The charts in reference 1 were each on a basis of 1 pound of air plus the appropriate fuel, and the coordinates were entropy S and internal energy E. A set of corresponding "unburned" charts on the same basis could be prepared, one corresponding to each "burned" chart. If, however, the basis for the properties of unburned mixtures is not 1 pound of air but 1 pound mol of mixture, the p-v-T relations for various mixture ratios are substantially the same - identical, of course, if the various air-fuel mixtures were perfect gases.

Furthermore, if the coordinates of the chart are entropy S and temperature T rather than S and E as previously, the representation of the properties of different mixtures on a single chart is facilitated. It will be shown that the small variations, with air-fuel mixture ratios, from a common p-v-T relation due to gas imperfections and from a common H-T or E-T relation due to molal-specific-heat variations from fuel to air, can be allowed for on a single chart. Such a chart can then be used for all mixtures, burned or unburned and including pure air, at the temperatures of interest here (up to 1800° R (1340° F) for unburned fuel-air mixtures, 2520° R (2060° F) for burned mixtures).

Although such a single chart has the disadvantage over a series of charts that a change in basis is involved during the calculation of some thermodynamic cycles, that change is not difficult (an example will be given); furthermore, the advantages of a single chart are many. Besides the physical simplification of handling a single chart there is the possibility of calculation of complete gas turbine cycles of any mixture ratio of present interest instead of only those ratios for which burned charts are available; a comparison of the air-standard cycle with the actual fuel cycle can be made directly on the single chart; the chart gives directly the properties of pure air for calculation of various pumping or power cycles.

In the previous charts zero values were assigned to various thermodynamic properties at a base of 100° F. Since calculations of high-altitude power-plant performance will involve the present chart at temperatures to -60° F or lower, it is desirable to drop the temperature base to a value below any anticipated in order to involve differences of positive numbers in engineering calculations. The base chosen was 200° K (360° R or -100° F) because basic thermodynamic data are tabulated in the literature at that temperature.

DESCRIPTION OF CHART

Used as an Air Chart

The chart is best viewed first without consideration of the various peripheral plots. It is then a representation of the p-v-T-S relations for pure air, due allowance having been made for departure from perfect gas. Lines of constant volume, cubic feet per pound mol (labeled V), and lines of constant pressure, pounds per square inch absolute (labeled P), are plotted on S-T coordinates, with temperature scale from 360° R (the base temperature) to 2520° R (2060° F). Zero value has been assigned to entropy at the base temperature and 1 atmosphere (14.696 psia).

The value at zero pressure (i.e., for perfect-gas conditions) of the enthalpy, called H^o (British thermal units per pound mol) can be read from the first vertical scale to the right of the T-scale. This scale consists of a number of diagonal curved lines at the bottom of which appear values of F, the ratio of fuel used to that required for stoichometrically complete combustion. For air, $F = 0$, the left edge of the H-scale is read. To allow for the effect of pressure on the enthalpy of air, refer to figure 2A or 2B, the line marked $F = 0$, where the value $(H - H^o)/P$ is found as a function of temperature. For example, when volume and pressure are 16 cubic feet per pound mol and 500 psia, the entropy is found to be -2.05, temperature is 740° R, $H^o = 2660$ Btu per pound mol. From figure 2A, at 740° R and $F = 0$, $(H - H^o)/P = -0.085$, from which $H - H^o = - 500 \times 0.085 = -42.5$, and $H = 2660 - 42 = 2618$ Btu per pound mol. It will be noted that the pressure correction to H^o to obtain H becomes negligible at pressures below 1 atmosphere or temperatures above 1000° R, and that, for many calculations, figures 2A and 2B may be ignored. Values of H^o are based on $H = 0$ at the base temperature and 1 atmosphere.[1]

Similar to H^o, E^o (the value of internal energy at zero pressure) can be read from the extreme right scale, and the pressure correction from figure 3A or 3B, using the line $F = 0$. For the previous example, when $T = 740°$ R, $E^o = 1180$ Btu per pound mol, $(E - E^o)/P = -0.10$, $E = 1180 - 0.10 \times 500 = 1130$. The base for E is consistent with

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[1] This gives H^o a value of 7 Btu per pound mol at the base temperature.

that for H; $E = \frac{-144PV}{777.75}$ at the base temperature and 1 atmosphere.

Used as a Mixture Chart

The use of the chart in determining the properties of an air-fuel mixture will next be described, without inclusion of the thermodynamic basis for the procedure. Suppose the mixture contains 20 percent more fuel than the stoichiometric mixture. Then $F = 1.20$. The mixture may, in addition, consist in part of unpurged combustion products from the previous cycle in an Otto cycle engine, together with some fresh fuel-air mixture. The weight fraction of the former in the total mixture is referred to as f, the "unpurged fraction," or weight-fraction of the fuel in the burned state. For Otto-cycle calculations, f may vary from 0.01 to 0.05; for combustion in a gas turbine cycle, f is 0 on entry and about 1.0 on leaving. As an example, consider a mixture with $F = 1.2$ and $f = 0.05$, at a temperature of 950° R and pressure of 100 psia. From figure 5, one pound of air produces 0.03545 mols of such a mixture. This is the conversion factor in going from the present chart to the burned charts. (See reference 1.) Because in many problems the oxygen of the air is partially or wholly combined with fuel, the ordinate of figure 5 is labeled "pound mols of mixture per pound of air constituents." From the main chart, at $T = 950^{\circ}$ R and $P = 100$, $V_{air} = 102$. This volume applies for air. Since the p-v-T relations for air and for the mixture are somewhat different, a correction is read from figure 7; $V_{mix} - V_{air} = 0.07$, $V_{mix} = 102.07$. Since the uncorrected volume can be read to no better than 1/2 percent, the correction at this temperature and pressure is obviously not worth making.

To obtain enthalpy, first determine H^{o} from the right-hand scale by moving horizontally along the $T = 950$-line to $F = 1.2$; and interpolate between the dashed-line scales corresponding to an f of 0.05, finding $H^{o} = 4590$. Similarly, $E^{o} = 2690$ (linear interpolation and extrapolation are valid for obtaining values at f other than 0 or 0.05). From figure 2A, $(H - H^{o})/P = -0.08$ and $(E - E^{o})/P = -0.12$. Then, $H = 4590 - 0.08 \times 100 = 4582$, and $E = 2690 - 0.12 \times 100 = 2678$. The corrections, for this example, were barely worth making.

The only additional property of interest is entropy. Absolute values of entropy for mixtures do not appear on the chart; but a change in entropy along a specified path or the change in other properties along a path of constant entropy may be evaluated. The variation, with temperature and pressure, of the entropy of a mixture differs from that of pure air because of differences in specific heats and in p-v-T relations for the two. Allowance for the specific-heat effect appears in families of curves running almost vertically along the left side of the chart, labeled $(S_{mix} - S_{air})$, and plotted against temperature. Allowance for the effect of differences in p-v-T relations of air and of gas mixtures is much less important, and may be neglected for many uses of the chart. (See later example.)

As an example, suppose the last given mixture is to be compressed isentropically from its temperature and pressure of 950° R and 100 psia, respectively, to a new pressure of 600 psia, The entropy of air at the first condition is found to be 2.99, and the difference between the entropy of the mixture of interest and that of air (exclusive of a constant which is independent of temperature and pressure) is read from the family of almost vertical lines at the left of the plot. It is found to be 0.63. The sum of these is 3.62. Now move upward from 950° R and 100 psia along such a path that the new value of the sum of S_{air} and $(S_{mix} - S_{air})$ is the same. This may be done by trial and error, choosing various temperatures until the condition is satisfied. Much simpler is the graphical procedure of laying the edge of a sheet of paper horizontally along the 950° isotherm and marking on it the distance between the points where the line $P = 100$ on the right, and $F = 1.2$, $f = 0.05$ on the left, cut the isotherm, Then, move the horizontal edge of the paper vertically upward keeping the left-hand point on the line labeled "$F = 1.2$; $f = 0.05$" until the right-hand point coincides with the line, $P = 600$. From this procedure it is apparent that the families of lines at the left may be thought of as direction lines for moving along a constant-entropy path with a given mixture of fuel, air, and combustion products. At $P = 600$ it is found that $T = 1435°$ R and $V_{air} = 26$. Strictly, a pressure correction to entropy should be made, using peripheral figure 8, The correction is appreciable only for the lower left region of the main chart (low temperature, high pressure). Furthermore, numerical values read from figure 8 indicate that, along paths of approximately constant entropy the pressure correction is substantially constant (within a ΔS of 0.005, i.e., one-tenth of a small square) and may therefore be neglected. The only remaining correction is to convert from V_{air} to $V_{mixture}$. At the initial temperature the difference of the two was negligible. (See previous example.) At the final temperature of 1435° R the correction is even less important. The work of compression in a flow system is ΔH. By rounding off the result from the previous example, $H_1 = 4580$; $H^o_2 = 8790$, $(H_2 - H^o_2)/P = 0.05$; $H_2 - H^o_2 = 30$, $H_2 = 8820$. Then, work = 8820 - 4580 = 4240 Btu. This number is established to about 10 Btu by careful use of the chart. Omission of the pressure corrections to H would have given the answer 4200 Btu - that is, 1 percent lower. Treatment of the whole problem as though the gas were air rather than a partially burned fuel-air mixture would have given a final temperature of 1540° R and a work of compression of 4390 Btu (3.5 percent high).

CONVERSION FROM PRESENT CHART TO "BURNED MIXTURE" CHARTS OF REFERENCE 1

The present chart will be referred to as the "modified-air" chart for brevity. Given a system located on the modified-air chart, unreacted, and of such composition that combustion would raise the temperature to a point where dissociation is important - that is, to a temperature not included on the chart - what is the procedure?

