REPORT 937

CONSTANT-PRESSURE COMBUSTION CHARTS INCLUDING EFFECTS OF DILUENT ADDITION

By L. Richard Turner and Donald Bogart

SUMMARY

Charts are presented for the calculation of (a) the final temperatures and the temperature changes involved in constant-pressure combustion processes of air and in products of combustion of air and hydrocarbon fuels, and (b) the quantity of hydrocarbon fuel required in order to attain a specified combustion temperature when water, alcohol, water-alcohol mixtures, liquid ammonia, liquid carbon dioxide, liquid nitrogen, liquid oxygen, or their mixtures are added to air as diluents or refrigerants. The ideal combustion process and combustion with incomplete heat release from the primary fuel and from combustible diluents are considered. The effect of preheating the mixture of air and diluents and the effect of an initial water-vapor content in the combustion air on the required fuel quantity are also included. The charts are applicable only to processes in which the final mixture is leaner than stoichiometric and at temperatures where dissociation is unimportant. A chart is also included to permit the calculation of the stoichiometric ratio of hydrocarbon fuel to air with diluent addition. The use of the charts is illustrated by numerical examples.

INTRODUCTION

Accurate computation of the combustion temperatures or of the quantity of hydrocarbon fuel required to attain specified combustion temperatures is complicated by the variation in composition and thermal properties of the fluid. Further difficulty is introduced by the addition of various diluents or refrigerants to the combustible mixture.

A need for such calculation arises in connection with processes of combustion of hydrocarbon fuels with air, reheating of products of combustion by the introduction and the burning of additional fuel, and in performance analyses of aircraft gas-turbine engines when diluents or refrigerants are used to augment the thrust or the power of the engine.

This report represents a synthesis of references 1 and 2, which were written in 1946 and 1948, respectively, at the NACA Cleveland laboratory, and presents charts for the computation of constant-pressure combustion temperatures or for the calculation of the quantity of a hydrocarbon fuel required to attain a specified combustion temperature when water, alcohol, water-alcohol mixtures, liquid ammonia, liquid carbon dioxide, liquid nitrogen, liquid oxygen, or combinations of these liquids are used as diluents or refrigerants. The ideal combustion process and combustion with incomplete heat release from the primary fuel and from combustible diluents are considered. The use of the charts is illustrated by numerical examples.

The effect of preheating the mixture of air and diluents and the effect of an initial water-vapor content in the combustion air on the required fuel quantity are also considered. The charts are applicable only to processes in which the final mixture is leaner than stoichiometric and at temperatures where dissociation is unimportant.

A chart for determining the stoichiometric fuel-air ratio with diluent addition is also presented.

PRINCIPLES OF CHARTS

The charts presented herein apply to processes in which the final mixture is leaner than stoichiometric and are exact below those temperatures at which dissociation becomes important. (For most calculations, dissociation may be neglected at all temperatures below about 3200° R.) The charts are readily used above 3200° R, without considering dissociation, for making approximate calculations for higher final temperatures.

The specific-heat data for the gases were taken from references 3 to 10. The thermodynamic properties of the various liquid diluents were taken from references 11 to 13.

The use of complicated subscripts has been partly avoided by the use of the notation $x\Big]_y^z$ to mean "the value of x at z minus the value of x at y."

The symbols are defined when first used. For the convenience of the reader, symbols used more than once are listed in appendix A.

Ideal combustion.—The lower enthalpy of combustion at constant pressure of a liquid fuel $h_{c,f}$ or of a liquid diluent $h_{c,d}$ is defined as the amount of heat $-h_c$ removed during the combustion at constant pressure of the fuel or diluent in oxygen when the initial and final temperatures are equal and the products of combustion are all in the gaseous phase. Because of this convention, enthalpies of combustion will appear in this report as negative quantities.

The first law of thermodynamics applied to an ideal constant-pressure combustion of a mixture of air, hydro-

carbon fuel, and diluent for leaner-than-stoichiometric mixtures leads to the following equation:

$$h_a\Big]_{T_r}^{T_a}-fh_{c,f}+(1+d')\frac{W_c}{J}+d\left(h_d\Big]_{T_r}^{T_d}-h_{c,d}\right)=(1+f+d)h_b\Big]_{T_r}^{T_b} \tag{1}$$

where

d total diluent-air ratio, (lb/lb air)

d' weight of diluent injected into air stream prior to compression of mixture, (lb/lb air)

f total fuel-air ratio, (lb/lb air)

h_a enthalpy of dry air, (Btu/lb air)

h_b enthalpy of final burned mixture, (Btu/lb mixture)

$h_{c,d}$ lower enthalpy of combustion of liquid diluent at 540° R, (Btu/lb diluent)

$h_{c,f}$ lower enthalpy of combustion of liquid fuel at 540° R, (Btu/lb fuel)

h_d enthalpy of liquid diluent, (Btu/lb diluent)

J mechanical equivalent of heat, 778 (ft-lb/Btu)

T_a initial total air temperature, (°R)

T_b total combustion temperature, (°R)

T_d temperature of diluent as liquid immediately before injection, (°R)

T_r reference temperature, 540° R

W_c work of compression on mixture entering compressor, (ft-lb/lb mixture)

The effects of preheating the fuel have been neglected in equation (1) for simplicity of notation. The correction to $-h_{c,f}$ for the liquid fuel introduced to the system at a temperature other than the reference temperature of 540° R is small (approximately 0.5 Btu/(lb)(°R) for fuel in liquid phase). Under ordinary circumstances, partly vaporized fuel would not be used; hence, no portion of the fuel is considered to be vaporized.

A term for energy addition to the mixture or preheating of the mixture by any means $(1+d')W_c/J$ is included in equation (1); the preheating is usually, although not necessarily, accomplished by work of compression on the mixture and is referred to in this manner.

For leaner-than-stoichiometric mixtures, the term $(1+f+d)h_b$ is given by

$$(1+f+d)h_b=h_a+f(F_{CO_2}H_{CO_2}+F_{H_2O}H_{H_2O}+F_{O_2}H_{O_2})+ d(D_{CO_2}H_{CO_2}+D_{H_2O}H_{H_2O}+D_{O_2}H_{O_2}+D_{N_2}H_{N_2}) \tag{2}$$

where

D_y increase per pound of diluent in number of moles of y in ultimate burned gas mixture due to addition and combustion of diluent, (lb mole/lb diluent)

F_y increase per pound of fuel in number of moles of y in ultimate burned gas mixture due to addition and combustion of fuel, (lb mole/lb fuel)

H_y molal enthalpy of y, (Btu/lb mole)

y variety of gas, specifically CO_2, H_2O, O_2, and N_2

The term $f(F_{CO_2}H_{CO_2}+F_{H_2O}H_{H_2O}+F_{O_2}H_{O_2})$ is equivalent to the term used in reference 3

$$f\frac{Am+B}{m+1}$$

where

$$A=\frac{H_{H_2O}-\frac{1}{2}H_{O_2}}{2.016}$$

$$B=\frac{H_{CO_2}-H_{O_2}}{12.010}$$

m hydrogen-carbon ratio of fuel

The term $\frac{Am+B}{m+1}$ accounts for the difference between the enthalpy of carbon dioxide and water vapor in the burned mixture and the enthalpy of oxygen removed from the air by their formation.

The term $d(D_{CO_2}H_{CO_2}+D_{H_2O}H_{H_2O}+D_{O_2}H_{O_2}+D_{N_2}H_{N_2})$ represents the increase in enthalpy of the molecular products resulting from the addition and the combustion of the diluent. The values of $F_{O_2}H_{O_2}$ and of $D_{O_2}H_{O_2}$ generally are negative.

If equation (2) is substituted in equation (1),

$$h_a\Big]_{T_r}^{T_a}-fh_{c,f}+\frac{(1+d')W_c}{J}+d\left(h_d\Big]_{T_r}^{T_d}-h_{c,d}\right) =h_a\Big]_{T_r}^{T_b}+f\frac{Am+B}{m+1}\Big]_{T_r}^{T_b}+ d(D_{CO_2}H_{CO_2}+D_{H_2O}H_{H_2O}+D_{O_2}H_{O_2}+D_{N_2}H_{N_2})\Big]_{T_r}^{T_b} \tag{3}$$

Upon collection of terms, equation (3) becomes

$$f=\frac{h_a\Big]_{T_a}^{T_b}+\Phi}{-h_{c,f}-\frac{Am+B}{m+1}\Big]_{T_r}^{T_b}} \tag{4}$$

where

$$\Phi=-(1+d')\frac{W_c}{J}-d\left\{h_d\Big]_{T_r}^{T_d}-h_{c,d}- (D_{CO_2}H_{CO_2}+D_{H_2O}H_{H_2O}+D_{O_2}H_{O_2}+D_{N_2}H_{N_2})\Big]_{T_r}^{T_b}\right\} \tag{5}$$

The term Φ considers all the effects of diluent addition and compressor work on the magnitude of the fuel-air ratio ideally required to attain the specified combustion temperature; Φ is a function of the kind and amount of diluent used, the initial temperature and state of the diluent, the compressor work, and the combustion temperature.

The denominator of equation (4) contains all the factors that depend on the nature of the fuel. The effect of variation of fuel characteristics can be computed by correction factors that depend only on this denominator. For convenience of chart representation, a standard hydrocarbon fuel having a hydrogen-carbon ratio of 0.175 and a lower

enthalpy of combustion of −18,700 Btu per pound was used. Correction factors K_m and K_h permit the calculation of the required fuel-air ratio for other hydrocarbon fuels. The value of the product K_mK_h is given by

$$K_mK_h=\frac{18{,}700-\left.\frac{0.175A+B}{1.175}\right]_{T_r}^{T_b}}{-h_{c,f}-\left.\frac{Am+B}{m+1}\right]_{T_r}^{T_b}} \tag{6}$$

The two correction factors have been so adjusted that the correction is exact for the average variation of the lower heating value with the hydrogen-carbon ratio of the gasolines, kerosenes, and light fuel oils currently available. The assumed average relation is

$$h_c=-(15{,}935+15{,}800m) \tag{7}$$

The corrections are also exact for a hydrogen-carbon ratio of 0.175 for any lower heating value. Small errors exist for other combinations of heating value and hydrogen-carbon ratio. For example, the fuel quantity calculated for a combustion temperature of 3000° R for a fuel with a hydrogen-carbon ratio of 0.084 will be in error about 1 percent for every 1500 Btu per pound that the lower heating value of the fuel varies from the value given by equation (7).

A correction factor K_w, which permits the calculation of the fuel-air ratio required to attain a given combustion temperature when the air at the initial temperature contains water vapor, is defined by the relation

$$K_w=\frac{\left.h_{m,a}\right]_{T_a}^{T_b}}{\left.h_a\right]_{T_a}^{T_b}} \tag{8}$$

where $h_{m,a}$ is the enthalpy of moist air in Btu per pound of moist air. The value of K_w is found to be practically independent of the initial temperature T_a and therefore can be represented as a function only of water-vapor-to-air ratio and of T_b. The working values of K_w have been based on a value of T_a of 900° R.

In terms of equations (4), (6), and (8), the total fuel-air ratio ideally required to attain a desired temperature by combustion of a mixture of air, hydrocarbon fuel, and diluents is given by

$$f=\frac{K_mK_h\left(K_w\left.h_a\right]_{T_a}^{T_b}+\Phi\right)}{18{,}700-\left.\frac{0.175A+B}{1.175}\right]_{T_r}^{T_b}} \tag{9}$$

$$=K_mK_hK_wf'+\Delta f \tag{10}$$

where the fuel-air ratio f' for the standard fuel without diluent addition is given by

$$f'=\frac{\left.h_a\right]_{T_a}^{T_b}}{18{,}700-\left.\frac{0.175A+B}{1.175}\right]_{T_r}^{T_b}} \tag{11}$$

and the increment in fuel-air ratio Δf due to diluent addition is equal to K_mK_hf'' for any hydrocarbon fuel, where the increase in fuel-air ratio f'' for the standard fuel is

$$f''=\frac{\Phi}{18{,}700-\left.\frac{0.175A+B}{1.175}\right]_{T_r}^{T_b}} \tag{12}$$

Specific expressions for increase in chart fuel-air ratio f'' due to addition of various diluents are presented in appendix B.

When the factor K_w is used in the form defined by equation (8), all fuel-air ratios and diluent-air ratios must be expressed in units of pounds per pound of moist air. Only water occurring as vapor at the initial temperature and pressure of the air is considered in computing K_w, fuel-air ratio, and diluent-air ratio. If the air initially contains liquid water, the unevaporated portion of the water must be separately treated in the same manner as a diluent or refrigerant.

A liquid-to-dry-air ratio may be computed by multiplying a liquid-to-moist-air ratio by the ratio of mass of moist air to mass of dry air $\left(1+\frac{\text{grains water vapor/lb dry air}}{7000}\right)$.

Combustion with incomplete heat release.—In actual combustion processes of gas-turbine engines, the heat of combustion of fuel and of combustible diluents is never fully released. In turbine engines when combustible diluents are injected at the compressor inlet, the diluent is distributed throughout the combustion air; as a result of this mixing and because only a small part of the total air passes through the flame zone, much of the diluent vapor never reaches a sufficiently high temperature to promote efficient combustion.

In order to discuss incomplete heat release quantitatively, a basis must be established for an estimate of the enthalpy of the products of incomplete combustion. The difference between the enthalpy of several possible residual molecules plus the oxygen required to burn them and the enthalpy of the corresponding masses of molecules of products CO_2, H_2O, and N_2 is later shown to be small as compared with the enthalpy of combustion of the assumed residual molecules. The enthalpy of the products of incomplete combustion has accordingly been assumed to be equal to that of the completely burned mixture at the actual temperature of the incompletely burned mixture.

A heat-release ratio η_f is defined as the fraction of the lower heat of combustion of the liquid fuel effective in increasing the enthalpy across the combustor

$$\eta_f=\frac{\text{actual enthalpy rise across the combustor}}{\text{heating value of liquid fuel supplied}}$$

The heat-release ratio for the hydrocarbon fuel is then given by the heat-balance equation

$$f_a\left(-h_{c,f}\eta_f-\left.\frac{Am+B}{m+1}\right]_{T_r}^{T_b}\right)=\left.h_a\right]_{T_a}^{T_b}+\Phi \tag{13}$$

where f_a is the actual total fuel-air ratio for the incompletely burned mixture and T_b is the actual combustion temperature.

The heat-balance equation for the ideal combustion process is

$$f_i\left(-h_{c,f}-\frac{Am+B}{m+1}\Big]_{T_r}^{T_b}\right)=h_a\Big]_{T_a}^{T_b}+\Phi \tag{14}$$

where f_i is the ideal fuel-air ratio.

The ratio of fuel actually required to fuel ideally required r_f from equations (13) and (14) is then

$$r_f=\frac{f_a}{f_i}=\frac{-h_{c,f}-\frac{Am+B}{m+1}\Big]_{T_r}^{T_b}}{-\eta_f h_{c,f}-\frac{Am+B}{m+1}\Big]_{T_r}^{T_b}} \tag{15}$$

The ratio r_f depends only on η_f, the composition of the fuel, and the combustion temperature; the ratio is independent of h_a and Φ.