Case I.- Combustion occurs at constant volume. It is necessary to evaluate E of the burned system above the older burned-chart base - that is, above a state in which zero value of internal energy is assigned to CO_2, $H_2O(v)$, N_2, O_2 at 100° F. From the "modified-air" chart, read E at state in question before reaction, and read E^o at 100° F (=560° R). To help the reader, a heavy line appears in the E-scale at 560° R. From the same chart (fig. 5), read y = pound mols of mixture per pound of air constituents. Then $(E - E^o_{560})\,y$ = sensible internal energy per pound of original air, above 560° base, of the gas, which contains both fresh fuel-air and unpurged gas. The internal energies of combustion of these, at the base temperature, must be added to obtain E.

$$E_{\text{burned chart}} = y\,[E - E^o_{560}]_{\text{modified-air chart}} + (1 - f)(\Delta E)_{c,560} + f\,Q_v$$

The term $-\Delta E_{c,560}$ is the internal energy of combustion of any fresh fuel in the mixture, and equals +2,151,000 Btu per pound mol of octene, or

$$\frac{2151000\ (0.01749\ F)}{28.95} = 1299\ F$$

per pound air constituents, where (0.01749 F) is mols fuel per mol air. (See fig. 4.) And Q_v is the internal energy of combustion, at 100° F, of any unburned fuel in the unpurged products of a previous cycle. It is read from the right-hand side of the burned charts, or from the following table:

F	0.8	0.9	1.0	1.1	1.2	1.5
Q_v	2	2	2	169	336	832

Obviously, Q_v has no importance for lean mixtures.

Recapitulating,

$$E_{\text{burned chart}} = y\,[E - E^{\circ}_{560}]_{\text{modified-air chart}}$$
$$+ (1 - f)1299\ F + fQ_v \qquad (1)$$

In addition to E, volume V must be known to locate the system on the burned chart. On the modified-air chart V is per mol of mixture; on the burned chart is is per pound of air constituents. Figure 5 gives the conversion factor y.

$$y(V_{\text{modified-air chart}}) = V_{\text{burned chart}}$$

Case II.- Combustion occurs at constant pressure. The condition to satisfy is that H is constant. On the burned charts H_s is the ΔH, to the temperature in question from that temperature where both $E_s = J(PV) = -NRT$ and $E_s = \Sigma NMC_v(T - 560)$. Solutions of these equations from the data used in calculating the burned charts indicate that, over the burned-chart range of F = 0.8 to 1.5, T = 405 is an adequate average base temperature, constant to within 1° F.

From the modified-air chart, read H at state in question before combustion; and read $H^{o}{}_{405^{o}\,R}$ (from the solid line on the H-scale); and from figure 5, read y = pound mols mixture per pound of air constituents. Then $(H - H^{o}{}_{405})\,y$ = sensible enthalpy, per pound of original air, above 405° R base, of the gases containing both fresh fuel and unpurged gas.

$$H_{\text{burned chart}} = y\,(H - H^{o}{}_{405})_{\text{modified-air chart}}$$

$$+ (1 - f)(1299\ F) + fQ_{v} \qquad (2)$$

It is to be noted that the chemical contributions to the value of $H_{\text{burned chart}}$ involve ΔE_{c} and Q_{v}, and not ΔH_{c} and Q_{p}. This is a consequence of the fact that the burned charts define H as $E + PV$, and H_{s} as $E_{s} + PV$, where $E_{s} = E - Q_{v}$. Therefore, $H = H_{s} + Q_{v}$ and <u>not</u> $H_{s} + Q_{p}$.

Examples of Cycle Calculations

I. Turbocompressor power plant.- Consider a turbine and compressor, direct-coupled. The compressor takes air at 0° F. and 8 psia, compresses it sevenfold in pressure, with an efficiency of 75 percent. Liquid fuel at 40° F is then sprayed in to give an air-fuel weight ratio of 73:1, combustion occurs at constant pressure, and the gases are expanded through a turbine with an efficiency of 90 percent to a pressure of 10 psia. Per pound of fuel burned per hour, what is the available shaft horsepower?

At 460° R and 8 psia, find $S = 2.92$, $H_{1}{}^{o} = 696$, $(H_{1} - H_{1}{}^{o})/P = -0.27$, $H_{1} = 696 - 0.27 \times 8 = 694$.

Perfect compression to $8 \times 7 = 56$ psi would give $T = 800$, $H = 3085 - 0.07 \times 56 = 3081$. Then ΔH would be $3081 - 694 = 2387$. Instead, because of imperfect compression process,

$$\Delta H = 2387/0.75 = 3183$$

Then $H_{2} = 694 + 3183 = 3877$, T_{2} = about 912° R, $(H_{2} - H_{2}{}^{o}) = -0.04 \times 56 = -2$, $H_{2}{}^{o} = 3879$, and $T_{2} = 912^{o}$ R.

Now, add liquid fuel. From figure 4, when pounds fuel per pound air = 1/73 = 0.01370,

$$F = \frac{0.0137}{0.06775} = 0.2021$$

H of liquid, per mol, from figure 9, = -13,200. And ΔH of combustion at base temperature of 360° R = 2,150,000 Btu per pound mol. Then

Total H of liquid = 2,150,000 - 13,200 = 2,137,000

From equation on figure 4,

Mols fuel per mol air = 0.01749 × 0.2021 = 0.003535

H_2 of mixture per mol of fresh mixture

$$= \frac{3877 + 0.003535 \times 2137000}{1.00354} = 11,390$$

Mols burned mixture/mol fresh mixture is read from figure 6, line marked $f = 0$, at $F = 0.2021$; it is 1.011.

When combustion occurs, H does not change. But, since the number of mols changed from 1 to 1.011 due to combustion, and since the chart basis is 1 mol

$$H_3 = \frac{H_2}{1.011} = 11,265 \text{ Btu per mol burned mixture}$$

From chart at $H_3 = 11,265$, T_3 is about 1865° R, $(H - H^o)/P = +0.04$ (fig. 2B), $H_3{}^o = 11,265 - 0.04 \times 56 = 11,263$, and $T_3 = 1863°$ R (1403° F)

S_3, air, from chart at $p_3 = 56$ psi and $T_3 = 1863°$ R, is 9.23; $S_{mix} - S_{air}$ is read from the group of nearly vertical lines at the left; at $F = 0.202$, $f = 1$, and $T_3 = 1863°$, it is 0.18. The pressure correction on S is negligible. $S_3 = 9.23 + 0.18 = 9.41$ (plus a constant of no interest here).

Let the gas expand through the turbine to 10 psia. If perfect expansion occurs, S(total) is still 9.41. To find the condition at end of this expansion, lay the edge of a paper horizontally at $T_3 = 1863$ from the initial coordinate, $S_{3,air} = 9.23$, to the extreme left to line $F = 0.2$, $f = 1$. The distance between marks on the paper now represents S_{total}. Move the paper downward with edge kept horizontal, and left mark kept on the line $F = 0.2$, $f = 1$, until the right-hand mark intersects the line $p = 10$. At this point, $T_4 = 1205^\circ$ R, $H_4{}^{o} = 6100$. (Actually, the left-hand S-guide line is so nearly vertical that an approximate method is frequently better than the exact graphical one described). If the expansion path had been assumed to occur along a line of constant S_{air}, a preliminary value of T_4 of 1195° R would be read, from which $S_{mix} - S_{air} = 0.11$. A considerable error in T_4 does not affect this quantity appreciably. Consequently, without further trial and error, $S_{4,air} = 9.42 - 0.11 = 9.30$, and $T_4 = 1205$, $H_4{}^{o} = 6100$, $H_4 = 6100 - 0.02 \times 10 = 6100$.

Then $-\Delta H$ during perfect expansion would be $11,263 - 6100 = 5163$. Actually, because of turbine inefficiency,

$$-\Delta H = 5163 \times 0.9 = 4647$$

$$H_4 = 11,263 - 4647 = 6616$$

The correction from H_4 to $H_4{}^{o}$ is negligible; then

$$T_4 = 1275^\circ \text{ R}$$

Basis of calculation of output; 1 mol air

Mols fuel = 0.00354
Pounds fuel = 0.00354 × 112.1 = 0.397
Mols unburned mixture = 1.0035
Mols burned mixture = 1.011 × 1.0035
= 1.0145
Work output of turbine = 4647 × 1.0145 = 4714
Work into compressor = 3183
1531

$$\text{Pounds fuel/hp-hr} = \frac{2545 \times 0.397}{1531} = 0.66$$

The low value of this figure is a consequence of assuming high values for the separate efficiencies of the compressor and turbine, without introducing compensating allowance for pressure drop in ducts and the combustion chamber.

There may be occasion to use the velocity of the exhaust gas to obtain additional thrust. If the exhaust gas expands reversibly from 10 psia to atmospheric pressure of 8 psia, the temperature changes from 1275° to 1202° R, and H^0 from 6616 to 6080. Corrections to H are negligible. Then $-\Delta H = 536$ per mol mixture.

$$\text{Pounds mixture per mol mixture} = \frac{\text{pounds fuel + pounds air}}{\text{mol mixture}}$$

$$= \frac{0.397 + 28.95}{1.0145} = 28.95$$

As expected with such a lean mixture, the molecular weight of the products is the same as that of air.

$$\Delta H \text{ per pound mixture} = \frac{536}{28.95} = 18.52 \text{ Btu}$$

This equals $\dfrac{u^2}{2gJ}$

$$u = \sqrt{64.4 \times 778 \times 18.52} = 962 \text{ feet per second}$$

Pounds mixture per pound fuel = 74

Then

$$\text{Pounds thrust per (lb fuel/hr)} = \frac{m\,u}{g}$$

$$= \frac{74 \times 962}{3600 \times 32.2} = 0.66$$

Otto-Cycle Engine with Supercharger

Supercharged engine operating in air at $P = 10$ psia and $T = 20°$ F ($T = 480°$ R), supercharging with 70 percent efficiency to 30 psia, after which liquid fuel is sprayed in at 60° F with 20 percent excess fuel. Engine compression ratio is 6.

First determine H of unburned air-fuel mixture entering manifold.

Isentropic compression of 1 mol of air from 10 to 30 pounds, starting at 480° R.

$$H_{before} = 835 + 0.25 \times 10 = 838; \quad S = 2.77$$

Compression at constant - S to 30 psi gives

$$T_{after} = 657$$

$$H_{after} = 2080 + 0.12 \times 30 = 2084$$

$$\text{Isentropic work} = 2084 - 838 = 1246$$

$$\text{Actual work input} = 1246/0.7 = 1780$$

If no thermal losses are assumed, all the extra work goes into temperature in the gas, and

$$H \text{ after compression} = 1780 + 838 = 2618$$

from which T is approximated as 740° R

$$(H - H^{o})/P = 0.09$$

$$H^{o} = 2618 - 0.09 \times 30 = 2615$$

T may now be determined exactly; it is 734° R

$$\text{Volume} = 263 \text{ cubic feet}$$

At this point, inject liquid fuel at 60° F (520° R). According to figure 9,

$$\text{Mols of liquid} = 1.2 \times 0.01749 = 0.0210$$
$$H \text{ of liquid} = -12,200 \times 0.0210 = -256$$
$$H \text{ of mixture, per mol mixture} = \frac{2618 - 256}{1.0210} = 2313$$

(Note that basis has changed here.)