The value of r_f is found to be practically independent of $h_{c,f}$ and m when η_f is greater than 0.7; for the lower values of η_f (to about 0.5), the quantity r_f varies a maximum of 1 percent for the range of liquid hydrocarbon fuels. The working values of r_f have therefore been based on the standard fuel.

Liquid combustible diluents whether burned or not will usually be completely vaporized. A heat-release ratio for combustible diluents η_d is then defined as the fraction of the lower heat of combustion of the vaporized diluent $-h_{c,d}'$ actually released

$$\eta_d=\frac{\text{actual heat released by vaporized diluent}}{\text{heating value of vaporized diluent supplied}}$$

Any defect in heat release must be compensated for by an increase in primary fuel rate. For any hydrocarbon fuel, the increment in fuel-air ratio Δf due to incomplete heat release is given by $K_mK_hf''_\eta$ where the increase in fuel-air ratio for the standard fuel f''_η is

$$f''_\eta=\frac{d(1-\eta_d)(-h_{c,d}')}{18{,}700-\frac{0.175\,A+B}{1.175}\Big]_{T_r}^{T_b}} \tag{16}$$

Specific equations for f''_η for water-alcohol mixtures and ammonia are given in appendix C.

The total fuel-air ratio actually required to attain a desired temperature by combustion of a mixture of air, hydrocarbon fuel, and diluents with incomplete heat release considered is given by

$$f=r_f(K_mK_hK_wf'+\Delta f) \tag{17}$$

COMBUSTION CHARTS

Two combustion charts, which are based on equation (4) with Φ equal to zero, are presented as figures 1 and 2. These two charts permit the determination for dry air of the ideal fuel-air ratio f' as a function of the initial temperature and the combustion temperature, respectively, for a single hydrocarbon fuel having a lower enthalpy of combustion of −18,700 Btu per pound and a hydrogen-carbon ratio of 0.175. The ideal fuel-air ratio f' for this standard fuel is called the chart fuel-air ratio.

The fuel correction factors K_m and K_h and the water-vapor correction factor K_w are included as inserts on figures 1 and 2. These correction factors permit the calculation of the ideal fuel-air ratio for hydrocarbon fuels other than the standard fuel and for combustion air that initially contains water vapor.

In the determination of the combustion temperature for any given fuel, fuel-air ratio, and initial air temperature, figure 1 is also readily employed, as illustrated later by an example.

Combustion-gas mixtures that have undergone work abstraction or heat-exchange processes in one portion of a gas-turbine engine are frequently required to undergo further combustion and subsequent thermodynamic processes. The problem of reheating a combustion gas by the burning of additional fuel, provided that the over-all fuel-air ratio is leaner than stoichiometric, is readily solved by the use of figures 1 and 2. The procedure in making such a calculation is illustrated later by an example.

The relation between the heat-release ratio η_f and the ratio of actual fuel-air ratio to ideal fuel-air ratio r_f is shown in figure 3. This relation may be used in conjunction with figures 1 and 2 to compute the required fuel-air ratio for an assigned combustion temperature and heat-release ratio or to determine the heat-release ratio from known values of combustion temperature, actual fuel-air ratio, and ideal fuel-air ratio.

Combustion charts for determining the increase in chart fuel-air ratio due to diluent addition f'' have been prepared from equation (12) for the following diluents:

(1) water, ethyl alcohol, methyl alcohol, isopropyl alcohol, and water-alcohol mixtures
(2) liquid ammonia
(3) liquid carbon dioxide
(4) liquid nitrogen
(5) liquid oxygen

The increase in fuel-air ratio due to incomplete heat release of the combustible diluents is determined by separate charts for water-alcohol mixtures and for ammonia.

Equations from which the increment in fuel-air ratio Δf due to diluent addition or to incompleteness of diluent combustion is computed are included on each chart.

ALCOHOLS AND WATER AS DILUENTS

The alcohols and water form a convenient group because of formal chemical similarity and because they are generally used as mixtures of alcohols or of water with one or more alcohols. The three alcohols commercially available in large quantities are methyl alcohol, ethyl alcohol, and

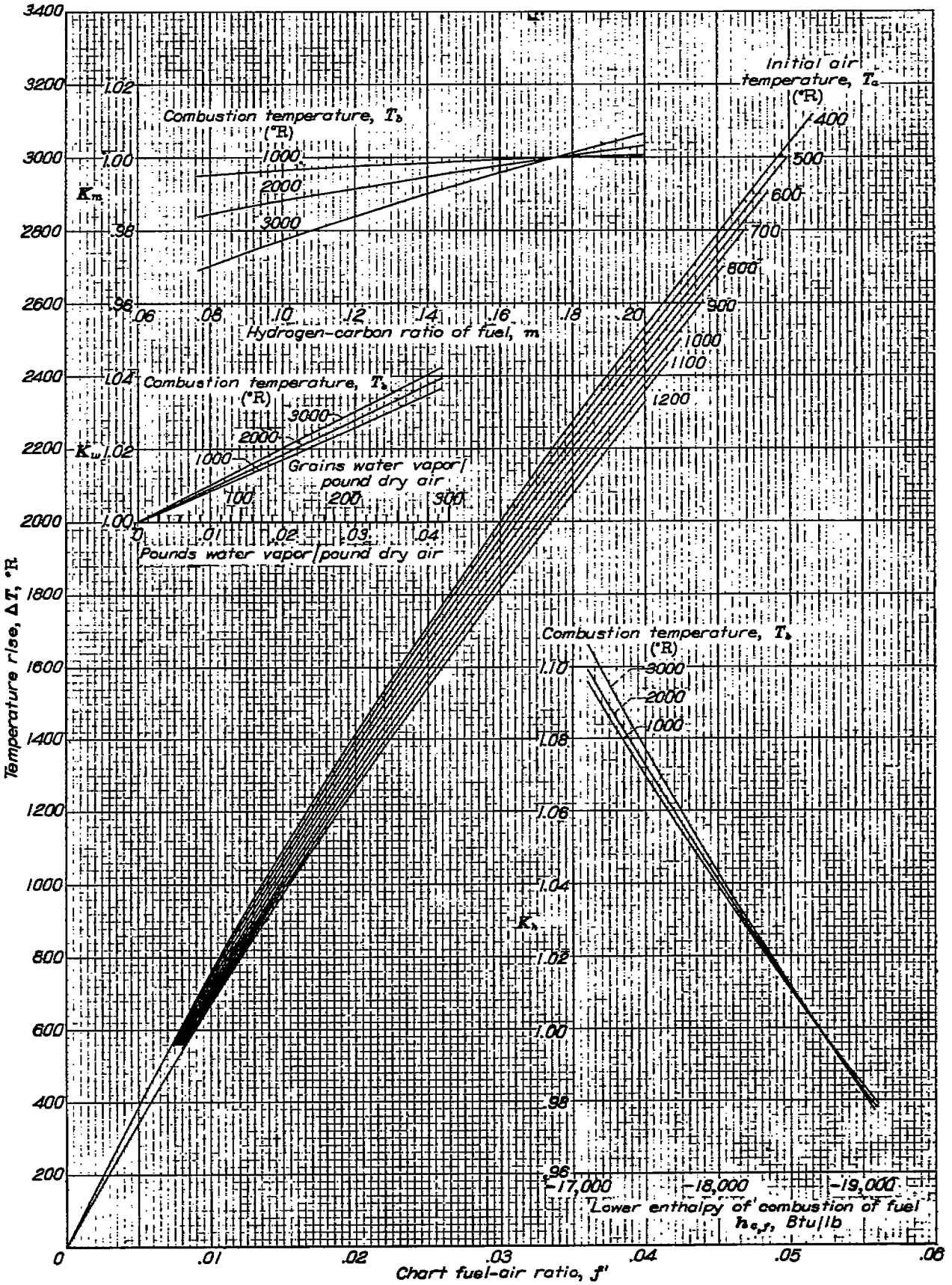


FIGURE 1.—Fuel-air ratio f for ideal constant-pressure combustion as function of initial temperature. $f=K_m K_h K_w f'$.

(A 13- by 18-in. print of this chart is available upon request from NACA.)

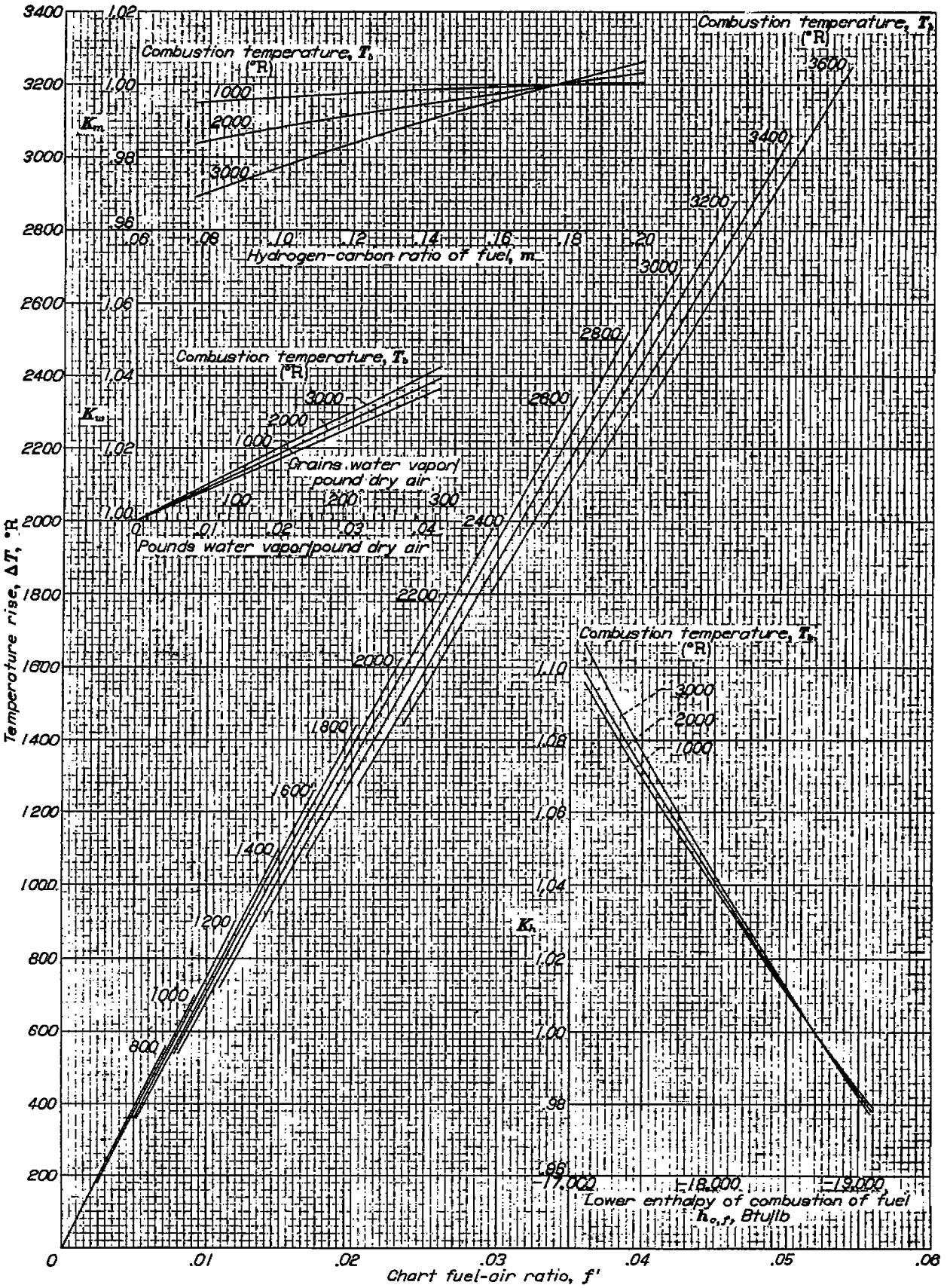


FIGURE 2.—Fuel-air ratio f for ideal constant-pressure combustion as function of combustion temperature. $f=K_mK_hK_wf'$.

(A 18- by 18-in. print of this chart is available upon request from NACA.)

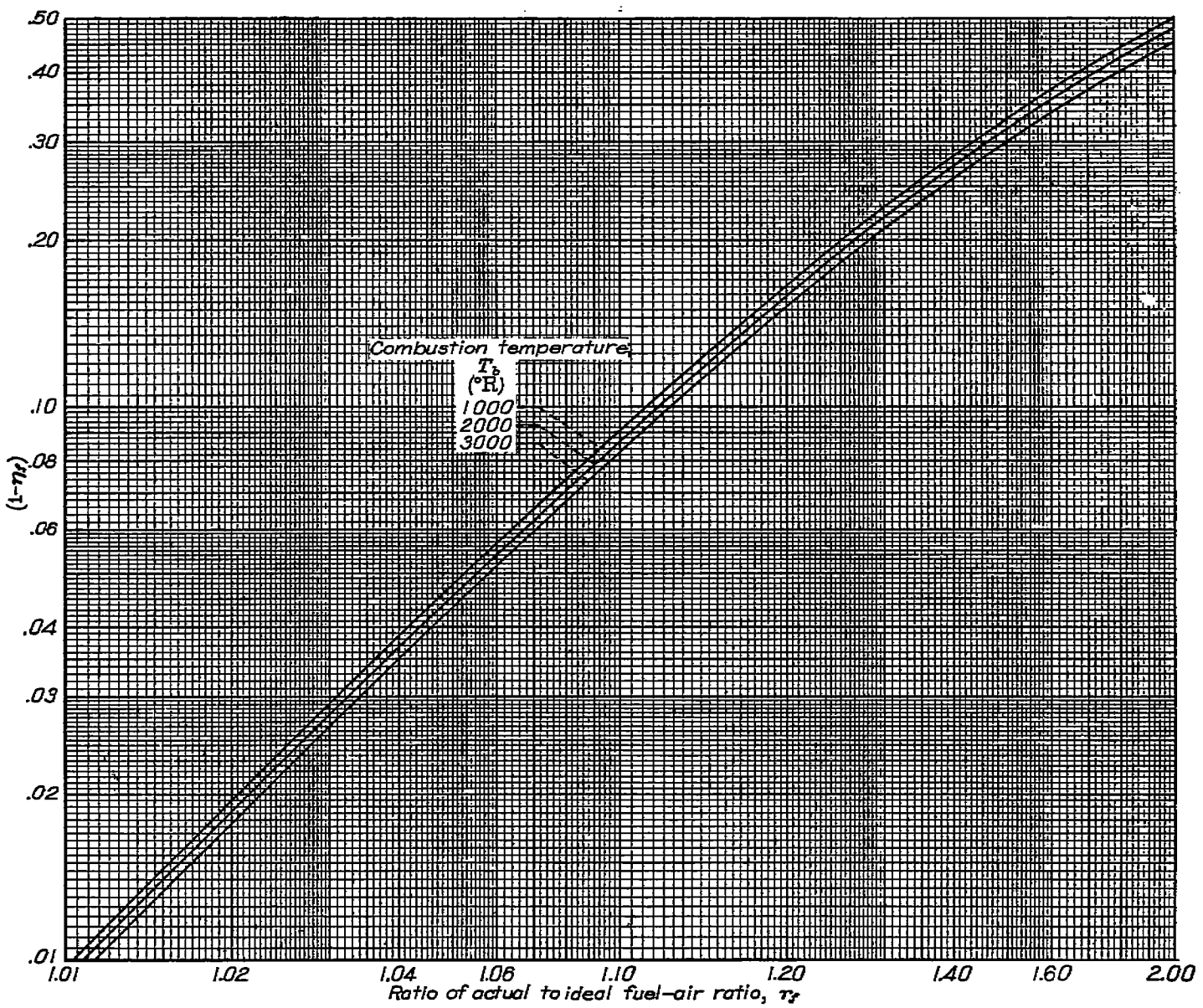


FIGURE 3.—Ratio of actual to ideal fuel-air ratio for incomplete combustion of hydrocarbon fuel as function of heat-release ratio η_f.

isopropyl alcohol. They may be grouped with water by the following formal scheme:

Isopropyl alcohol	$(CH_2)_3H_2O$
Ethyl alcohol	$(CH_2)_2H_2O$
Methyl alcohol	CH_2H_2O
Water	H_2O

The various alcohols, water, and water-alcohol mixtures only differ in the amount of CH_2 radical; thus a mixture of water and alcohols can be presented by the average chemical formula $(CH_2)_xH_2O$. The value of the formula weight M_m of the water-alcohol mixture may be expressed either as a function of the mixture characteristic x or in terms of the fractions by weight of the mixture constituents. In terms of x

$$M_m = M_{H_2O} + xM_{CH_2} \tag{18}$$

where

M_{H_2O} molecular weight of water
M_{CH_2} molecular weight of CH_2 radical

When the sum of the weights of constituents of the mixture is taken as unity by definition, the reciprocal formula weight of the mixture is given by

$$\frac{1}{M_m} = \frac{1}{M_0} + \left(\frac{1}{M_1} - \frac{1}{M_0}\right)W_1 + \left(\frac{1}{M_2} - \frac{1}{M_0}\right)W_2 + \left(\frac{1}{M_3} - \frac{1}{M_0}\right)W_3 \tag{19}$$

where

M molecular weight of each constituent
W fraction by weight of each constituent

and subscripts 0, 1, 2, and 3 refer to water, methyl alcohol, ethyl alcohol, and isopropyl alcohol, respectively.

The quantity $1/M_m$ serves as a parameter of a given mixture and may be computed from equation (19) or determined with the aid of figure 4, which is a graphical representation of equation (19). The determination of $1/M_m$ for a mixture containing equal parts of water and of each of the three alcohols (0.25 lb/lb diluent mixture) is illustrated in figure 4 ($1/M_m=0.0313$).

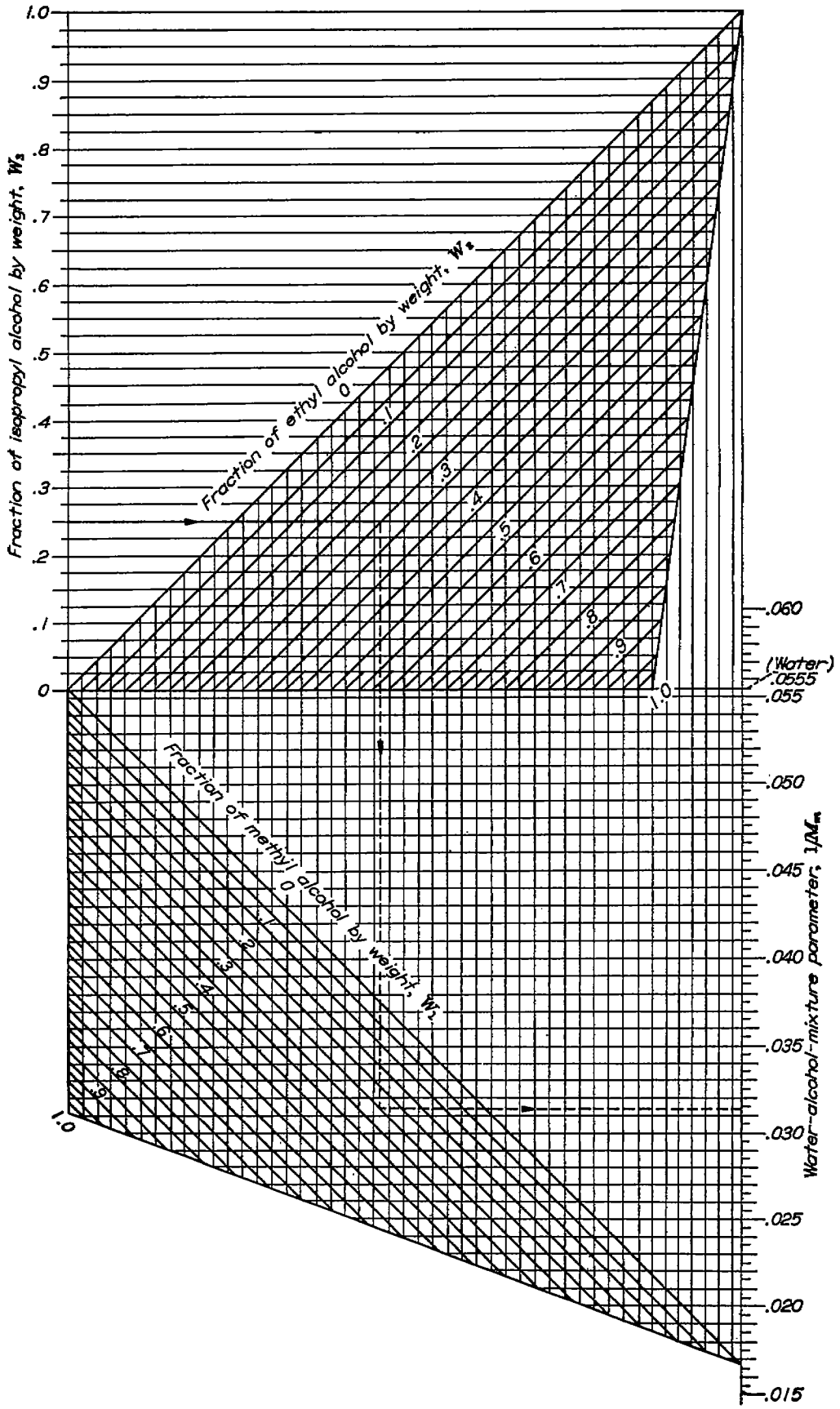


FIGURE 4.—Water-alcohol-mixture parameter as function of mixture composition by weight.

Ideal combustion.—The increment in fuel-air ratio Δf required to attain a specified combustion temperature T_b with water-alcohol addition to the fuel-air mixture may be calculated by the use of figure 5. The water-alcohol mixture is assumed to be completely burned. The equations on which figure 5 are based are discussed in appendix B. The increase in chart fuel-air ratio f'' required by water-alcohol addition is proportional to the diluent-air ratio d expressed in pounds per pound of air and is principally a function of the mixture parameter $1/M_m$, the initial temperature and state of the water-alcohol mixture, and the combustion temperature. The diluent-air ratio d is expressed as pounds of diluent per pound of air, which may be initially either dry or moist. The principal chart is exactly correct for mixtures of water and methyl alcohol at an initial liquid temperature of 540° R; small additive corrections to f'' must be applied for water-alcohol mixtures containing ethyl or isopropyl alcohols. (See appendix B.) When the mixture contains ethyl alcohol or isopropyl alcohol, the required corrections are $\delta_2 f''$ and $\delta_3 f''$, respectively, and may be found by means of the right insert on figure 5. If both ethyl and isopropyl alcohols are present, corrections for each alcohol are added successively.

If the diluent mixture is initially injected as a liquid at a temperature other than 540° R, an additional correction $\delta_h f''$ is required. This correction depends on the difference between the enthalpy of the diluent at injection temperature and the enthalpy of the diluent in the liquid phase at 540° R. A sufficiently accurate value of this enthalpy for liquid diluents is obtained by the assumption that the specific heat of the three alcohols is 0.60 and the specific heat of water is 1.00 Btu per pound per °R. Hence

$$h_d\Big]_{T_r}^{T_d}=(0.40W_0+0.60)(T_d-540) \qquad (20)$$

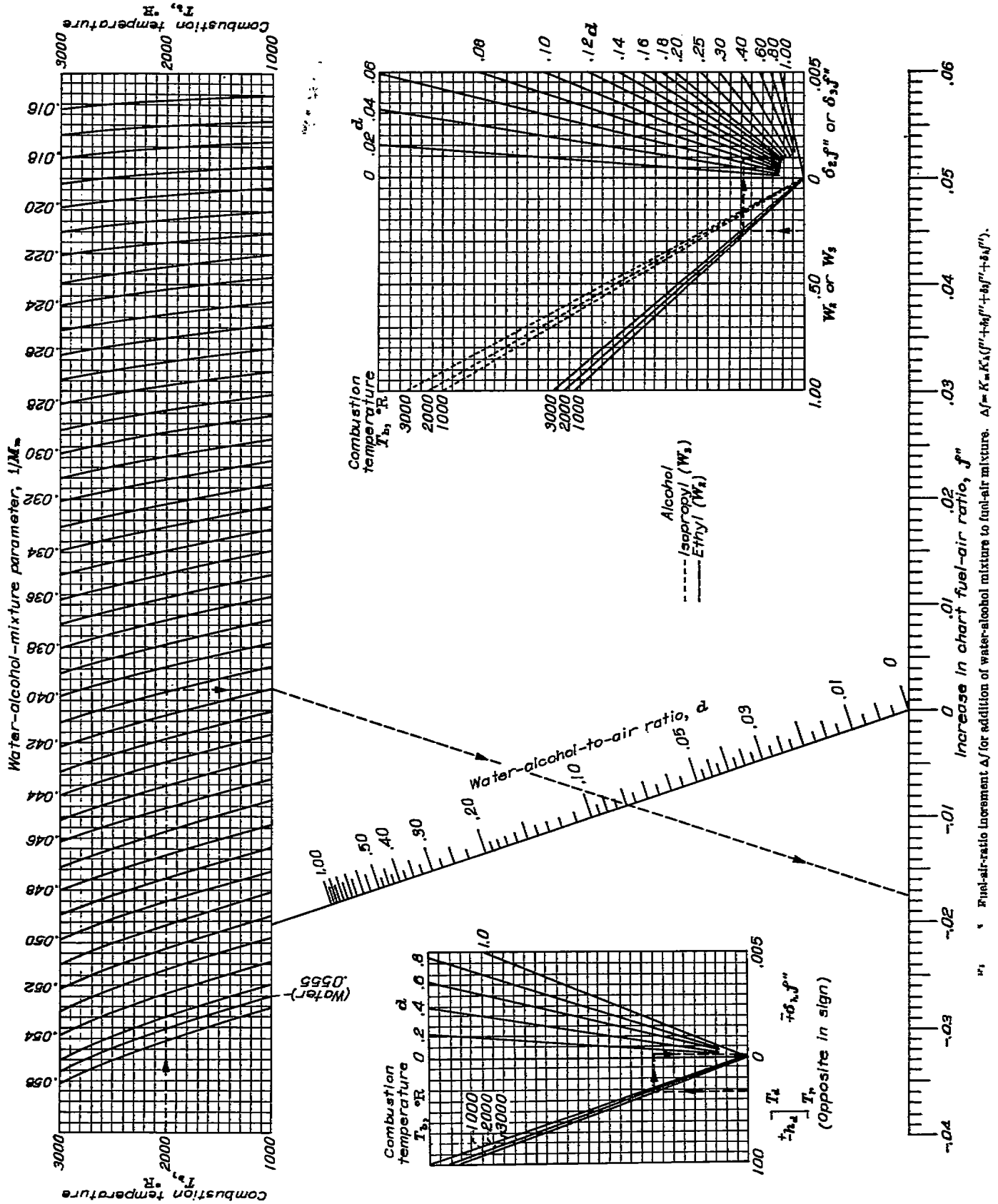
where W_0 is the fraction by weight of the water in the mixture of diluents.

The correction $\delta_h f''$ may be obtained from a known value of $h_d\Big]_{T_r}^{T_d}$ with the aid of the left insert on figure 5.

The increase in chart fuel-air ratio required for water-alcohol-mixture addition for the standard hydrocarbon fuel is

$$(f''+\delta_2 f''+\delta_3 f''+\delta_h f'')$$

and the increment in fuel-air ratio Δf for other hydrocarbon



Fuel-air-ratio increment Δf for addition of water-alcohol mixture to fuel-air mixture. $\Delta f=K_w K_h(f''+\delta_2 f''+\delta_3 f''+\delta_h f'')$.

fuels is

$$K_m K_h (f'' + \delta_2 f'' + \delta_3 f'' + \delta_h f'')$$

An example illustrating the use of figure 5 is given in a subsequent section.