H^{o} of mixture = 2313 - 0.24 × 30 = 2306, and corresponding temperature 690° R and V = 246, Correction on V is 0.2 (negligible).

Now, assume that temperature in cylinder at end of exhaust stroke and after expansion to 10 psi is 2100° R. (This is subject to check by completion of the cycle calculations.) One mol products ($f = 1$) at 2100° R and 10 psi, has $E = 9720$, $V = 2260$. For the process of mixing fresh mixture at 30 psi through a throttling valve into combustion products initially at 10 psi and rising ultimately to 30 psi, while the volume remains constant, the enthalpy of the entering charge plus the initial internal energy of the combustion products must equal the internal energy of the final mixture. The basis of calculation will be 1 mol of unpurged mixture from previous cycle, left in engine at top dead center.

Let x = mols fresh charge entering at top dead center by throttling through intake valve and mixing with unpurged gas, but not yet including any fresh charge entering during intake stroke. One mol of fresh mixture of composition $F = 1.2$ produces 1.10 mols products (fig. 6). To find the weight fraction of burned material in the resultant mixture, convert burned and unburned parts to a common state, either burned or unburned, and then determine the mol or volume fraction. By converting the fresh mixture to the burned state,

$$f' = \frac{1}{1 + 1.1\,x}$$

The prime indicates that this f is an intermediate value and not the one corresponding to the introduction of all the fresh charge; that comes in a later step.

$$E_{\text{per mol of resultant mixture}} = \frac{2313x + 9720}{x + 1}$$

and

$$V_{\text{per mol of resultant mixture}} = \frac{2260}{1 + x}$$

Given V, f', and E in terms of unknown x and given $P = 30$, use the chart to solve for x by trial and error.

Assumed values of x	$V = \frac{2260}{1+x}$	$f' = \frac{1}{1+1.1x}$	Values of E corresp. to V and f', and at $P' = 30$	E from above equation	Diff. in E's
5	377-	0.154	3320 - 3	3550-	-230
4.6	404-	.165	3800 - 3	3638	+160
4.76	392+	.160	(3590 + 10)-3	3600	-7

Therefore, $x = 4.76$, $f' = 0.160$, $V = 392$, $E = 3600$, from which $H = 5770$.

This mixture now mixes further at a pressure assumed constant at 30 psi, with more fresh mixture entering as the piston recedes to six times the previous volume. The enthalpy of the resultant mixture then equals the sum of the H's of the two components.

$$6 \times 2260 = 13,560$$

total volume of new mixture containing 1 mol of burned gases, 4.76 mols of fresh charge, and x_1 additional mols of fresh charge now entering. By this process, point (1) on the p-v diagram of the cycle is reached. (See fig. 10.) The resultant enthalpy H_1 is given by

$$H_1(1 + 4.76 + x_1) = 5770(1 + 4.76) + 2313\ x_1$$

$$V_1 = \frac{13560}{1 + 4.76 + x_1}$$

$$f = \frac{1}{1 + (4.76 + x_1)1.1}$$

As before, x_1 is obtained by trial and error.

Assumed x_1	$V_1 = \frac{13560}{5.76+x_1}$	$f = \frac{1}{6.236+1.1x_1}$	H corresp. to V and F at $P=30$	H from above equation	Diff. in H's
45	267	0.01794	2910-6	2704	+200
48	252	.0169	2620-6	2684	-70
47.3	255.5	.01716	2690-6	2688	-4

Therefore, $x_1 = 47.3$, $V_1 = 255.5$, $f = 0.0172$, and $H_1 = 2688$. The corresponding $E_1 = 1280$.

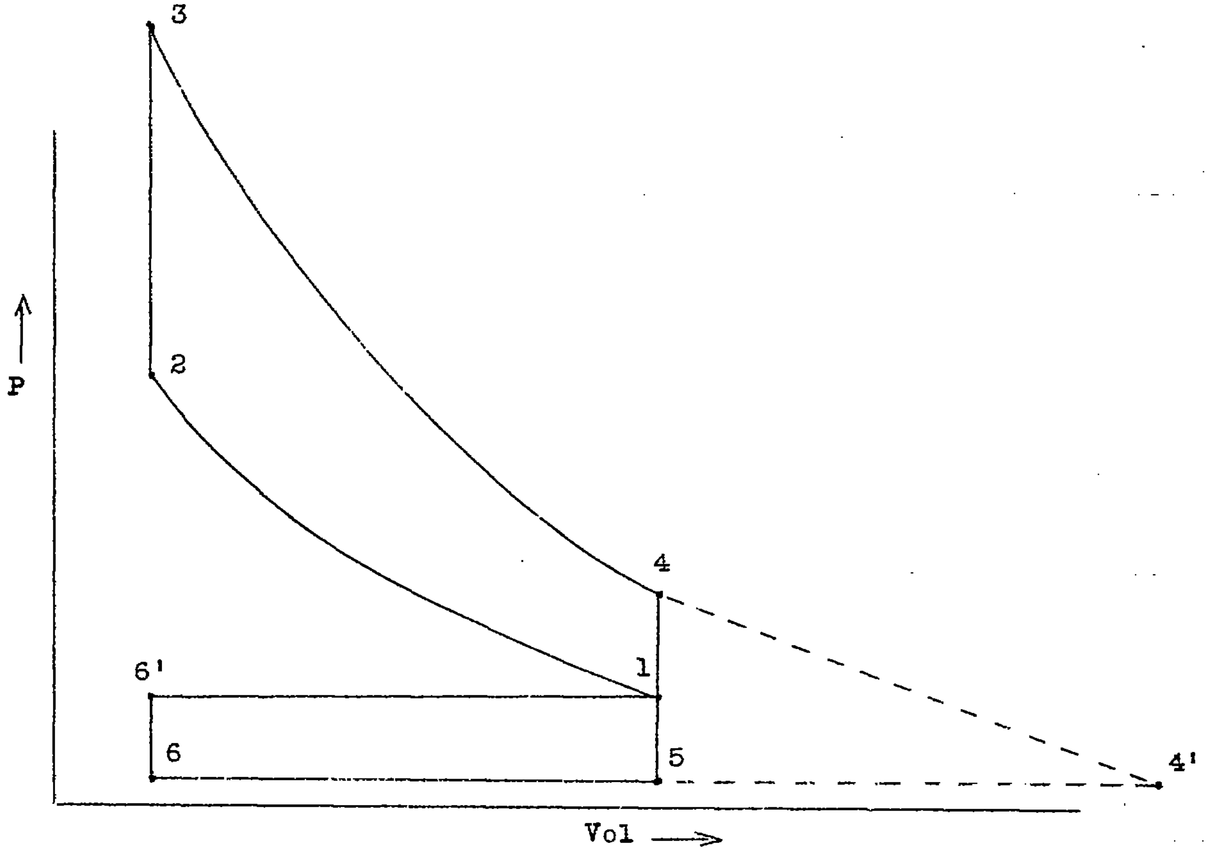

Figure 10.- The supercharged Otto cycle.

The next step is compression to state 2, assumed isentropic. The volume correction on V_1 is -0.16 (negligible). The entropy S_1 is 3.37 and the entropy correction is -0.00013×30 (negligible). The isentropic compression is followed by measuring the horizontal distance from point P_1, V_1 to the entropy-direction line for $F = 1.2$, $f = 0.017$, then moving the measuring device upward with left end on the entropy-direction line until the right end is on the line $V_2 = 255.3/6 = 42.6$. The correction on volume is negligible. (As a check on the graphical procedure,

$$S_1 + (S_{mix} - S_{air})_1 = 3.37 + 0.38 = 3.75$$

and

$$S_2 + (S_{mix} - S_{air})_2 = 2.74 + 1.01 = 3.75)$$

From figure 8, the correction on S_1 is negligible. At the new point, $P_2 = 321$, $T_2 = 1260$, and $E_2 = 4735 - 0.08 \times 321 = 4710$. (Note that the E-correction is the only one not negligible so far.)

The next step is a constant-volume combustion, assumed adiabatic and to thermodynamic equilibrium. The temperature reached is so high as to make the assumption of frozen chemical equilibrium on which the present chart is based, no longer valid. On the other hand, the new high temperature makes allowance for gas imperfection unimportant. The set of thermodynamic-property charts presented in a previous report must be used at this point. As previously explained, the burned-mixture charts are of necessity on a different basis, since the number of mols associated with a given system changes along various thermodynamic paths and the basis must be one of mass rather than number of mols.

The constant-volume combustion process is one at constant E. From equation (1),

$$E_{\text{burned chart}} = (E - E^{o}_{560})_{\text{modified air chart}} \times y$$

$$+ (1 - f)(-\Delta E_{c,560}) + f\ Q_v$$

$$= (4710 - 390)0.0353 + 0.983 \times (1299 \times 1.2) + 0.017 \times 336$$

$$= 152 + 1532 + 6 = 1690 \text{ Btu}, \quad E_3$$

$$V_{3\ \text{per pound air}} = 42.6\ y = 42.6 \times 0.0353 = 1,504 \text{ cubic feet}$$

From the burned chart for $F = 1.2$, T_3, P_3, and S_3 corresponding to E_3 and V_3 are 5230° R (4770° F), 1482 psi, and 0.518. (It is to be understood that the cycle has been calculated assuming compression and combustion to be adiabatic, and that the pressure and temperature are consequently high.)

The next step is isentropic expansion to $V_4 = 6 \times 1.504 = 9.02$. Reading from the burned chart, $P_4 = 160$, $E_4 = 1085$. As the exhaust valve opens, the mixture at state 4 expands irreversibly through the valve, but that part remaining in the engine expands isentropically, doing work on the effluent gases. Expansion is to $P_4' = 10$ psi, and from the chart $T_4' = 1900°$ R and $V_4' = 79$. The fraction of the mixture staying in the cylinder is then $V_4/V_4' = 9.02/79 = 0.1142$. As the piston returns to top dead center, it expels five-sixths of this burned residue, leaving $0.1142/6 = 0.0190$ which is the f, or unpurged fraction, for the cycle. This does not agree exactly with the value 0.0172 previously determined in steps 6-6'-1 because the temperature of the clearance gases was assumed to be 2100° R against the value 1900 just determined. The cycle calculation using a clearance-gas temperature of 1900° R instead of 2100° R could be repeated, but the result would be found to differ negligibly from those just obtained.