The use of figure 5 for values of $1/M_m$ corresponding to mixtures that are composed mostly of water is subject to some inaccuracy because of the small angles with which the slant lines used in the determination of f'' intersect the multiplier scale. An enlargement of part of figure 5 in the range of $1/M_m$ from 0.0480 to 0.0555 (water-alcohol mixtures containing 75 percent or more of water) is presented in figure 6 to improve the accuracy in this region. Problems

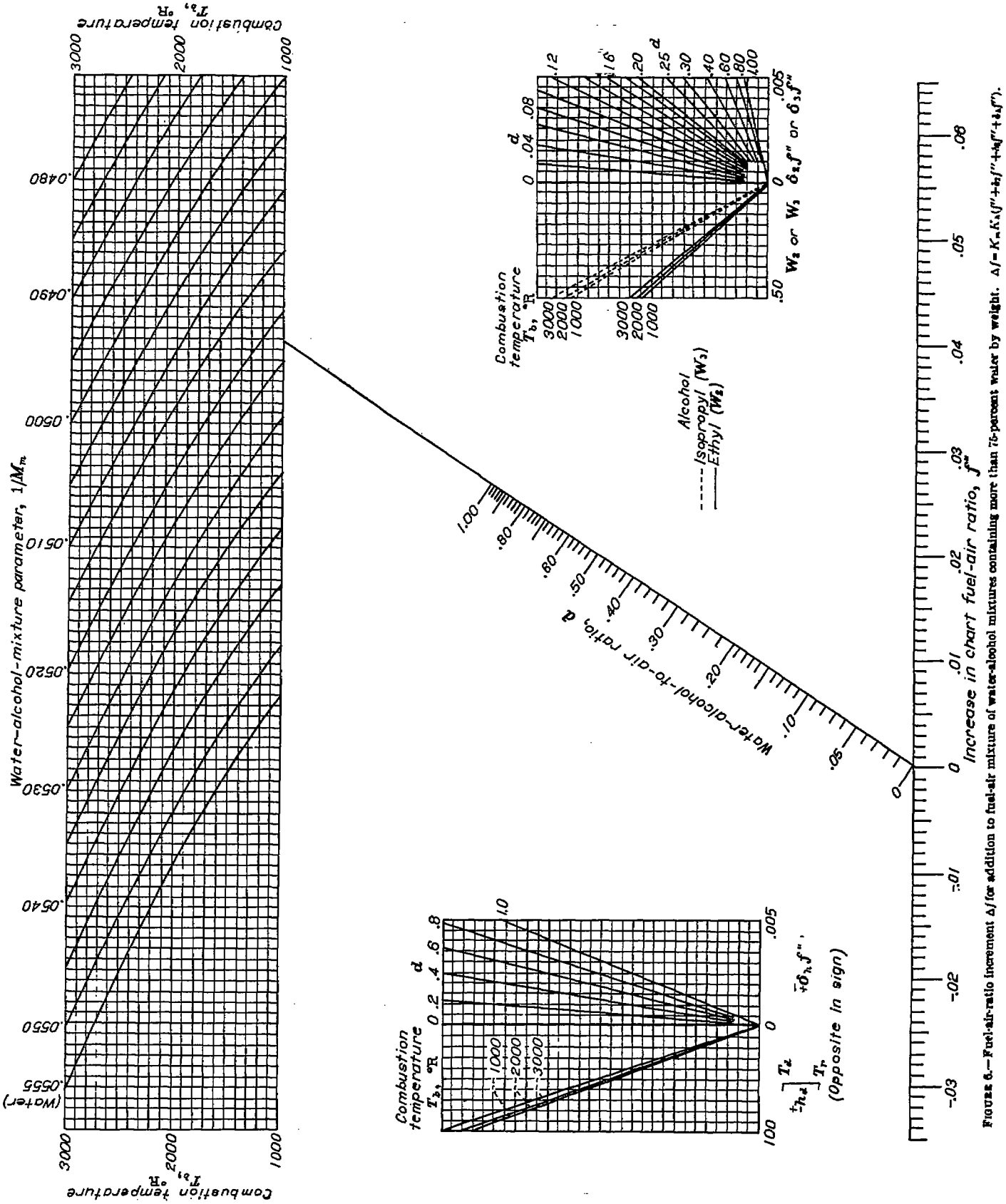


FIGURE 6.—Fuel-air-ratio increment Δf for addition to fuel-air mixture of water-alcohol mixtures containing more than 75-percent water by weight. $\Delta f = K_m K_h (f'' + \delta_2 f'' + \delta_3 f'' + \delta_h f'')$.

of the addition of water-alcohol mixtures containing mostly water, and which ideally require little or no additional fuel to maintain a given combustion temperature, are more readily handled by figure 6, which is used in precisely the same manner as figure 5.

Combustion with incomplete heat release.—The increment in fuel-air ratio Δf due to incomplete combustion of the water-alcohol mixture may be determined from figures 7 and 8 and is given by $K_m K_k f''_\eta$. Figure 7 applies to any water-alcohol mixture and is used in conjunction with

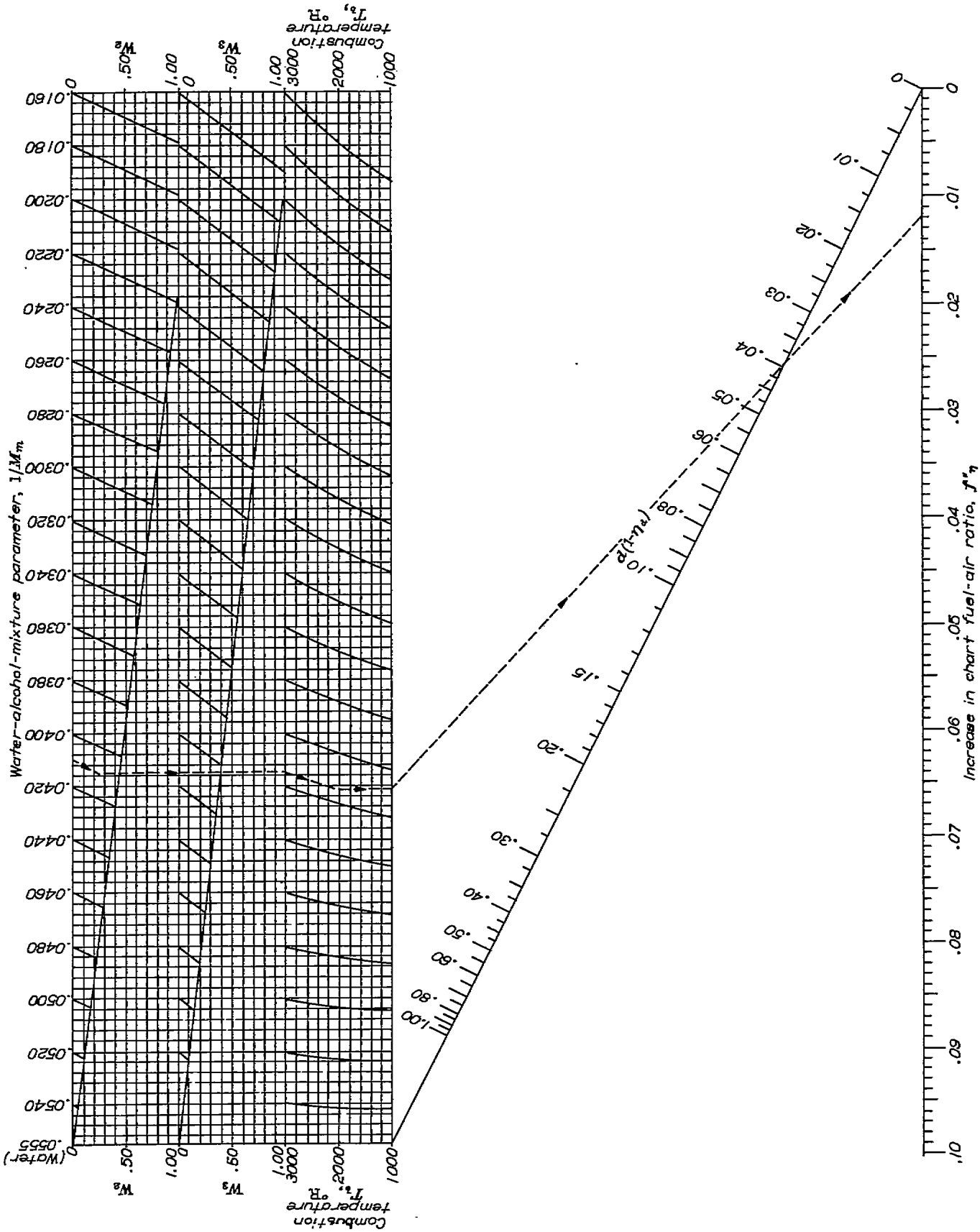


FIGURE 7.—Fuel-air-ratio increment Δf due to incomplete combustion of water-alcohol mixtures. $\Delta f = K_m K_k f''_\eta$.

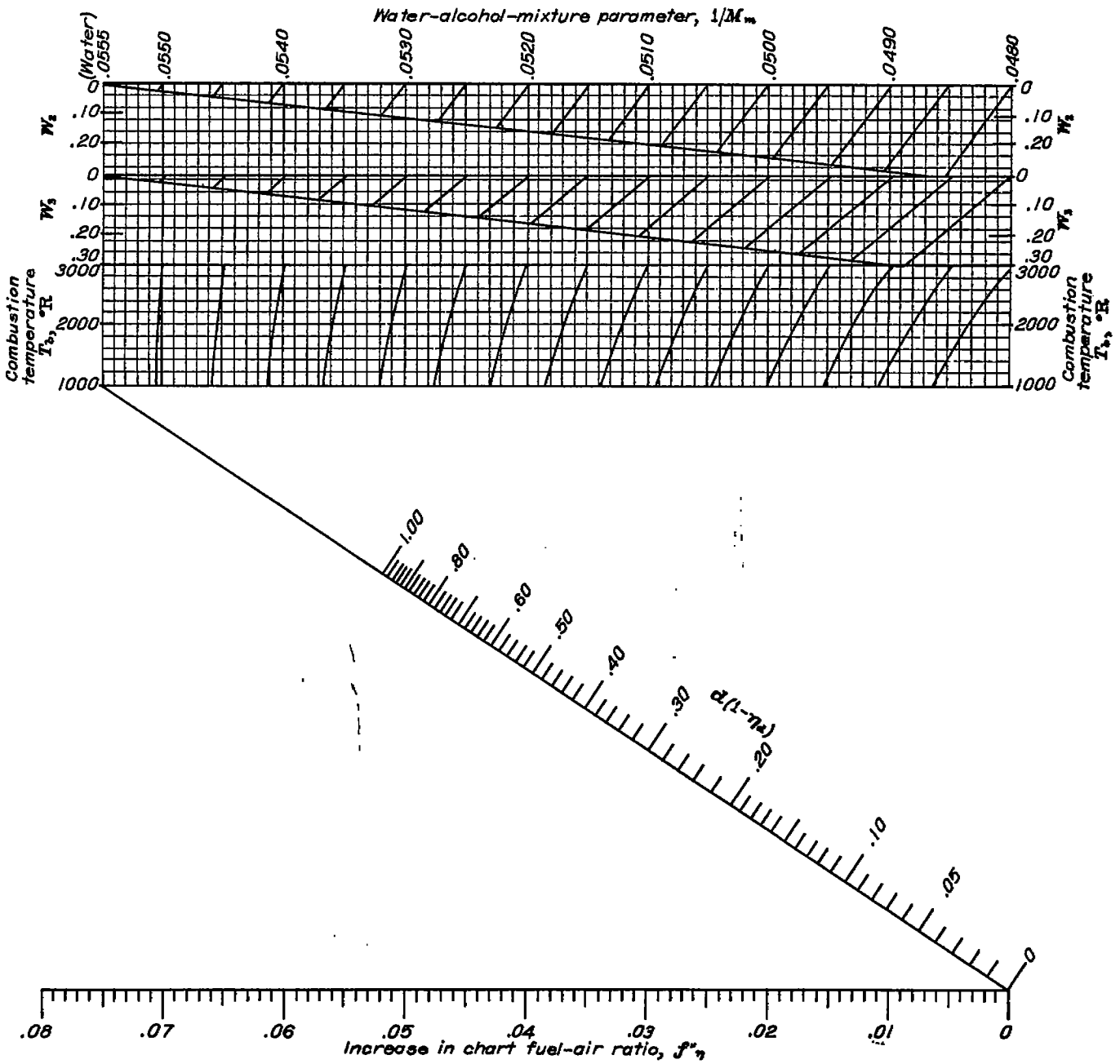


FIGURE 8.—Fuel-air-ratio increment Δf due to incomplete combustion of water-alcohol mixtures containing 75-percent water by weight or more. $\Delta f = K_m K_h f''_\eta$.

figure 5; figure 8 applies to water-alcohol mixtures containing 75-percent water or more and is used in conjunction with figure 6.

The increase in chart fuel-air ratio f''_η over the fuel-air ratio ideally required for water-alcohol-mixture addition is a function of mixture parameter $1/M_m$, diluent-air ratio d, heat-release ratio η_d, and combustion temperature T_b (appendix C). The small corrections for mixtures of water and alcohol containing fractions of ethyl or isopropyl alcohols and the effect of combustion temperature are incorporated at the top of the chart. The use of figure 7 is later illustrated by an example.

LIQUID AMMONIA AS DILUENT

Ideal combustion.—When dry liquid ammonia is used as a diluent, the increase in chart fuel-air ratio f'' is proportional to the weight of added ammonia in pounds per pound of air d; the fuel-air ratio is a function of the combustion temperature T_b and is substantially independent of initial temperature T_d (appendix B). The increment in fuel-air ratio Δf, which is negative for ammonia, may be computed by figure 9 and is given by $K_m K_h f''$.

Combustion with incomplete heat release.—The increment in fuel-air ratio Δf due to incomplete combustion of ammonia vapor may be calculated by the use of figure 10 and is given by $K_m K_h f''_\eta$. The increase in chart fuel-air ratio f''_η over that ideally required for ammonia addition is a function of combustion temperature T_b, diluent-air ratio d, and heat-release ratio η_d (appendix C). An example that illustrates the use of figure 10 is given later.

LIQUID CARBON DIOXIDE AS DILUENT

The increment in fuel-air ratio Δf resulting from the use of liquid carbon dioxide as a diluent may be computed with the

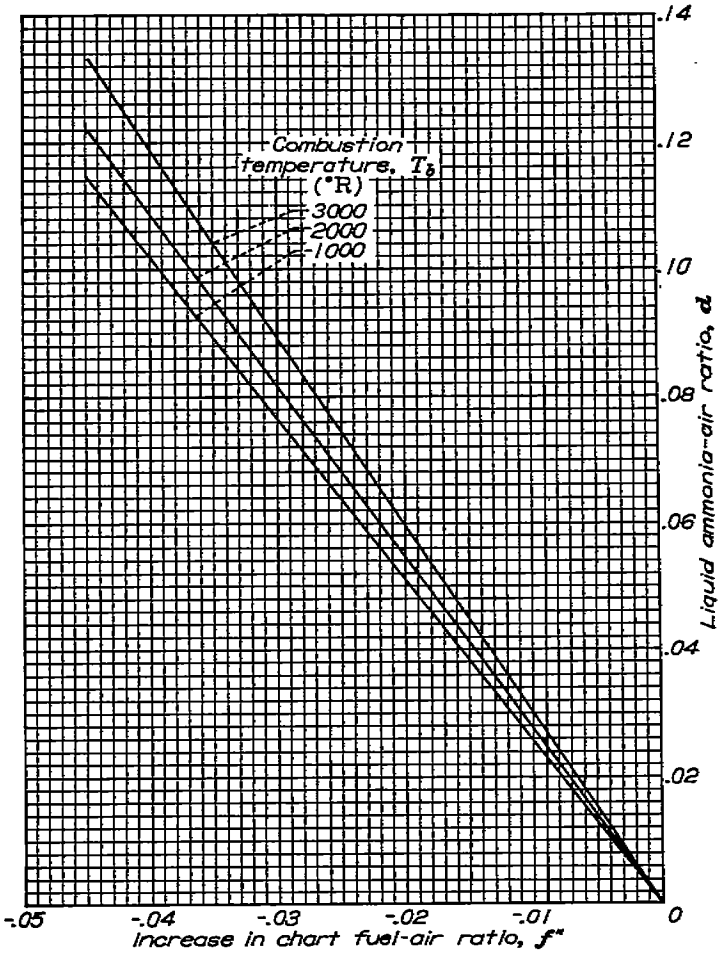


FIGURE 9.—Fuel-air-ratio increment Δf for addition of liquid ammonia to fuel-air mixture. $\Delta f = K_m K_h f''$.

aid of figure 11. Carbon dioxide exists as a liquid at pressures in excess of 5 atmospheres and at temperatures in the range from 391° to 548° R. The carbon dioxide is presumed to be stored as a saturated or subcooled liquid under pressure at a temperature T_d and injected into the combustion-air stream as a liquid; although the chart is based on saturated liquid carbon dioxide, it may be used with accuracy for the subcooled liquid except in the vicinity of the critical temperature (548° R). For convenience, a scale of saturation pressure is included in figure 11. Use of nonsaturated mixtures of liquid and vapor were considered impractical because of the difficulty of controlling rate of discharge and economy of storage space.