The work of the cycle may now be calculated. The basis is 1 mol of unpurged gas left in the engine at top dead center. To this were added

$$4.76 + 47.3 = 52.06 \text{ mols fresh charge}$$

Each mol of this contained 1/0.03531 or 28.32 pounds fresh air. The work of the cycle, exclusive of the pumping loop, is

$$(E_3 - E_4) - (E_2 - E_1)$$

$$= (1690 - 1085)\ 52.06 \times 28.32 - (4710 - 1280)52.06$$

$$= 892{,}500 - 178{,}500 = 714{,}000 \text{ Btu}$$

The work of the pumping loop, positive in a supercharged engine,

$$= (V_1 - V_2)(P_1 - P_{atm})\ \frac{144}{778}$$

$$= (13{,}560 - 2260)(30 - 10)\ \frac{144}{778} = 41{,}800 \text{ Btu}$$

The work put into the supercharger (assumed mechanically geared to the engine) was found to be 1780 Btu per mol of air. Mols of air entering

$$= \frac{52.06 \times 28.32}{28.95} = 50.95$$

Work into supercharger = 1780 × 50.95 = 90,600 Btu

Net work of cycle = 714,000 + 41,800 - 90,600 = 665,200 Btu

Finally, the mols fuel entering, per mol air, = 0.01749F (from fig. 9); so

Mols fuel = 50.95 × 0.01749 × 1.2 = 1.069
Pounds fuel = 1.069 × 112.13 = 119.9

Conventionally, the enthalpy of the liquid fuel at a standard temperature is used in the denominator to express efficiency. The values for ΔH and ΔE for combustion are given in the table below the nomenclature for the main chart. At 560° R, ΔH = 2,148,000 Btu per pound mol, from vaporized gasoline to water as vapor. The heat of vaporization of octene at 560° R is obtainable from the chart, inset figure 9, by taking the difference between the enthalpies of the vapor and the liquid. It is 6100 – (–10200), or 16,300 Btu per pound mol. Then, ΔH from liquid gasoline to combustion products (water as vapor) is 2,148,000 – 16,300 = 2,132,000 (1904 Btu/lb).

Then, cycle efficiency (engine–supercharger combined)

$$= \frac{665200}{119.9 \times 1904}$$

$$= 29.1 \text{ percent}$$

The obtaining of displacement volume per horsepower–hour is straightforward, and will not be included here.

Massachusetts Institute of Technology,
Cambridge, Mass., April 1945.

APPENDIX

I. FUNDAMENTAL DATA

Constants used throughout these calculations are identical with those used in the previous paper. The only others involved are constants for the Beattie-Bridgeman equations of state used in this report; see later.

Specific Heat of Octene

Specific heats of hydrocarbon vapors may be calculated by a summation of a number of Einstein functions, each representing a bond energy in the molecule. (See reference 2.) Dobratz (reference 3) has improved the method of Bennewitz and Rossner by adding allowance for molecular rotation. Values for the specific heat of propane have been plotted, from the papers of Bennewitz and Rossner, Dobratz, Fugassi and Rudy (reference 4), and Edmister (reference 5), for comparison with the experimental data of Konz and Brown (reference 6) and of Brown (reference 7). Dobratz' method fits the experimental data more closely than the others (within 1 percent at 800° K), and furthermore predicts a high-temperature variation much more in accord with expectations from theory than any straight-line extrapolation of the experimental data. Consequently, Dobratz' correction to the calculations of Bennewitz and Rossner has been accepted for the calculation of the specific heat of octene.

The formula for C_p^o $(p=0)$ given by Dobratz is

$$C_p^o = 4R + aR/2 + \Sigma v_1 P_1 + \frac{3n - 6 - \Sigma v_1 - a}{\Sigma v_1} \Sigma v_1 Q_1 \qquad (3)$$

where

a number of bonds permitting free rotation, C-C or similar

v_1 number of bonds of type 1

P_1, Q_1 energy associated with each bond of type 1

n total number of atoms in molecule

If m = number of C atoms in the molecule, this becomes, for normal or branched olefines,

$$C_p^o = (6 + m)R/2 + (m - 2)P_1 + P_2 + 2mP_3 + \frac{5m - 3}{3m - 1}\left[(m - 2)Q_1 + Q_2 + 2mQ_3\right] \qquad (4)$$

For octene, for which $m = 8$,

$$C_p^o = 7R + 6P_1 + P_2 + 16P_3 + \frac{37}{23}(6Q_1 + Q_2 + 16Q_3) \qquad (5)$$

The Einstein function by which P_1 and Q_1 may be determined is

$$P \text{ or } Q = R\left(x^2 \frac{e^x}{(e^x - 1)^2}\right) \qquad (6)$$

where

$x = h\upsilon/kT$

h Planck's constant

υ characteristic frequency

k gas constant per molecule

T temperature, °K

$$h/k = 4.778 \times 10^{-11} \text{ degree seconds}$$

$$\upsilon = c/\lambda = 2.99796(1/\lambda) \times 10^{10} \text{ cm/sec/cm}$$

$$\frac{h\upsilon}{kT} = \frac{1.4324(1/\lambda)}{T}$$

Wave numbers $1/\lambda_1$, $1/\lambda_2$, and $1/\lambda_3$ for P-energy are 990, 1620, and 2990, and for Q-energy are 390, 845, and 1320. A table of Einstein functions may be found in Physik.-Chem. Tab., Landolt-Börnstein, 1927, p. 702, fifth ed., first enlarged volume.

By applying these values to the equation, the C_p^o of octene at 210°, 230°, 250°, . . ., 990° K is determined. Then

$$H^o_{\text{above } 200^\circ \text{ K}} = 20 \Sigma C_p^o$$

and

$$S_p = 20 \ \Sigma (C_p^o/T)$$

Finally, $E^{o\prime}$ (= change in internal energy above zero-base for E at 200° K) $= \int_{200}^{T} C_v \, dT = H^o - R(T - T_o)$

Entropies and Internal Energies of Other Gases

The previous report gives values of E and S above 300° K for the various gases involved (tables II and III of that report). For the present purpose it is necessary only to determine values from 300° down to 200°, and put all values on a new base corresponding to 0-value at 200° K for all gases. The results are given in tables I and II.

CRITICAL CONSTANTS

For n-octane, the critical temperature, T_c, is 296° C (569° K); the critical pressure, P_c, is 24.6 atm. (See reference 8.) From ethylene-ethane and propylene-propane critical-constant relations (temperature down 22.4° and 5.1° C, respectively; pressure up 1.9 and 3.0 atm, respectively), assume that octene has T_c and P_c which are 5° C lower and 2 atm higher, respectively, than octane. Then

$$T_{c,\text{octene}} = 564^\circ \text{ K}; \quad P_{c,\text{octene}} = 26.6 \text{ atm}$$

Considering the fact that gasoline is a mixture, the above procedure for determining critical constants is entirely adequate for estimating corrections due to gas imperfections, which in any case are small.

For water, $T_c = 374.0^\circ$ C(647.2° K)

and $P_c = 217.7$ atm

SUMMARY OF BEATTIE-BRIDGEMAN CONSTANTS FOR GASES

Gas	Octene[1]	(Air-N_2 (reference 9)	CO_2 (reference 10)	H_2O (reference 11)
$\frac{B_oP_c}{RT_c}$	0.1620			0.1384
$\frac{A_oP_c}{R^2T_c^2}$	.4253			.3140
$\frac{C\ P_c}{R\ T_c^4}$	.0667			.1438
B_o	0.2819	0.04070	0.10476	0.03377
A_o	34.248	1.0763	5.0065	4.0686
C	2.082×10^7	12×10^4	66×10^4	951×10^4

[1] From a private communication by J. A. Beattie.

For octene, the bottom half of the table was obtained from the top half and from the previously given critical data, as follows:

$$B_o = \left(\frac{B_oP_c}{R\ T_c}\right) \times \frac{0.08206 \times 564}{26.6} = 0.2819 \text{ liters/gm mol}$$

$$A_o = \left(\frac{A_oP_c}{R^2T_c^2}\right) \times \frac{(0.08206 \times 564)^2}{26.6} = 34.248(\text{liters/gm mol})^2(\text{atm})$$

$$C = \left(\frac{C\ P_c}{R\ T_c^4}\right) \times \frac{0.08206 \times 564^4}{26.6} = 2.082 \times 10^7(\text{liters/gm mol})(^\circ\text{K})^3$$

The Beattie-Bridgeman constants for water vapor were obtained in like manner.

It was assumed that all diatomic species (CO, O_2, H_2, OH, NO), because of the minute quantity present, had the same B.B. constants as Air-N_2.

II. CALCULATION OF TEMPERATURE AT WHICH H = 0 ON BURNED-MIXTURE CHARTS

F = 0.8 Composition of gas is from page 55 of M.I.T. file-notes.

	Composition	(ΔE, 200 to 300° K)/100 = MC_v (cal/gm mol)	$N.MC_v$
N_2	1	4.95	4.9500
NO	.00119	5.21	.0062
O_2	.05248	5.02	.2635
CO_2	.14176	6.40	.9080
H_2O	.14154	6.00	.8500
CO	.00001	4.97	---
H_2	---	4.78	---
OH	.00045	5.21	.0027
	ΣN=1.33743		ΣNMC_v=6.9804

$$-NRT = \Sigma NMC_v(T - T_o)$$

$$-1.33743 \times 1.987 \times T = 6.9804(T - 560) = 6.9804T - 3910$$

$$T = \frac{3910}{6.9804 + 2.655} = 406^\circ R$$

F = 1.5

	Composition	MC_v	$N.MC_v$
N_2	1.0	4.95	4.9500
CO_2	.09667	6.40	.6185
H_2O	.16897	6.00	1.0140
CO	.16900	4.97	.8400
H_2	.09669	4.78	.4625
H	.00002	3.00	.0001
	ΣN=1.53134		ΣNMC_v=7.8851

$$-1.53134 \times 1.987 \times T = 7.8851(T - 560)$$

$$-3.04\,T = 7.8851\,T - 4415$$

$$T = \frac{4415}{10.925} = 404^\circ R$$

Spread of but 2° F between the two extremes of composition suggests an average $T = 405^\circ$ R at which $H = 0$. This produces a maximum error in H of about 7 Btu per mol, or about 0.25 Btu per pound, which on the burned charts is one-thirtieth of one small division on the H-scale. A heavy line has been drawn on the H-scale of the Modified Air chart at $T = 405^\circ$ R.

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11. Beattie, J. A., and Stockmayer, W. H.: Equations of State. Phys. Soc. Rep. Progress Physics, vol. 7, 1940, pp. 195-229.

TABLE I.- INTERNAL ENERGY IN PERFECT GAS STATE ($p = 0$), ABOVE BASE OF 200°K ($E^{o\prime}$)

(cal/gm mol)

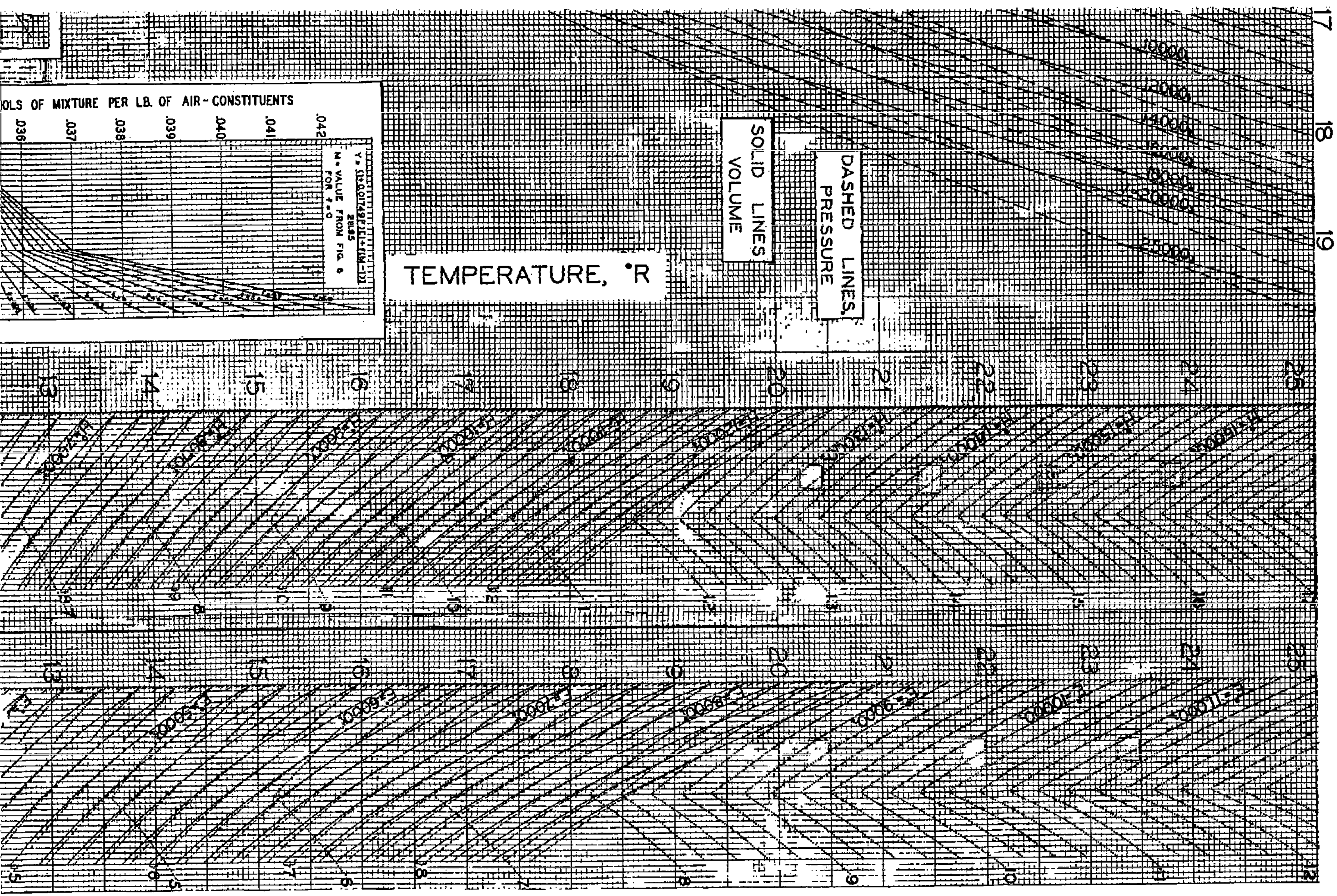
T (°K)	Air	Octene	Air-N_2	O_2	CO_2	H_2O	H_2	CO	NO	OH	O,H
200	0	0	0	0	0	0	0	0	0	0	0
250	248	1,295	248	249	307	299	235	248	263	262	149
300	496	2,830	495	502	640	600	478	497	521	521	298
400	997	6,748	992	1014	1,385	1221	974	997	1047	1032	596
600	2026	17,876	2006	2103	3,118	2508	1975	2025	2101	2046	1192
800	3118	32,563	3075	3282	5,090	3907	2986	3118	3237	3067	1788
1000	4275	49,864	4207	4529	7,229	5428	4017	4279	4439	4116	2384
1200	5483		5394	5819	9,485	7071	5083	5495	5691	5198	2980
1400	6733		6624	7144	11,825	8816	6188	6751	6979	6338	3576

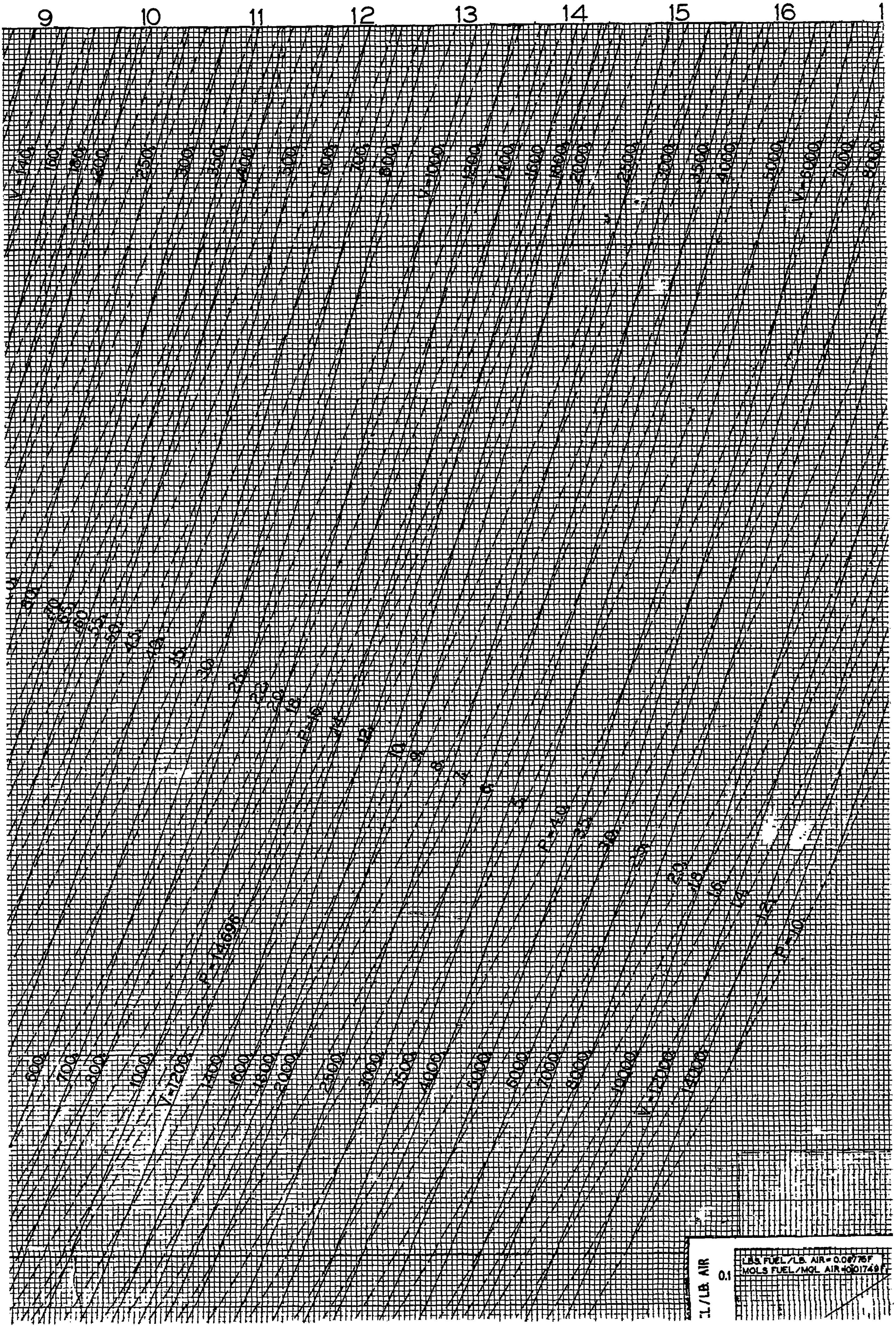
TABLE II.- CONSTANT-PRESSURE CHANGE OF ENTROPY WITH TEMPERATURE, S_p^o