For carbon dioxide, f'' is always positive, is a function of T_d and T_b, and is proportional to the weight of carbon dioxide in pounds per pound of air d (appendix B). The fuel-air-ratio increments Δf for liquid carbon dioxide addition is $K_m K_h f''$. The use of figure 11 is illustrated later by an example.

LIQUID NITROGEN AS DILUENT

The increment in fuel-air ratio Δf caused by the use of liquid nitrogen as a diluent may be computed by using figure 12. For liquid nitrogen, f'' is always positive, is a function of the combustion temperature T_b, is proportional to the weight of liquid nitrogen in pounds per pound of air d, and is independent of initial temperature T_d (appendix B). The fuel-air-ratio increment Δf for liquid nitrogen addition is $K_m K_h f''$.

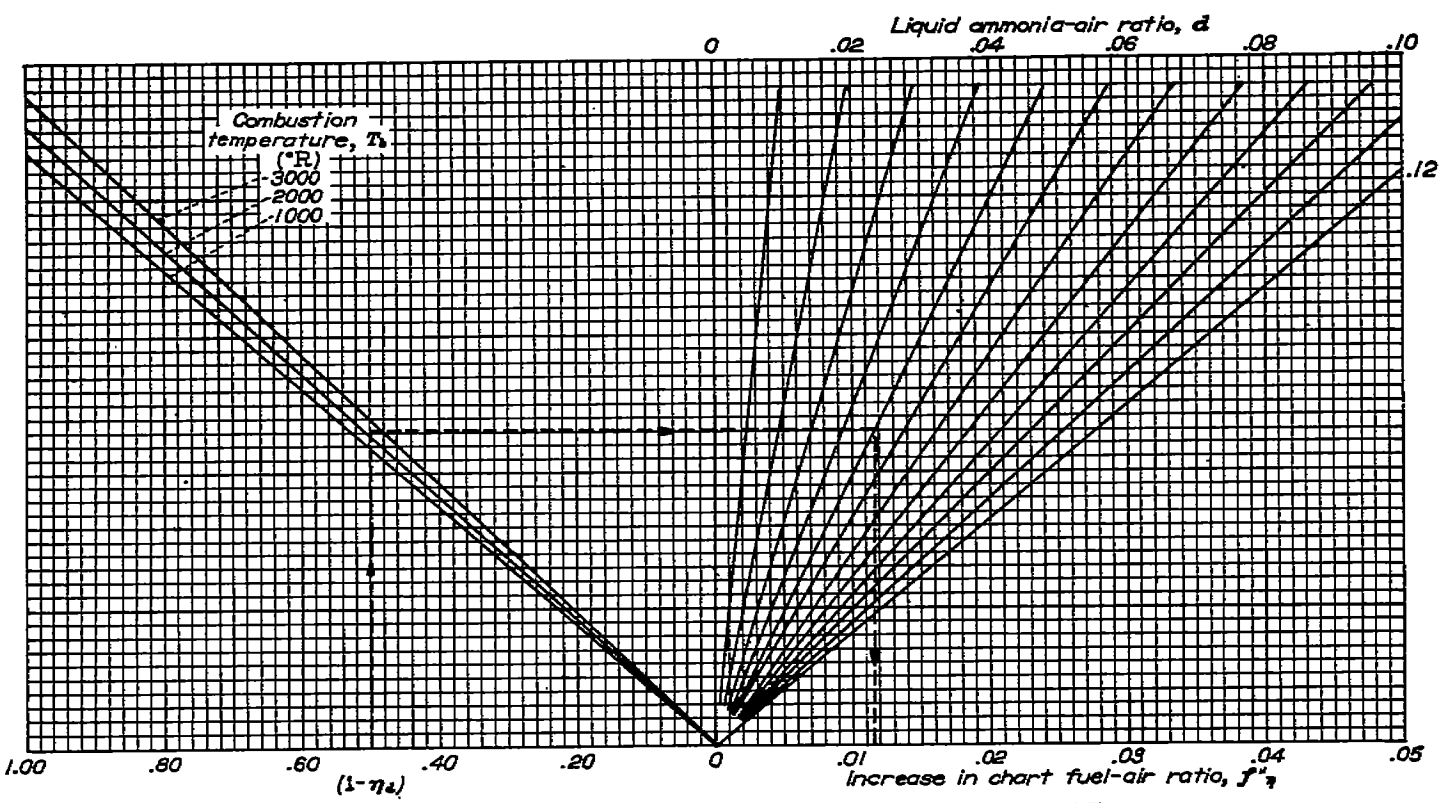


FIGURE 10.—Fuel-air-ratio increment Δf due to incomplete combustion of ammonia. $\Delta f = K_m K_h f''_\eta$.

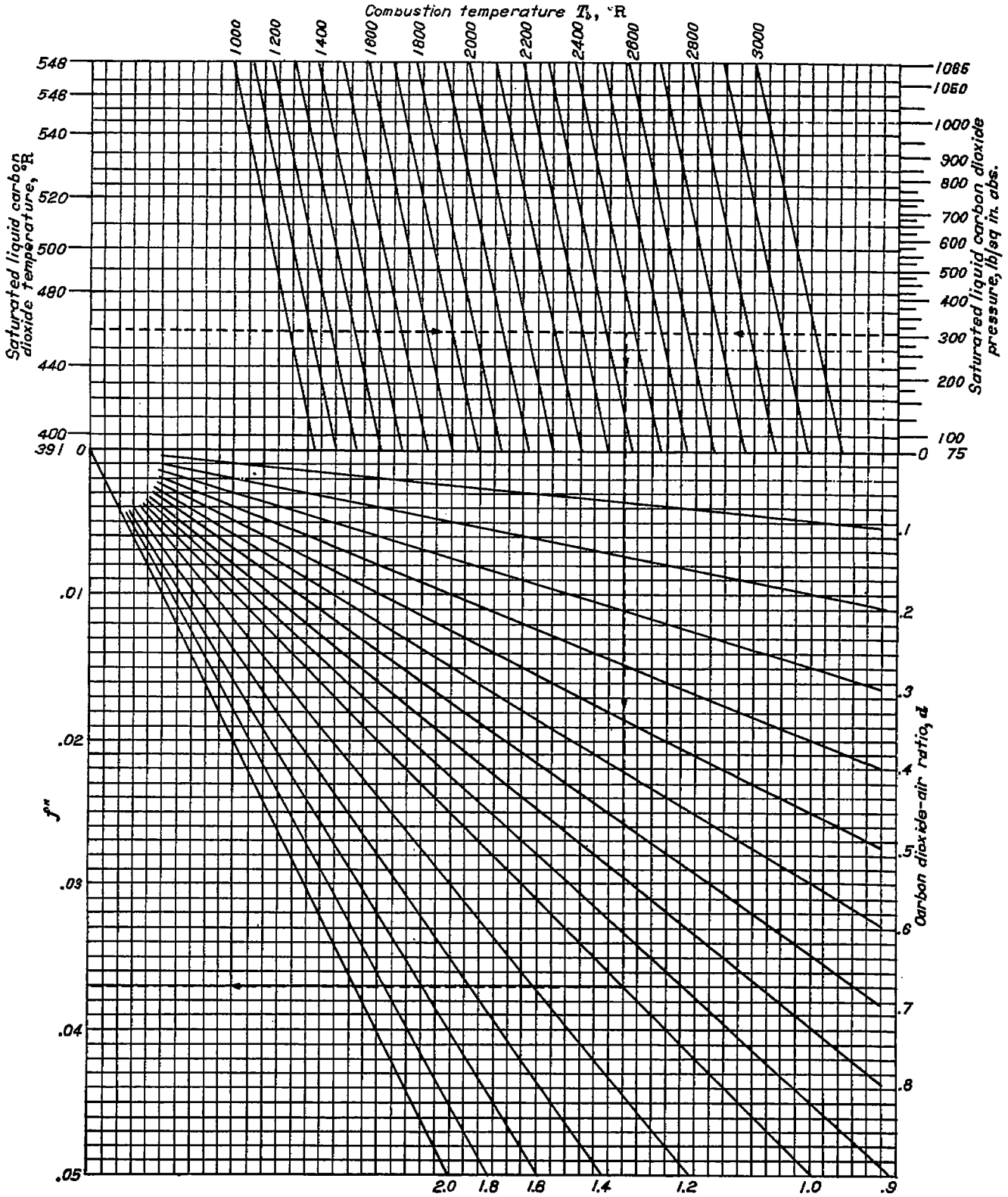


FIGURE 11.—Fuel-air-ratio increment Δf for addition of saturated liquid carbon dioxide to fuel-air mixture. $\Delta f = K_m K_h f''$.

LIQUID OXYGEN AS DILUENT

The increment in fuel-air ratio Δf caused by the use of liquid oxygen as a diluent may be computed by figure 13. For liquid oxygen, f'' is a function of T_b, is proportional to the weight of liquid oxygen in pounds per pound of air d, and is independent of initial temperature T_d (appendix B). For liquid oxygen, f'' is always positive in the range of fuel-air ratio less than stoichiometric. The fuel-air-ratio increment Δf for liquid oxygen addition is $K_m K_h f''$.

EFFECT OF COMPRESSOR WORK OR PREHEATING OF DILUENTS

In the case of turbine engines, a part of the diluent frequently is added to the air stream ahead of the compressor to reduce the air temperature and to increase the compressor

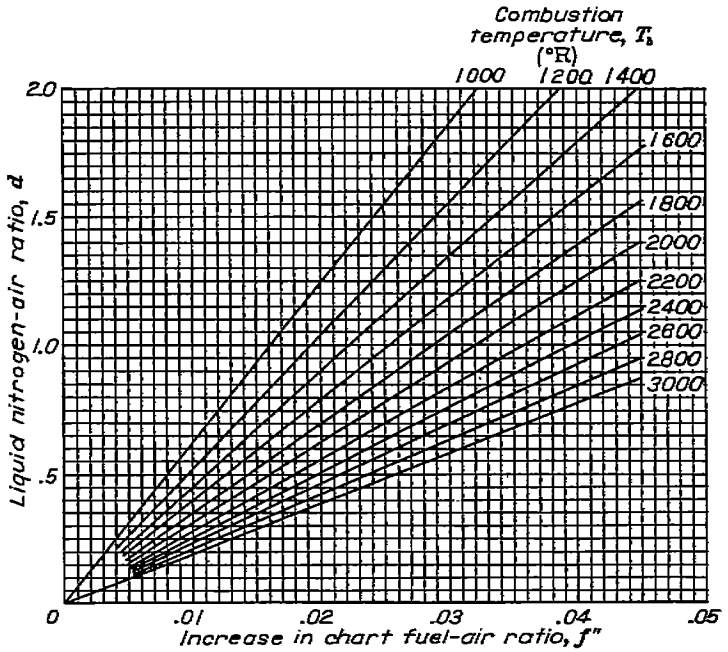


FIGURE 12.—Fuel-air-ratio increment Δf for addition of liquid nitrogen to fuel-air mixture. $\Delta f = K_m K_h f''$.

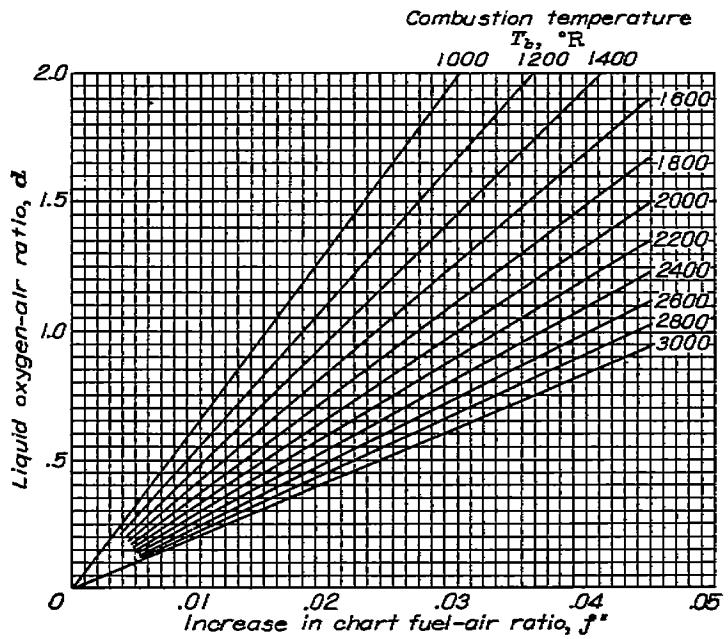


FIGURE 13.—Fuel-air-ratio increment Δf for addition of liquid oxygen to fuel-air mixture. $\Delta f = K_m K_h f''$.

pressure ratio. The addition of the diluent before compression of the working fluid increases the compressor work term of equation (1) and thus increases the enthalpy of the working fluid. The effect of compressor work on the negative increment in fuel-air ratio Δf may be computed by means of figure 14, which includes the work done by the compressor on both air and diluent. The increase in chart fuel-air ratio f'' is a function of the compressor work per pound of compressed mixture W_c, the combustion temperature T_b, and the weight of diluent per pound of air added before compression d (appendix B). When this correction is applied, the air temperature to be used in computing f' by means of figure 1 is the temperature at a point immediately ahead of the diluent injection. The fuel-air-ratio increment Δf for compressor work addition is $K_m K_h f''$. The use of figure 14 is illustrated later by an example.

USE OF MORE THAN ONE DILUENT

When more than one diluent is used or when work of compression is done on the air after diluent addition, all the previous fuel-air-ratio increments Δf corresponding to each of the diluents or to work addition as indicated by figures 5 to 14 are algebraically added. The total fuel-air ratio f is then the algebraic sum of $K_m K_h K_w f'$ and of all the increments Δf multiplied by the ratio r_f. The equation for f is given by

$$f = r_f(K_m K_h K_w f' + \Sigma \Delta f) \tag{21}$$

CALCULATION OF STOICHIOMETRIC FUEL-AIR RATIO WITH DILUENT ADDITION

The use of a mixture of diluents containing a combustible diluent or an oxidant changes the value of the stoichiometric fuel-air ratio. The stoichiometric fuel-air ratio of the mixture as a function of the various pertinent diluent-air ratios is presented in figure 15. (See appendix D for details.) The upper right part of figure 15 is used for evaluation of the stoichiometric fuel-air ratio when water-alcohol mixtures are

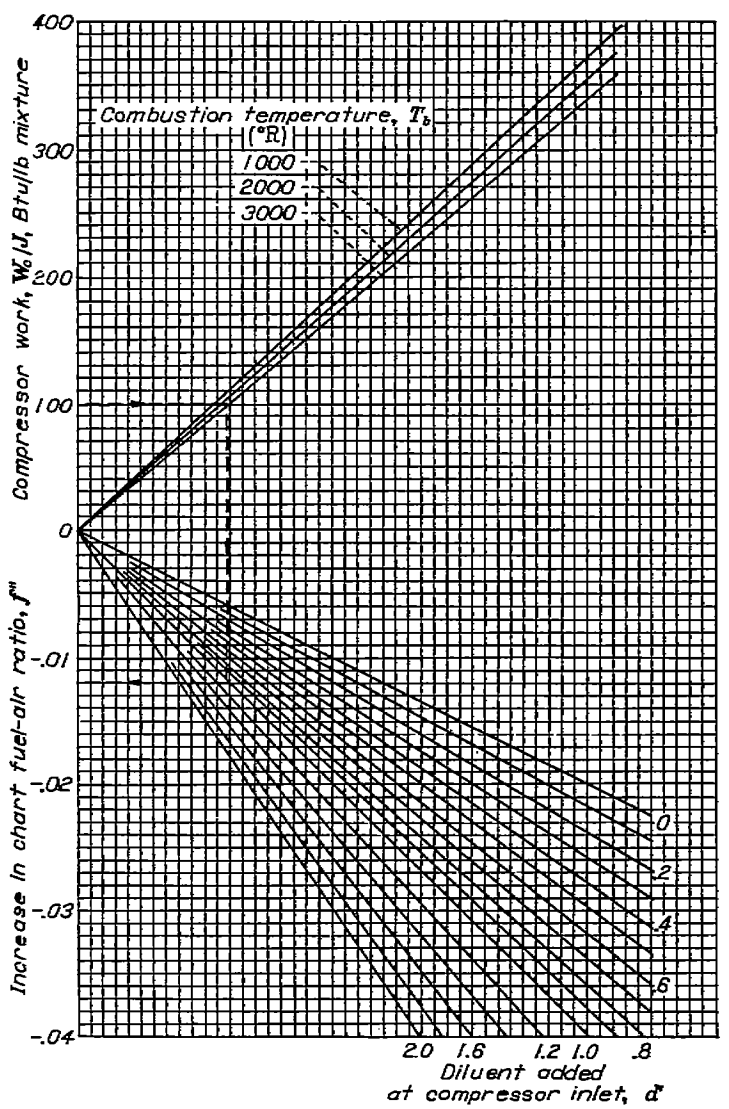


FIGURE 14.—Fuel-air-ratio increment Δf for work addition by compressor to diluent-air mixture. $\Delta f = K_m K_h f''$.

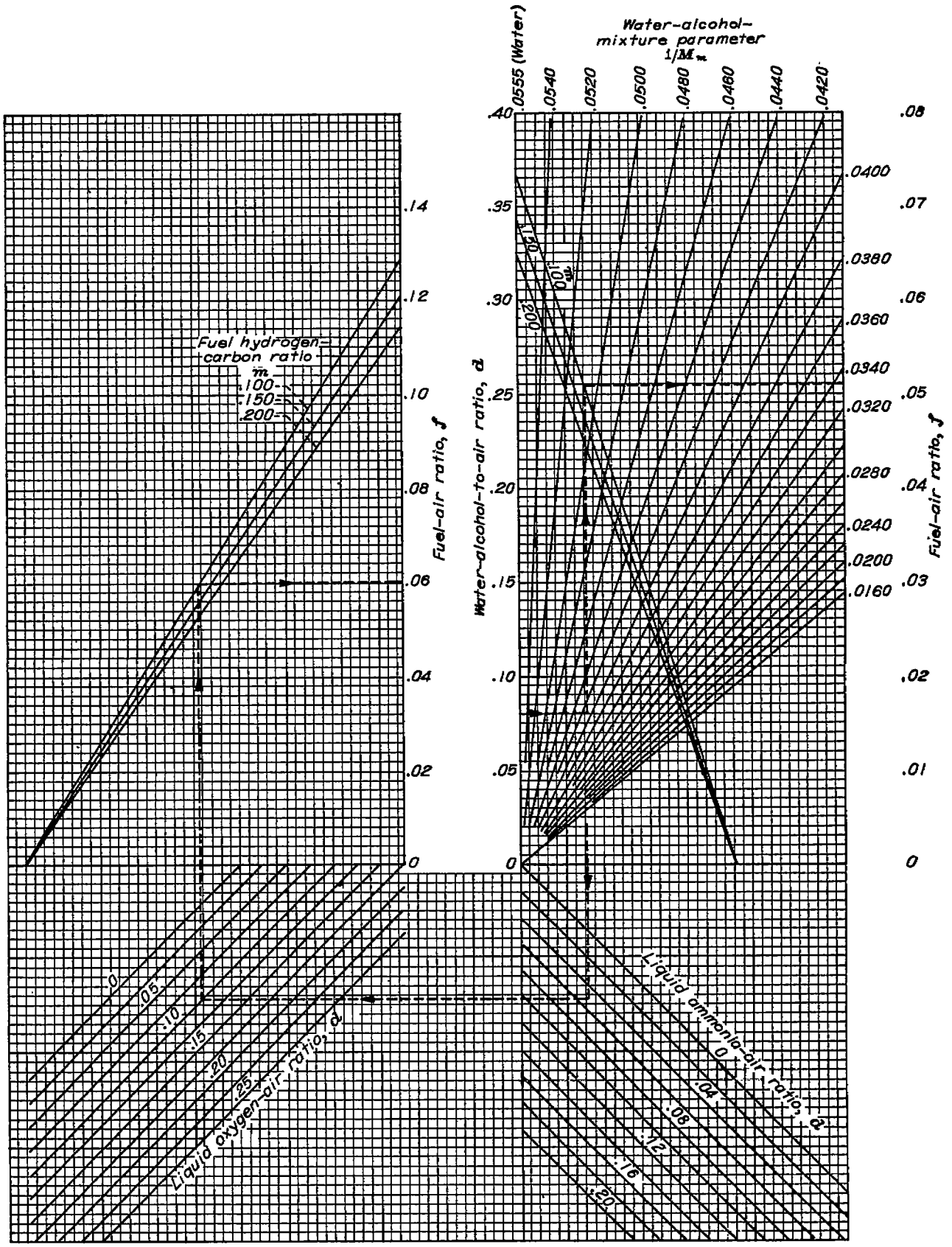


FIGURE 15.—Stoichiometric fuel-air ratio for hydrocarbon fuel-air mixture with diluent addition.

used. The entire figure is used in cases where liquid ammonia and liquid oxygen are separately used, used together, or used in combination with water-alcohol mixtures. The use of the figure is illustrated later by examples.

USE OF COMBUSTION CHARTS WITH DILUENT ADDITION

The use of the combustion charts with diluent addition is illustrated by the following examples. The fuel employed in

the examples has a hydrogen-carbon ratio m of 0.100 and a lower enthalpy of combustion $h_{c,f}$ of −18,300 Btu per pound.

The total fuel-air ratio required to attain a desired combustion temperature is given by the following equation:

$$f=r_f(K_mK_hK_wf'+\Sigma\Delta f) \tag{21}$$

Example 1—Ideal combustion with dry air; no diluent addition.—The amount of fuel necessary to produce a combustion temperature T_b of 2000° R when burned with 1 pound of dry air at an initial temperature of 600° R is to be determined. Because the combustion air is dry, K_w is unity; because combustion is ideal, r_f is unity; and because no diluents are added, $\Sigma\Delta f$ equals zero.

For a temperature rise ΔT of 1400° R and T_b of 2000° R, a chart fuel-air ratio f' of 0.0203 is obtained from figure 2.

From the inserts on figure 2 at a T_b of 2000° R, the correction factors K_m and K_h are obtained and the total fuel-air ratio is calculated from equation (21). For a value of m of 0.100, K_m is 0.9885; for a value of $h_{c,f}$ of −18,300 Btu per pound, K_h is 1.023.

$$f=K_mK_hf'=(0.9885)(1.023)(0.0203)$$
$$=0.0205 \text{ pound per pound dry air}$$

The inverse problem of determining the combustion temperature when the fuel-air ratio is known necessitates an estimation of the combustion temperature from figure 1 using an approximate chart fuel-air ratio, as

$$f'=-fh_c/18{,}700=(0.0205)(18{,}300)/18{,}700=0.0201$$

From figure 1, for an approximate chart fuel-air ratio f' of 0.0201 and an initial air temperature of 600° R, ΔT is 1380° R; therefore, T_b is approximately 600°+1380°=1980° R. The correction factors K_m and K_h corresponding to T_b of 1980° R closely approximate those given previously, so that

$$f'=f/K_mK_h=0.0205/(0.9885)(1.023)=0.0203$$

The calculation of ΔT is repeated using the new chart fuel-air ratio of 0.0203. For this value of chart fuel-air ratio, ΔT=1400° R; therefore, T_b=600°+1400°=2000° R.

Example 2—Ideal combustion with moist air; no diluent addition.—If the combustion air of the preceding example contains water vapor in the amount of 70 grains per pound of dry air, additional fuel is required to achieve a T_b of 2000° R.

From the insert on figure 2, correction factor K_w corresponding to 70 grains of water vapor per pound of dry air and a combustion temperature of 2000° R is 1.0095. The ideal total fuel-air ratio is then calculated.

$$f=K_mK_hK_wf'=(0.9885)(1.023)(1.0095)(0.0203)$$
$$=0.0207 \text{ pound per pound moist air}$$

Example 3—Reheating by burning additional fuel.—The combustion gas of the foregoing example is cooled to 1800° R and reheated to a temperature of 3000° R by burning additional fuel; the additional fuel required is to be determined. This calculation is made by effectively "unburning" the combustion gas so as to find a reference initial air temperature that would give the combustion-gas temperature of 1800° R on combustion of the original fuel quantity corresponding to a fuel-air ratio of 0.0207 pound per pound of moist air. This reference initial temperature is used to calculate the fuel-air ratio required to produce the desired reheat temperature. The additional fuel required per pound of original air is the difference between the new fuel-air ratio and the original fuel-air ratio.

The correction factors K_m, K_h, and K_w are determined from the inserts on figure 1 at a temperature of 1800° R for the known values of m of 0.100, $h_{c,f}$ of −18,300 Btu per pound, and water vapor content of 70 grains per pound of dry air. The original chart fuel-air ratio f'_1 is then calculated.

$$f'_1=f_1/K_mK_hK_w=0.0207/(0.9900)(1.023)(1.0095)=0.0202$$

The corresponding ΔT for T_b of 1800° R is obtained from figure 2; the value of ΔT is 1430° R. The corresponding reference initial temperature is then

$$T_a=T_b-\Delta T=1800°-1430°=370° \text{ R}$$

The chart fuel-air ratio required to produce a combustion temperature of 3000° R by burning fuel with the reference initial temperature of 370° R is then determined. For a ΔT of 2630° R, a new chart fuel-air ratio is obtained from either figure 1 or 2 as

$$f'_2=0.0417$$

The correction factors K_m, K_h, and K_w corresponding to 3000° R are read from figure 1. The new fuel-air ratio f_2 is then

$$f_2=K_mK_hK_wf'_2=(0.9775)(1.025)(1.010)(0.0417)=0.0422$$

The additional fuel required is then

$$f_2-f_1=0.0422-0.0207$$
$$=0.0215 \text{ pound fuel per pound of original moist air}$$

Example 4—Calculation of heat-release ratio for incomplete combustion.—If a fuel-air ratio of 0.0225 were experimentally required to produce a combustion temperature of 2000° R for the conditions of example 2, the ratio of actual fuel-air ratio to ideal fuel-air ratio r_f is 0.0225/0.0207 or 1.0870. For the combustion temperature of 2000° R, the heat-release ratio η_f from figure 3 is found to be 0.9240.

Example 5—Ideal combustion with water-alcohol-mixture addition.—The addition of 0.08 pound of water-alcohol mixture per pound of moist air at a temperature T_d of 500° R to the combustion process of example 2 is now considered; both hydrocarbon fuel and diluent are assumed to be completely burned. The diluent mixture is composed of the following fractions by weight:

Water, W_0=0.50
Methyl alcohol, W_1=0.25
Ethyl alcohol, W_2=0.25

The total fuel-air ratio necessary to obtain a combustion temperature of 2000° R is to be determined.

The value of the mixture parameter $1/M_m$ from figure 4 is 0.0410. On figure 5, drop vertically from T_b of 2000° R and $1/M_m$ of 0.0410 to the base line (line of T_b of 1000° R). From this point, draw a line through the point corresponding to a value of d of 0.08 to the f'' scale, from which f'' has a value of -0.0176. From the right insert on figure 5 for 0.25 fraction by weight of ethyl alcohol and T_b of 2000° R, move to the right to a value of d of 0.08; correction $\delta_2 f''$ is equal to 0.0008. Because no isopropyl alcohol is added, $\delta_3 f''$ is zero.

Correction for the water-alcohol mixture introduced at a temperature other than 540° R is made from equation (20) and the left insert on figure 5.

$$h_d\Big]_{540}^{T_d}=(0.40W_0+0.60)(T_d-540) \tag{20}$$
$$=(0.20+0.60)(500-540)=-32 \text{ Btu per pound}$$

From the left insert on figure 5, for h_d of -32 Btu per pound, T_b of 2000° R, and d of 0.08, $\delta_h f''$ is 0.0002. The required increment in fuel-air ratio is

$$\Delta f=K_m K_h(f''+\delta_2 f''+\delta_h f'')$$
$$=(0.9885)(1.023)(-0.0176+0.0008+0.0002)$$
$$=-0.0168 \text{ pound per pound moist air}$$

The total fuel-air ratio is from equation (21)

$$f=K_m K_h K_w f'+\Delta f$$
$$=0.0207-0.0168$$
$$=0.0039 \text{ pound per pound moist air}$$

Example 6—Effect of incomplete heat release for water-alcohol-mixture addition.—Consider example 5 with a heat-release ratio for the hydrocarbon fuel η_f of 0.900 and a heat-release ratio for the diluent η_d of 0.500. The total fuel-air ratio for the combustion process is to be determined.

The fuel-air ratio ideally required for combustion with no diluent addition is 0.0207 from example 2. The required increment in fuel-air ratio Δf for the ideal combustion of the water-alcohol mixture added is -0.0168 from example 5. Additional increments in fuel-air ratio that must be determined are due to the incompletely burned fuel and the incompletely burned water-alcohol mixture.

For a value of $(1-\eta_f)$ of 0.10 and a T_b of 2000° R, the value of r_f is 1.1175, as found in figure 3.