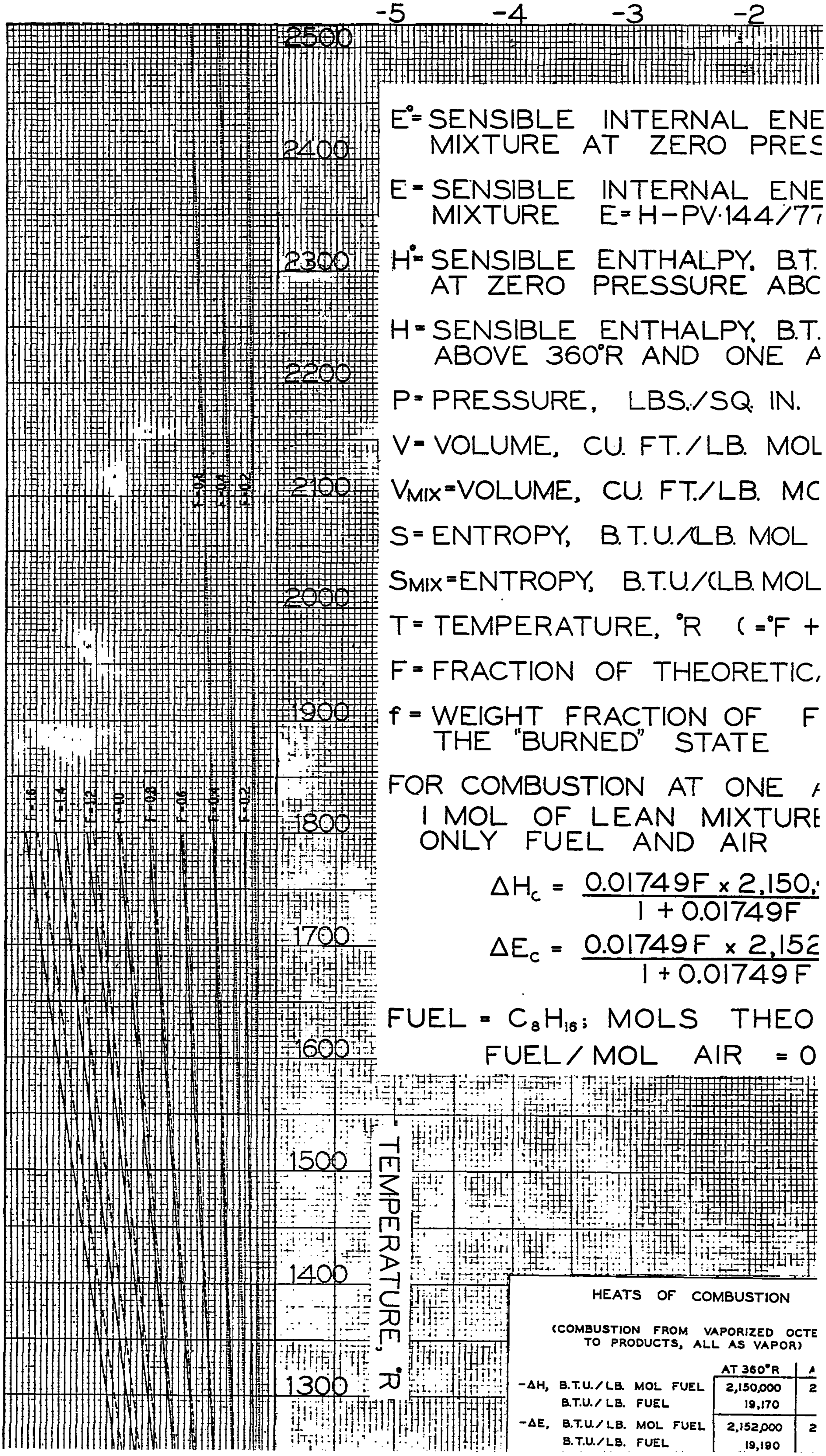
(cal/gm mol °K or Btu/lb mol °R)

[Zero value assigned at 200°K]

T (°K)	Air	Octene	Air-N_2	O_2	CO_2	H_2O	H_2	CO	NO	OH	O,H
200	0	0	0	0	0	0	0	0	0	0	0
250	1.544	6.176	1.542	1.553	1.809	1.773	1.495	1.553	1.615	1.609	1.11
300	2.815	12.141	2.812	2.826	3.384	3.230	2.742	2.821	2.921	2.913	2.02
400	4.824	23.905	4.812	4.869	6.090	5.556	4.739	4.829	4.978	4.98	3.45
600	7.714	46.987	7.671	7.876	10.389	8.959	7.573	7.717	7.937	7.84	5.46
800	9.854	68.579	9.778	10.141	13.790	11.531	9.594	9.859	10.136	9.88	6.89
1000	11.585	88.277	11.482	11.972	16.617	13.657	11.190	11.596	11.921	11.49	8.00
1200	13.049		12.927	13.510	19.034	15.508	12.523	13.065	13.39	12.84	8.90
1400	14.319		14.181	14.837	21.143	17.161	13.680	14.339	14.69	14.01	9.67


OLS OF MIXTURE PER LB. OF AIR - CONSTITUENTS
.036
.037
.038
.039
.040
.041
.042
Y = (1+0.01749F)(1+(N-1)) / 28.95
N = VALUE FROM FIG. 6 FOR F = 0
TEMPERATURE, °R
SOLID LINES VOLUME
DASHED LINES, PRESSURE
17
18
19
10000
12000
14000
16000
18000
20000
25000
13
14
15
16
17
18
19
20
21
22
23
24
25
H=7000
H=8000
H=9000
H=10000
H=11000
H=12000
H=13000
H=14000
H=15000
H=16000
E=5000
E=6000
E=7000
E=8000
E=9000
E=10000
E=11000
5
6
7
8
9
10
11
12


9
10
11
12
13
14
15
16
1
V=140
160
180
200
250
300
350
400
500
600
700
800
V=1000
1200
1400
1600
1800
2000
2500
3000
3500
4000
5000
V=6000
7000
8000
70
65
60
55
50
45
40
35
30
25
22
20
18
P=16
14
12
10
9
8
7
6
5
P=4.0
3.5
3.0
2.5
2.0
1.8
1.6
1.4
1.2
P=1.0
P=14.696
600
700
800
1000
V=1200
1400
1600
1800
2000
2500
3000
3500
4000
5000
6000
7000
8000
10000
V=12000
14000
L/LB. AIR
0.1
LBS. FUEL/LB. AIR = 0.06776F
MOLS FUEL/MOL AIR = 0.01749F



E°= SENSIBLE INTERNAL ENE
MIXTURE AT ZERO PRES

E = SENSIBLE INTERNAL ENE
MIXTURE E = H − PV·144/77

H°= SENSIBLE ENTHALPY, B.T.
AT ZERO PRESSURE ABC

H = SENSIBLE ENTHALPY, B.T.
ABOVE 360°R AND ONE A

P = PRESSURE, LBS./SQ. IN.

V = VOLUME, CU. FT./LB. MOL

V_{MIX}=VOLUME, CU. FT./LB. MC

S = ENTROPY, B.T.U./(LB. MOL

S_{MIX}=ENTROPY, B.T.U./(LB. MOL

T = TEMPERATURE, °R (=°F +

F = FRACTION OF THEORETIC

f = WEIGHT FRACTION OF F
THE "BURNED" STATE

FOR COMBUSTION AT ONE
1 MOL OF LEAN MIXTURE
ONLY FUEL AND AIR

$$\Delta H_c = \frac{0.01749F \times 2{,}150,}{1 + 0.01749F}$$

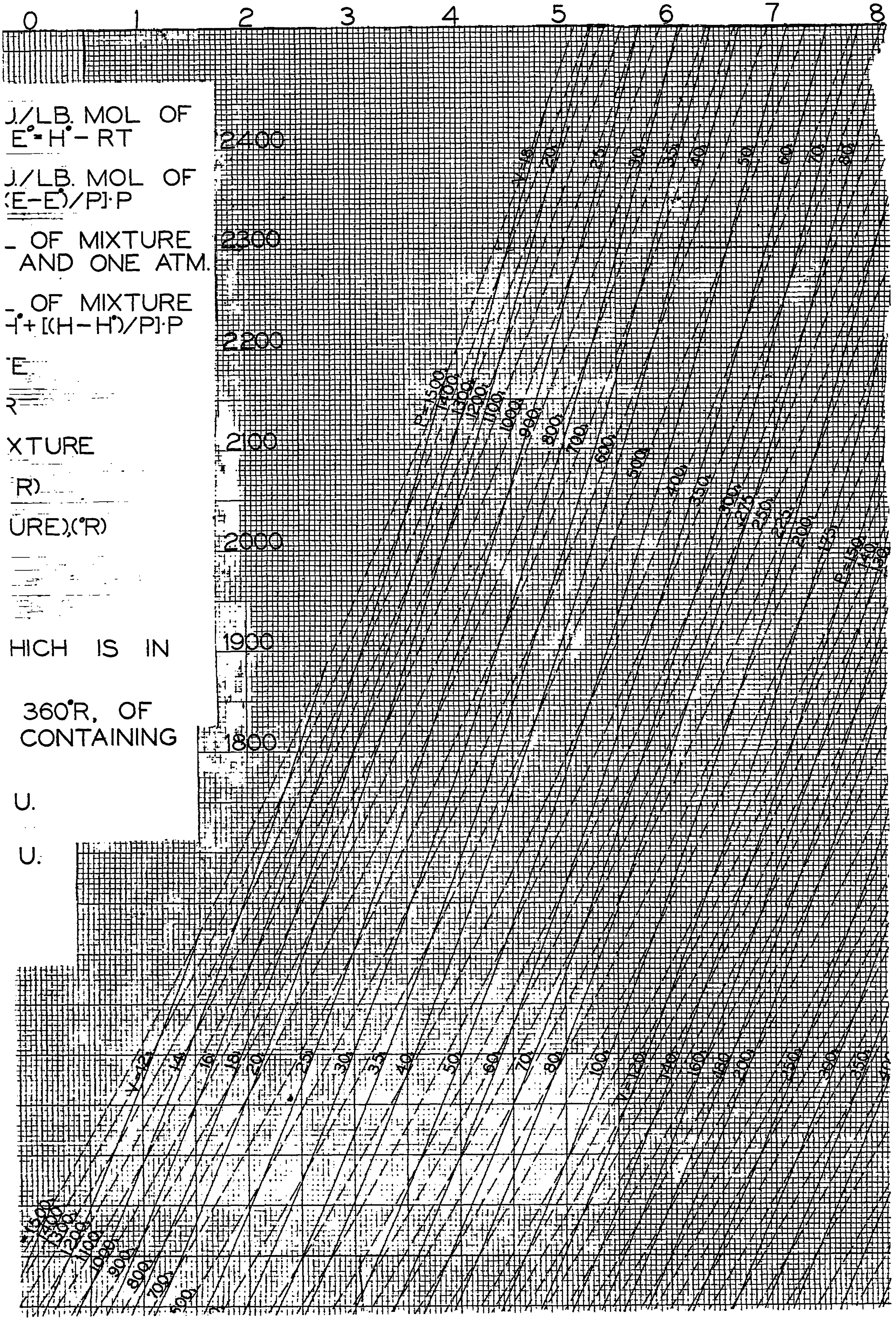
$$\Delta E_c = \frac{0.01749F \times 2{,}152}{1 + 0.01749F}$$