For the same water-alcohol mixture used in the previous example, in figure 7, for a value of $1/M_m$ of 0.041, move down parallel to the slant lines to a fraction by weight of ethyl alcohol W_2 of 0.25. Inasmuch as no isopropyl alcohol is present in this mixture, move directly down to the base line corresponding to a T_b value of 3000° R. (If isopropyl alcohol is present in the mixture, the slant lines for isopropyl alcohol are used in the same manner as those for ethyl alcohol.) From here, locate the pertinent combustion temperature, in this example a T_b of 2000° R, by following the curved guide lines and drop to the base line corresponding to a T_b of 1000° R. From this point, draw a line through the pertinent value of $d(1-\eta_d)$; in this example with a d value of 0.08 pound per pound of moist air and a diluent heat-release ratio η_d of 0.50, $d(1-\eta_f)$ has a value of 0.040. The required increase in chart fuel-air ratio f''_η is then 0.0118. The required increment in fuel-air ratio due to incomplete combustion of the water-alcohol mixture is

$$\Delta f=K_m K_h f''_\eta$$
$$=(0.09885)(1.023)(0.0118)$$
$$=0.0119 \text{ pound per pound moist air}$$

The total fuel-air ratio is from equation (21):

$$f=r_f\,(K_m K_h K_w f'+\Sigma\Delta f) \tag{21}$$
$$=1.1175[(0.9885)(1.023)(1.0095)(0.0203)-0.0168+0.0119]$$
$$=0.0179 \text{ pound per pound moist air}$$

Example 7—Effect of incomplete heat release for liquid ammonia and liquid carbon dioxide added at compressor inlet.—A mixture of 1 pound of liquid carbon dioxide stored at a temperature of 460° R and 0.05 pound of liquid ammonia is added to 1 pound of moist air at the compressor inlet of a turbojet engine. The inlet air is at 560° R and contains 140 grains of water vapor per pound of dry air. The compressor increases the enthalpy of the diluent-air mixture at the rate of 100 Btu per pound of fluid. The fuel-air ratio necessary to produce a combustion temperature of 2360° R when the heat-release ratio for the fuel η_f is 0.950 and the heat-release ratio for the ammonia η_d is 0.50 is to be determined.

The necessary corrections to the ideal chart fuel-air ratio f' are K_m, K_h, K_w, and r_f. Four values of fuel-air-ratio increments Δf are required for the liquid ammonia addition with complete combustion, the incomplete combustion of ammonia, the liquid carbon dioxide addition, and the compressor work input.

From figure 1 for a temperature rise ΔT of 1800° R and an initial temperature of 560° R, a chart fuel-air ratio f' of 0.0270 is obtained. The factors K_m of 0.9885 and K_h of 1.023 are the same as before because the same fuel is used in all the examples.

From the insert on figure 1, the correction factor K_w, corresponding to 140 grains of water vapor per pound of dry air and T_b of 2360° R, is 1.0195.

For a value of $(1-\eta_f)$ of 0.050 and T_b of 2360° R, r_f has a value of 1.0565 in figure 3.

For an ammonia addition d of 0.05 pound per pound of air and T_b of 2360° R, f'' is equal to -0.0177 pound per pound of air in figure 9. The required increment in fuel-air ratio for complete combustion of ammonia is

$$\Delta f=K_m K_h f''=(0.9885)(1.023)(-0.0177)$$
$$=-0.0179 \text{ pound per pound moist air}$$

For a value of $(1-\eta_d)$ of 0.50, T_b of 2360° R, and d of 0.05, f''_η has a value of 0.0115 as found in figure 10. The required

increment in fuel-air ratio due to incomplete combustion of ammonia is

$$\Delta f = K_m K_h f''_1 = (0.9885)(1.023)(0.0115)$$
$$= 0.0116 \text{ pound per pound moist air}$$

For a saturated liquid carbon dioxide temperature of 460° R, T_b of 2360° R, and d of 1.00 pound per pound of air, f'' is equal to 0.0370 as found in figure 11. The required increment in fuel-air ratio is

$$\Delta f = K_m K_h f'' = (0.9885)(1.023)(0.0370)$$
$$= 0.0374 \text{ pound per pound moist air}$$

For a compressor work input W_c/J of 100 Btu per pound of fluid, T_b of 2360° R, and a mass of diluent added at the compressor inlet d' of 1.05 pounds per pound of air, the value of f'' is equal to -0.0118 pound per pound of air as found in figure 14. The required increment in fuel-air ratio is

$$\Delta f = K_m K_h f'' = (0.9885)(1.023)(-0.0118)$$
$$= -0.0119 \text{ pound per pound moist air}$$

The total fuel-air ratio required is then

$$f = r_f(K_m K_h K_w f' + \Sigma \Delta f) \tag{21}$$
$$= 1.0565[(0.9885)(1.023)(1.0195)(0.0270) - 0.0179 + 0.0116 + 0.0374 - 0.0119]$$
$$= 0.0498 \text{ pound per pound of moist air}$$

The effects of the addition of liquid ammonia and liquid carbon dioxide on the required fuel-air ratio are independent but are combined in this example to illustrate conveniently the use of the charts. The addition of liquid oxygen and liquid nitrogen as diluents is handled in the same manner as liquid ammonia in the present example.

Determination of stoichiometric fuel-air ratio with diluent addition.—The stoichiometric fuel-air ratio for a mixture of air, hydrocarbon fuel, and diluents may be determined by means of figure 15.

For example, the determination of the stoichiometric fuel-air ratio for 0.08 pound of water-alcohol mixture having a mixture parameter $1/M_m$ of 0.0410 added to each pound of air for combustion with a fuel of hydrogen-carbon ratio m of 0.100 is shown in the upper right part of figure 15; the stoichiometric fuel-air ratio is 0.0510.

If the diluents ammonia and liquid oxygen are individually added or added in combination with a water-alcohol mixture, the stoichiometric fuel-air ratio is found by the entire figure. For example, the determination of the stoichiometric fuel-air ratio for a water-alcohol-to-air ratio d of 0.08, a mixture parameter $1/M_m$ of 0.0410, and ammonia-air ratio d of 0.05, a liquid oxygen-air ratio d of 0.10, and a hydrogen-carbon ratio m of 0.100 is shown; the stoichiometric fuel-air ratio is 0.060.

Flight Propulsion Research Laboratory,
National Advisory Committee for Aeronautics,
Cleveland, Ohio, *March 31, 1948.*

APPENDIX A

SYMBOLS

The following symbols are used in this report:

A $\quad \dfrac{H_{H_2O}-\frac{1}{2}H_{O_2}}{2.016}$

B $\quad \dfrac{H_{CO_2}-H_{O_2}}{12.010}$

D_y increase per pound of diluent in number of moles of y in ultimate burned gas mixture due to addition and combustion of diluent, lb mole/lb diluent

d total diluent-air ratio, lb/lb air

d' weight of diluent injected into air stream prior to compression of mixture, lb/lb air

f total fuel-air ratio, lb/lb air

Δf fuel-air ratio increment due to diluent addition to fuel-air mixture, lb/lb air

f' chart fuel-air ratio, function of T_a and T_b only, lb/lb air

f'' increase in chart fuel-air ratio due to diluent addition, function of specific diluent mixture, lb/lb air

f''_η increase in chart fuel-air ratio due to incomplete combustion of diluent, lb/lb air

$\delta_2 f''$ correction of f'' with use of ethyl alcohol, lb/lb air

$\delta_3 f''$ correction to f'' with use of isopropyl alcohol, lb/lb air

$\delta_h f''$ correction to f'' due to injection of water-alcohol mixture at temperature other than 540° R, lb/lb air

H_y molal enthalpy of y, Btu/lb mole

h_a enthalpy of dry air, Btu/lb air

h_b enthalpy of final burned mixture, Btu/lb mixture

$h_{c,d}$ lower enthalpy of combustion of liquid diluent at 540° R, Btu/lb diluent

$h_{c,f}$ lower enthalpy of combustion of liquid fuel at 540° R, Btu/lb fuel

h_d enthalpy of liquid diluent, Btu/lb diluent

J mechanical equivalent of heat, 778 ft-lb/Btu

K_h correction factor to f or f'' for change in lower enthalpy of combustion of fuel from value of 18,700 Btu/lb fuel

K_m correction factor to f' or f'' for change in hydrogen-carbon ratio of fuel from value of 0.175

K_w correction factor to f' due to water vapor in combustion air

M_m molecular weight of water-alcohol mixture, lb/(lb) (mole)

m hydrogen-carbon ratio of fuel

r_f ratio of actual fuel-air ratio to ideal fuel-air ratio

T_a initial total air temperature, °R

T_b total combustion temperature, °R

T_d temperature of diluent as liquid immediately before injection, °R

T_r reference temperature, 540° R

ΔT temperature rise in combustion process, °R

W fraction by weight of components of water-alcohol mixtures

W_c work of compression of mixture entering compressor, ft-lb/lb mixture

x water-alcohol-mixture characteristic

y variety of gas, specifically CO_2, H_2O, O_2, and N_2

Φ factor accounting for effects of diluent addition and compressor work on ideal fuel-air ratio

η_f heat-release ratio for hydrocarbon fuel

η_d heat-release ratio for combustible diluent

Subscripts 0, 1, 2, and 3 refer to water, methyl alcohol, ethyl alcohol, and isopropyl alcohol, respectively.

The atomic weights used are:

Carbon	12.010
Hydrogen	1.008
Oxygen	16.000
Nitrogen	14.008

APPENDIX B

EXPRESSIONS FOR INCREASE IN CHART FUEL-AIR RATIO DUE TO DILUENT ADDITION

WATER-ALCOHOL MIXTURES AS DILUENT

The molal lower enthalpies of combustion for the liquid phase $-Q$ of water and of the three alcohols considered are given in the following table; the values cited are for a pressure of 1 atmosphere and have been evaluated at the reference temperature of 540° R:

Diluent	Equivalent formula	Molecular weight	$-Q$ (Btu/(lb) (mole))	Reference
Water	H_2O	18.016	−18,870	11
Methyl alcohol	$(CH_2)H_2O$	32.042	274,700	11
Ethyl alcohol	$(CH_2)_2H_2O$	46.068	531,300	11
Isopropyl alcohol	$(CH_2)_3H_2O$	60.094	786,300	12

The general mixture may be represented by the average formula $(CH_2)_xH_2O$. A quantity $-Q'$ is arbitrarily chosen as a linear function of the diluent-mixture characteristic x such that it is exactly equal to $-Q$ for mixtures of water and methyl alcohol

$$-Q'=293{,}570x-18{,}870 \tag{22}$$

Because $-Q$ does not vary linearly with x, small corrections are required when ethyl or isopropyl alcohols are used.

The gravimetric lower enthalpy of combustion of the mixture may be written as a function of $1/M_m$ from equations (18) and (22)

$$-h_{c,d}=\frac{293{,}570x-18{,}870}{M_m}$$

$$=20{,}930-\frac{395{,}950}{M_m}\ \text{Btu/lb} \tag{23}$$

The net increase in enthalpy of the combustion gases due to diluent addition and compressor work is from equation (5):

$$\Phi=-(1+d')\frac{W_c}{J}-d\left\{h_d\Big]_{T_r}^{T_d}-h_{c,d}-(D_{CO_2}H_{CO_2}+D_{H_2O}H_{H_2O}+D_{O_2}H_{O_2}+D_{N_2}H_{N_2})\Big]_{T_r}^{T_b}\right\} \tag{5}$$

The term accounting for compressor work $(1+d')W_c/J$ is considered later in this appendix. The term $\left(h_d\Big]_{T_r}^{T_d}-h_{c,d}\right)$ reduces to $-h_{c,d}$ when the water-alcohol mixture is introduced to the system as a liquid at a temperature T_d equal to the base temperature T_r of 540° R; for those cases in which the diluent is introduced as a liquid at a temperature other than 540° R, a correction is to be applied.

The remaining term of equation (5) is evaluated by consideration of the combustion reaction

$$(CH_2)_xH_2O+\frac{3}{2}xO_2\rightarrow xCO_2+(1+x)H_2O$$

The increase per pound of diluent in the enthalpy of the various species in the ultimate gas mixture due to the addition of diluent is then

$$\begin{aligned}(D_{CO_2}H_{CO_2}+D_{H_2O}H_{H_2O}+D_{O_2}H_{O_2}+D_{N_2}H_{N_2})\Big]_{T_r}^{T_b}&=\frac{1}{M_m}\left\{xH_{CO_2}+(1+x)H_{H_2O}-\frac{3}{2}xH_{O_2}\right\}\Big]_{T_r}^{T_b}\\&=\left\{\left(\frac{1}{14.026}-\frac{1.28447}{M_m}\right)H_{CO_2}+\left(\frac{1}{14.026}-\frac{0.28447}{M_m}\right)H_{H_2O}-\right.\\&\quad\left.\frac{3}{2}\left(\frac{1}{14.026}-\frac{1.28447}{M_m}\right)H_{O_2}\right\}\Big]_{T_r}^{T_b}\end{aligned} \tag{24}$$

The quantity $D_{N_2}H_{N_2}$ is zero because the nitrogen content of the ultimate gas mixture is not increased as a result of the water-alcohol-mixture addition.

The relation for Φ (equation (5)) may therefore be expressed only as a function of d, M_m, and T_b for diluents of mixtures of water and alcohol.

From equations (5), (12), (23), and (24)

$$f''=d\left\{\frac{-20{,}930+\dfrac{395{,}950}{M_m}+\left\{\left(\dfrac{1}{14.026}-\dfrac{1.28447}{M_m}\right)H_{CO_2}+\left(\dfrac{1}{14.026}-\dfrac{0.28447}{M_m}\right)H_{H_2O}-\dfrac{3}{2}\left(\dfrac{1}{14.026}-\dfrac{1.28447}{M_m}\right)H_{O_2}\right\}\Big]_{T_r}^{T_b}}{18{,}700-\dfrac{0.175A+B}{1.175}\Big]_{T_r}^{T_b}}\right\} \tag{25}$$

The small corrections required when ethyl and isopropyl alcohols are used are accounted for by additive terms $\delta_2 f''$ and $\delta_3 f''$, respectively. For pure ethyl alcohol, equation (22) yields a value of $-Q'$ of 568,270 Btu per pound mole. The discrepancy between this value and the actual value of $-Q$ is 36,970 Btu per pound mole. For pure isopropyl alcohol, the discrepancy between the value of $-Q'$ from equation (22) and the actual value is 75,540 Btu per pound mole.

The corrections are therefore given by

$$\delta_2 f''=\frac{d\,\dfrac{W_2}{46.068}\,36{,}970}{18{,}700-\dfrac{0.175A+B}{1.175}\Big]_{T_r}^{T_b}} \tag{26}$$

$$\delta_3 f''=\frac{d\,\frac{W_3}{60.094}\,75{,}540}{18{,}700-\left.\frac{0.175A+B}{1.175}\right]_{T_r}^{T_b}} \tag{27}$$

The numerators proportion the error introduced by the use of the linear expression for $-Q$ (equation (22)) in accordance with the fraction by weight of either ethyl or isopropyl alcohols in the mixture of diluents.