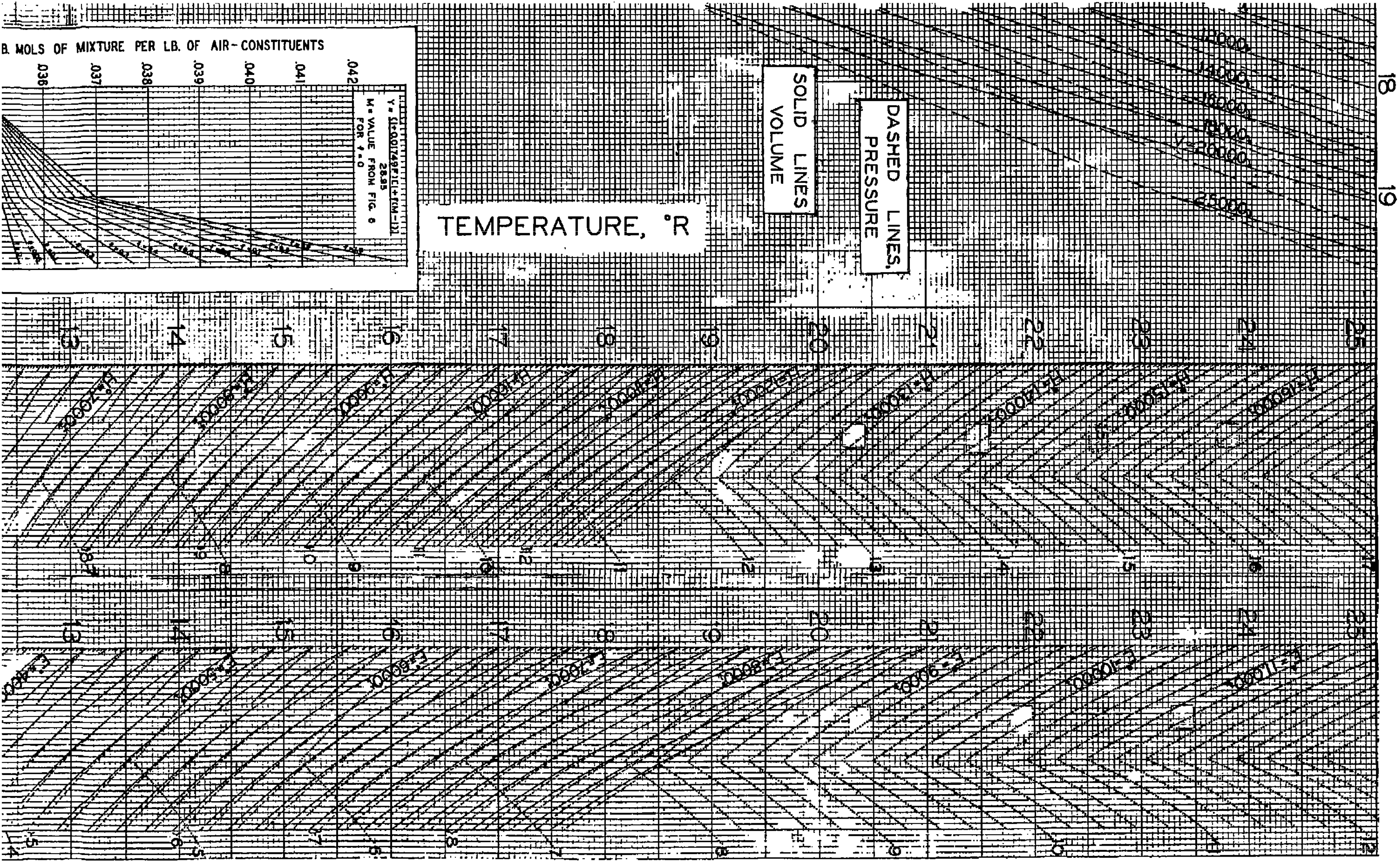
FUEL = C_8H_{16}; MOLS THEO
FUEL/MOL AIR = 0

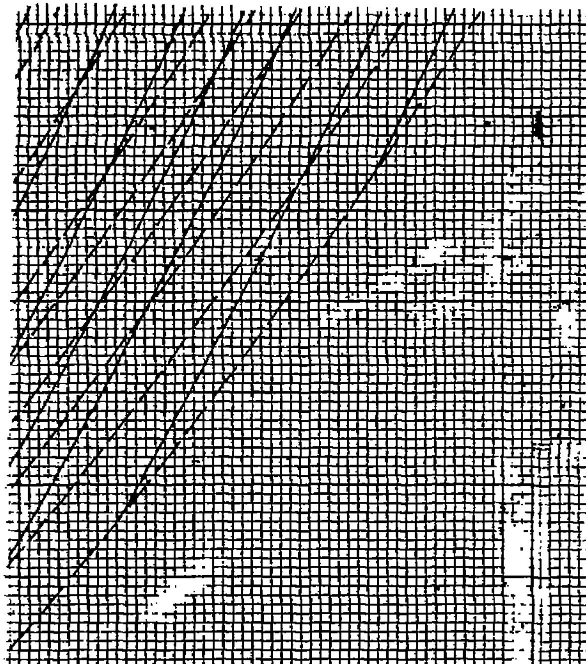
HEATS OF COMBUSTION

(COMBUSTION FROM VAPORIZED OCTE
TO PRODUCTS, ALL AS VAPOR)

	AT 360°R	
−ΔH, B.T.U./LB. MOL FUEL	2,150,000	2
B.T.U./LB. FUEL	19,170	
−ΔE, B.T.U./LB. MOL FUEL	2,152,000	2
B.T.U./LB. FUEL	19,190	


0
1
2
3
4
5
6
7
8
J./LB. MOL OF
E°=H°−RT
J./LB. MOL OF
(E−E°)/P]·P
_ OF MIXTURE
AND ONE ATM.
_ OF MIXTURE
H°+[(H−H°)/P]·P
E
R
XTURE
R)
URE),(°R)
HICH IS IN
360°R, OF
CONTAINING
U.
U.
2400
2300
2200
2100
2000
1900
1800
V=18
20
25
30
35
40
50
60
70
80
P=1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
350
300
275
250
225
200
175
P=150
140
130
V=12
14
16
18
20
25
30
35
40
50
60
70
80
100
V=120
140
160
180
200
250
300
350
P=1500
1400
1300
1200
1100
1000
900
800
700
600


LB. MOLS OF MIXTURE PER LB. OF AIR-CONSTITUENTS
.036
.037
.038
.039
.040
.041
.042
M = VALUE FROM FIG. 8 FOR φ = 0
TEMPERATURE, °R
SOLID LINES VOLUME
DASHED LINES, PRESSURE
V=20000
25000
18
19
13
14
15
16
17
18
19
20
21
22
23
24
25
H=12000
H=13000
H=14000
H=15000
H=16000
E=8000
E=9000
E=10000
E=11000



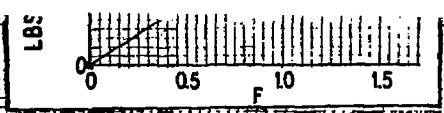


FIG. 4

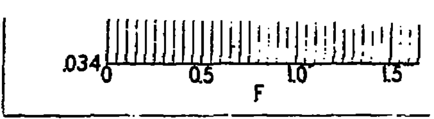


FIG. 5

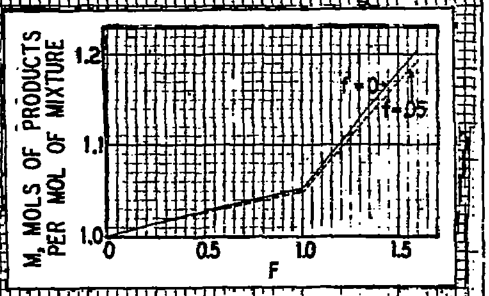


FIG. 6

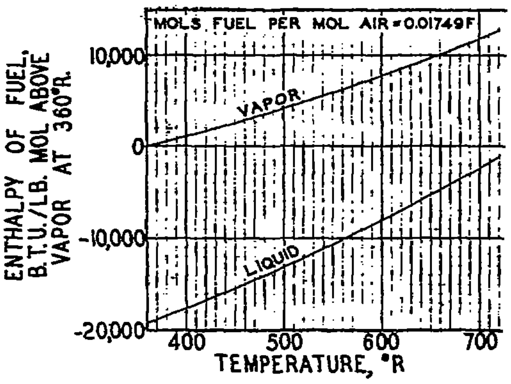


FIG. 9

THERMODYNAMIC PROPERTIES OF GASOLINE-AIR MIXTURES OR PRODUCTS OF COMBUSTION THEREOF,

INCLUDING VARIOUS AIR-FUEL RATIOS AND PROPORTIONS OF BURNED AND UNBURNED GASES

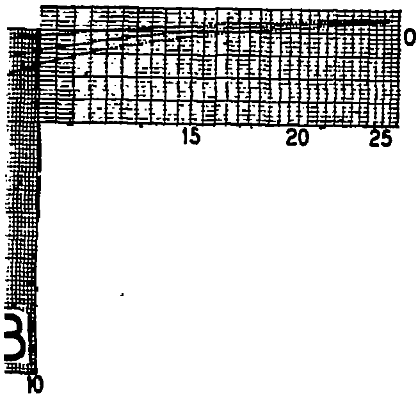
BASIS - 1 LB. MOL OF MIXTURE WHETHER BURNED OR UNBURNED

M. I. T., CAMBRIDGE, MASS. 1945

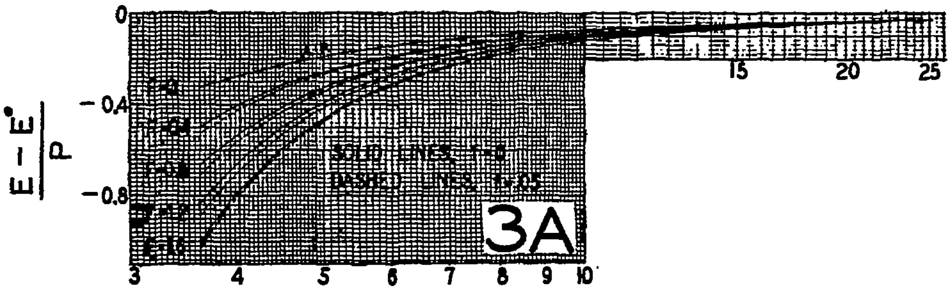
12 13 14 15 16 17 18 19

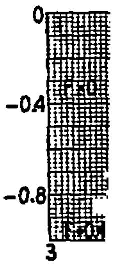
NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL NOTE NO. 1026

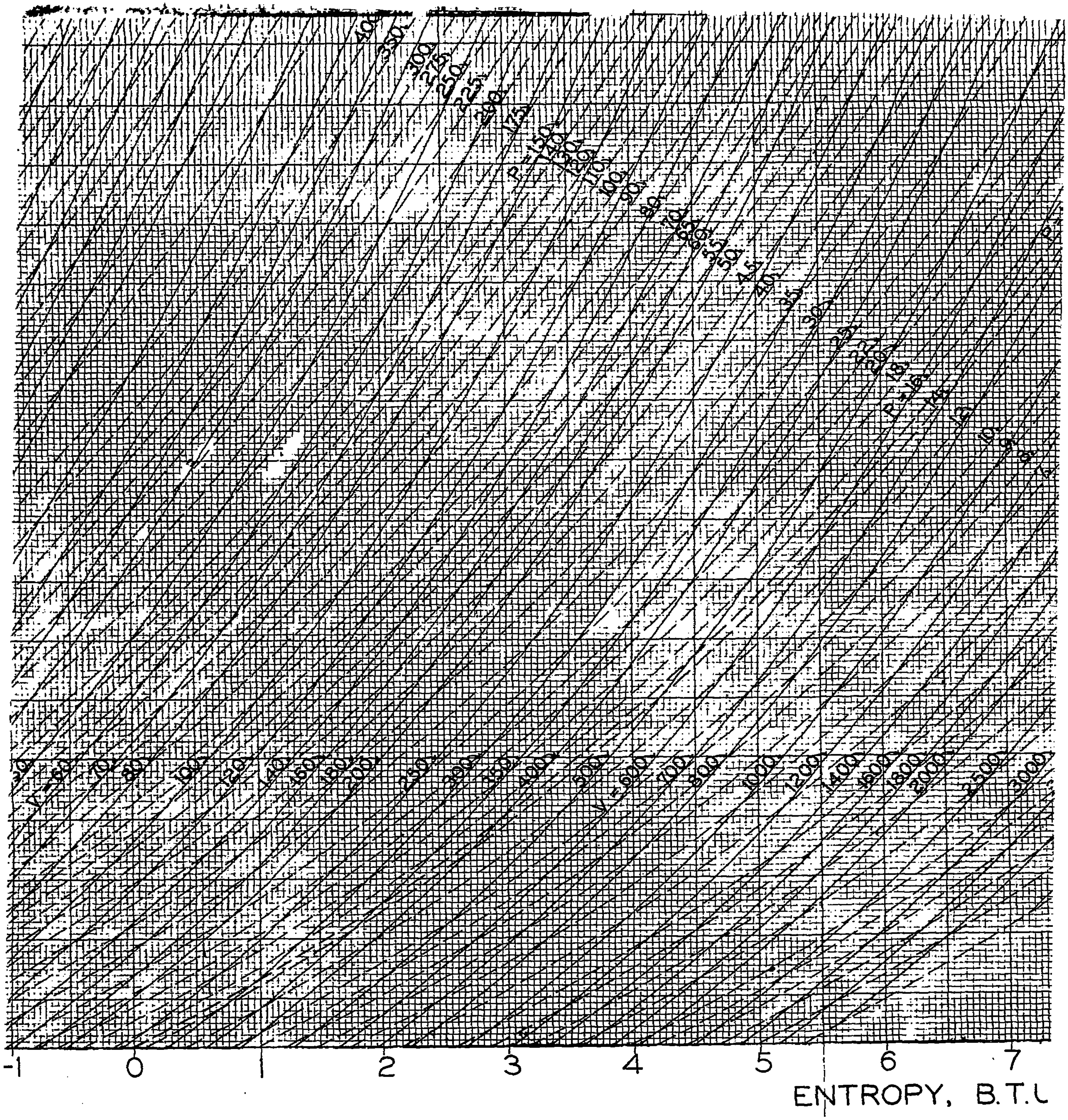


E- CORRECTION FOR

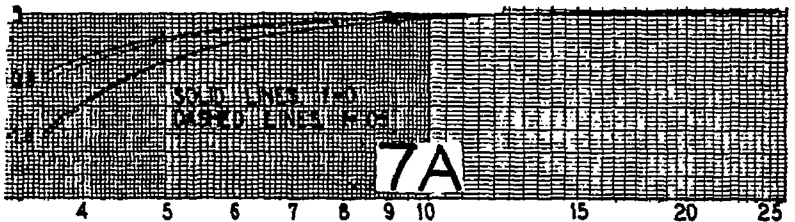




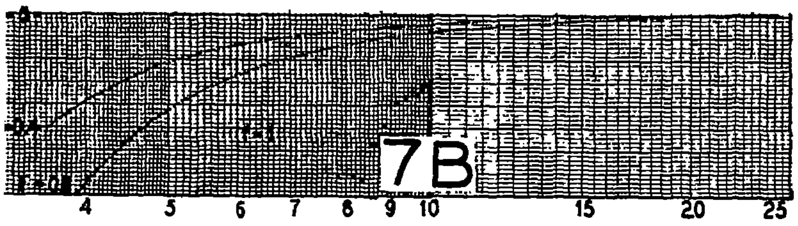
TEMPERATURE, DEGREES

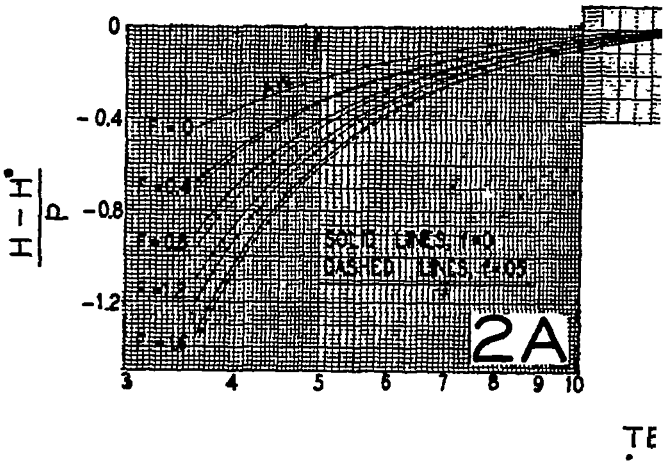


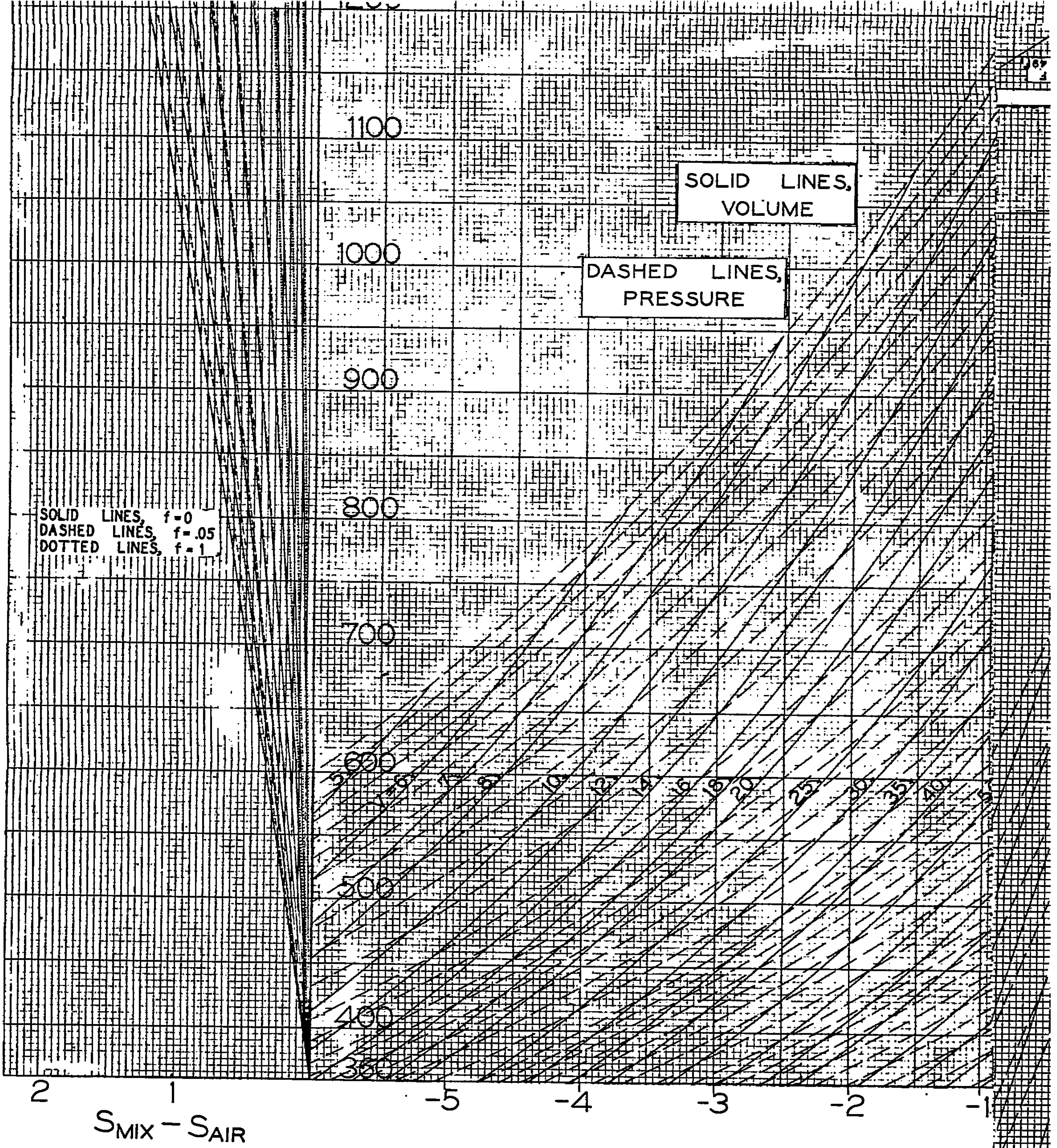
VOLUME CORRECTION FOR MIXTURE



TEMPERATURE, DEGREES R/100







($S_{MIX} - S_{AIR}$)—CORRECTION FOR PRESSURE