LIQUID AMMONIA AS DILUENT

The enthalpy of combustion of liquid ammonia is evaluated to be 7500 Btu per pound at a pressure of 1 atmosphere and a temperature of 540° R (reference 11). The combustion reaction and the assumption that all the ammonia burns to nitrogen and water yields

$$4NH_3+3O_2\rightarrow 2N_2+6H_2O$$

The increase per pound of diluent in the enthalpy of the various species in the ultimate gas mixture due to the addition of diluent is then

$$\left.(D_{H_2O}H_{H_2O}+D_{O_2}H_{O_2}+D_{N_2}H_{N_2})\right]_{T_r}^{T_b}$$
$$=\frac{1}{17.032}\left.\left(\frac{3}{2}H_{H_2O}-\frac{3}{4}H_{O_2}+\frac{1}{2}H_{N_2}\right)\right]_{T_r}^{T_b} \tag{28}$$

The expression for Φ from equation (5) becomes

$$\Phi=d\left\{-7500+\frac{1}{17.032}\left.\left(\frac{3}{2}H_{H_2O}-\frac{3}{4}H_{O_2}+\frac{1}{2}H_{N_2}\right)\right]_{T_r}^{T_b}\right\} \tag{29}$$

Therefore f'' may be written from equation (11) as a function of d and T_b

$$f''=\frac{d\left\{-7500+\frac{1}{17.032}\left.\left(\frac{3}{2}H_{H_2O}-\frac{3}{4}H_{O_2}+\frac{1}{2}H_{N_2}\right)\right]_{T_r}^{T_b}\right\}}{18{,}700-\left.\frac{0.175A+B}{1.175}\right]_{T_r}^{T_b}} \tag{30}$$

Ammonia may be stored either as a liquid under elevated pressures or as a chilled liquid at atmospheric pressure. In either case, the variation of the enthalpy of combustion of liquid ammonia with storage temperature is small. Hence, addition of liquid ammonia as diluent at a temperature other than 540° R introduces a negligible error in the expression for f''.

LIQUID CARBON DIOXIDE AS DILUENT

The enthalpy of liquid carbon dioxide relative to the vapor at 540° R and 1 atmosphere pressure for various conditions is taken from a temperature-entropy diagram for carbon dioxide appearing in reference 13. The value of $\left.h_d\right]_{T_r}^{T_d}$ is then a function of the diluent temperature immediately before injection. Because the most feasible arrangement is to store and to inject carbon dioxide as a liquid in the completely saturated state, $\left.h_d\right]_{T_r}^{T_d}$ becomes a function of the saturation temperature or its concomitant saturation pressure.

The expression for f'' is then

$$f''=\frac{d\left(\left.h_d\right]_{T_r}^{T_d}+\left.\frac{H_{CO_2}}{44.01}\right]_{T_r}^{T_b}\right)}{18{,}700-\left.\frac{0.175A+B}{1.175}\right]_{T_r}^{T_b}} \tag{31}$$

and is a function of T_b, d, and T_d or saturation pressure. Equation (31) accurately applies for use of the liquid carbon dioxide in the subcooled state except in the vicinity of the critical temperature (548° R).

LIQUID NITROGEN AND LIQUID OXYGEN AS DILUENTS

Enthalpies for liquid nitrogen and liquid oxygen are evaluated relative to the vapor at 540° R and 1 atmosphere pressure as the sum of the enthalpy of vaporization and the enthalpy difference of the diluent vapor at the liquid temperature and 540° R. Enthalpies of vaporization for both liquids are taken from reference 11. The liquids are generally stored in containers vented to the atmosphere. Hence variations in enthalpy in the liquid phase may be neglected because of the small temperature range in which the diluents exist as liquids at atmospheric pressure.

The enthalpy relative to the vapor at the reference condition $\left.h_d\right]_{T_r}^{T_d}$ is 186 Btu per pound for liquid nitrogen and 175 Btu per pound for liquid oxygen.

The expression for f'' for nitrogen is then

$$f''=\frac{d\left(186+\left.\frac{H_{N_2}}{28.016}\right]_{T_r}^{T_b}\right)}{18{,}700-\left.\frac{0.175A+B}{1.175}\right]_{T_r}^{T_b}} \tag{32}$$

for oxygen

$$f''=\frac{d\left(175+\left.\frac{H_{O_2}}{32.000}\right]_{T_r}^{T_b}\right)}{18{,}700-\left.\frac{0.175A+B}{1.175}\right]_{T_r}^{T_b}} \tag{33}$$

Therefore f'' is a function of d and T_b.

EFFECT OF COMPRESSOR WORK OR PREHEATING OF DILUENTS

The decrease in fuel-air ratio f'' associated with the work done in any compressor through which 1 pound of air plus d' pounds of diluent pass before combustion is given by the following expression:

$$f''=\frac{-(1+d')W_c/J}{18{,}700-\left.\frac{0.175A+B}{1.175}\right]_{T_r}^{T_b}} \tag{34}$$

Therefore f'' is a function of d', W_c, and T_b.

APPENDIX C

COMBUSTION WITH INCOMPLETE HEAT RELEASE

Justification of the assumption that the enthalpy of the actual burned products is negligibly different from that of the completely burned products for any given fuel-diluent-air mixture and given combustion temperature requires a measure of this difference in enthalpy.

Inasmuch as the heat-release ratio η_f is defined as the ratio of the actual enthalpy rise to the enthalpy of combustion of the liquid fuel, the true heat-release ratio η_f' would be given by

$$\eta_f' = \eta_f + (1-\eta_f)\frac{\Delta h}{(-h_{c,f})}$$

where Δh is the enthalpy difference between products and reactants.

The difference between the true heat-release ratio and the defined heat-release ratio is then given by

$$\eta_f' - \eta_f = (1-\eta_f)\frac{\Delta h}{(-h_{c,f})}$$

If, for example, normal octane vapor is considered to be present in the burned mixture, there will be oxygen present, which would not exist if the combustion were complete, according to the relation

$$C_8H_{18} + \frac{25}{2}O_2 \rightarrow 8CO_2 + 9H_2O$$

At 2700° R, the enthalpy of the left side is 483,130 Btu per mole of octane; the enthalpy of the right side is 469,650 Btu per mole of octane. The enthalpy of the left side is therefore 13,480 Btu per mole greater than the right side. The molecular weight of octane is 114.224; the enthalpy of the products is thus decreased 118 Btu per pound of unburned octane as contrasted with a defect in heat release of 19,110 Btu per pound of unburned octane.

For this example, the assumption that the enthalpy of the actual products (unburned normal octane vapor) is equal to the enthalpy of the completely burned products is in error by 118 Btu per pound of unburned octane at a temperature of 2700° R. The difference in heat-release ratios is then

$$\eta_f' - \eta_f = (1-\eta_f)\frac{118}{19{,}100}$$

For an η_f of 0.90, this difference in enthalpy corresponds to an error in the calculated value of heat-release ratio of only 0.06 percent.

The enthalpy of the products minus the enthalpy of the reactants Δh expressed as a percentage of the lower heat of combustion of the reactant is presented in figure 16 as a function of combustion temperature for a number of likely reactants; curves are given for methane, normal octane, ethyl alcohol, formaldehyde, ethylene, ammonia, carbon monoxide, and hydrogen. Data for the hydrocarbons were taken from reference 14; data for ethyl alcohol, formaldehyde, and ammonia were taken from references 15, 16, and 17, respectively.

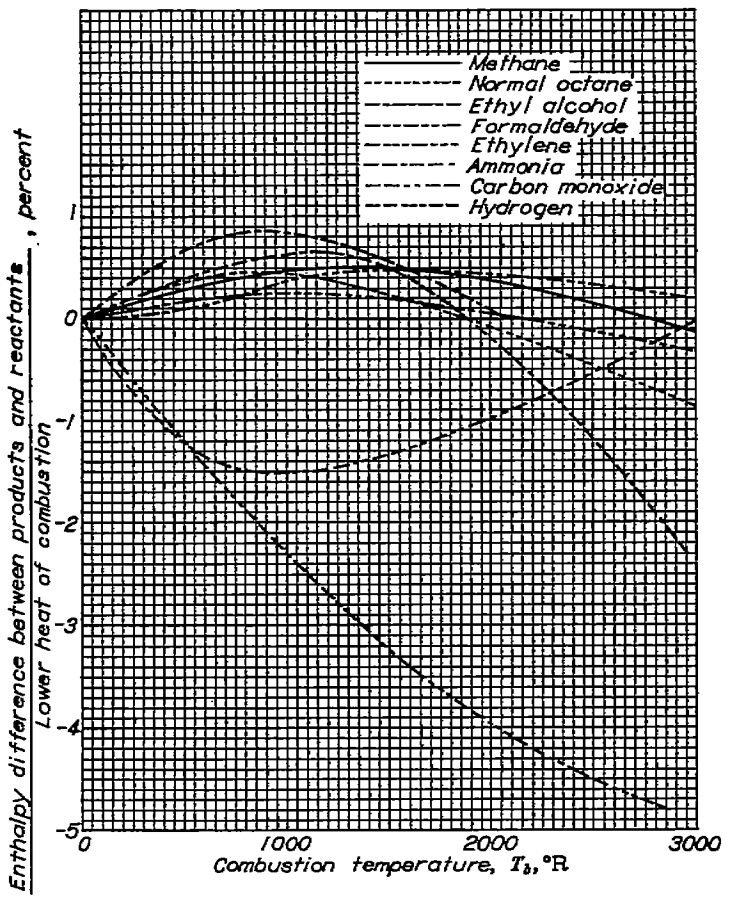


FIGURE 16.—Enthalpy difference between products and reactants as percentage of lower heat of combustion.

Except for hydrogen, the enthalpy difference generally is less than 1 percent of the lower heat of combustion, which corresponds to an error in the calculated value of heat-release ratio of less than 0.1 percent at an η_f of 0.90. Appreciable concentrations of hydrogen will probably not be present so that the enthalpy differences of 4 to 5 percent of the lower heat of combustion of hydrogen at the higher temperature will not affect the general validity of the assumption.

It has been shown that for each of the likely products of incomplete combustion, the difference between the enthalpy of the incompletely burned gas and the enthalpy of a gas at the same temperature that has a composition corresponding to complete combustion is small compared with the defect in heat release.

Water-alcohol mixtures.—The molal lower heats of combustion for the vapor phase $-q$ for water and for the three

alcohols considered are given in the following list for a pressure of 1 atmosphere and a temperature of 540° R:

Diluent	$-q$ (Btu/(lb)(mole))
Water	0
Methyl alcohol	290, 950
Ethyl alcohol	549, 710
Isopropyl alcohol	806, 330

As in appendix B, $-q$ is expressed as a linear function of the mixture parameter $1/M_m$; thus it is exact for mixtures of water and methyl alcohol. Inasmuch as $-q$ does not vary linearly with $1/M_m$, small corrections are required when ethyl or isopropyl alcohols are used.

The gravimetric lower enthalpy of combustion of the vapor mixture $-h_{c,d}'$ may then be written as

$$-h_{c,d}'=20,744-\frac{373,717}{M_m}-699\,W_2-1107\,W_3 \tag{35}$$

From equation (16), the increase in fuel-air ratio for the standard hydrocarbon fuel f''_η due to a defect in heat release is

$$f''_\eta=\frac{d(1-\eta_d)\left(20,744-\frac{373,717}{M_m}-699\,W_2-1107\,W_3\right)}{18,700-\left.\frac{0.175A+B}{1.175}\right]_{T_r}^{T_b}} \tag{36}$$

Ammonia.—The lower heat of combustion of gaseous ammonia $-h_{c,d}'$ is evaluated to be 8000 Btu per pound at a pressure of 1 atmosphere and a temperature of 540° R.

From equation (16), the increase in fuel-air ratio for the standard hydrocarbon fuel f''_η due to a defect in heat release is

$$f''_\eta=\frac{8000\,d(1-\eta_d)}{18,700-\left.\frac{0.175A+B}{1.175}\right]_{T_r}^{T_b}} \tag{37}$$

APPENDIX D

STOICHIOMETRIC FUEL-AIR RATIO WITH DILUENT ADDITION

The stoichiometric fuel-air ratio of a mixture containing combustible diluents is found by determining the net amount of oxygen available to the hydrocarbon fuel after complete oxidation of the combustible diluents.

The gross amount of oxygen available in the air is 0.23186 pound per pound of air.

The oxygen consumed by combustion of the alcohol in the water-alcohol mixture is

$$\frac{48\,d}{M_m}\ \text{lb/lb air}$$

Oxygen required for combustion of ammonia is

$$\frac{24\,d}{17.032}\ \text{lb/lb air}$$

The addition of oxygen itself supplies

$$d\ \text{lb/lb air}$$

The oxygen required for combustion of the hydrocarbon fuel is

$$\frac{f}{1+m}\left(\frac{16m}{2.016}+\frac{32}{12.01}\right)\ \text{lb/lb air}$$

The net amount of oxygen available to the hydrocarbon fuel after diluent combustion determines the magnitude of the stoichiometric fuel-air ratio, inasmuch as the mass of oxygen required for stoichiometric combustion is equal to the mass of oxygen available.

REFERENCES

1. Turner, L. Richard, and Lord, Albert M.: Thermodynamic Charts for the Computation of Combustion and Mixture Temperatures at Constant Pressure. NACA TN 1086, 1946.
2. Bogart, Donald, Okrent, David, and Turner, L. Richard: Thermodynamic Charts for the Computation of Fuel Quantity Required for Constant-Pressure Combustion with Diluents. NACA TN 1655, 1948.
3. Pinkel, Benjamin, and Turner, L. Richard: Thermodynamic Data for the Computation of the Performance of Exhaust-Gas Turbines. NACA ARR 4B25, 1944.
4. Davis, Clyde O., and Johnston, Herrick L.: Heat Capacity Curves of the Simpler Gases. V. The Heat Capacity of Hydrogen at High Temperatures. The Entropy and Total Energy. A Corrected Table of the Free Energy above 2000°. Jour. Am. Chem. Soc., vol. 56, no. 5, May 5, 1934, pp. 1045–1047.
5. Johnston, Herrick L., and Davis, Clyde O.: Heat Capacity Curves of the Simpler Gases. IV. Extension of the "Free Energy" Formula of Giauque and Overstreet to Yield Reliable Approximation Formulas for the Calculation of Entropy and of Heat Capacity from Spectroscopic Data. Entropy and Heat Capacity of Carbon Monoxide and of Nitrogen from near Zero Absolute to 5000° K. Jour. Am. Chem. Soc., vol. 56, no. 2, Feb. 7, 1934, pp. 271–276.
6. Johnston, Herrick L., and Walker, Margery K.: Heat Capacity Curves of the Simpler Gases. II. Heat Capacity, Entropy and Free Energy of Gaseous Oxygen from near Zero Absolute to 5000° K. Jour. Am. Chem. Soc., vol. 55, no. 1, Jan. 1933, pp. 172–186.
7. Johnston, Herrick L., and Walker, Margery K.: Heat Capacity Curves of the Simpler Gases. VII. The High Temperature Heat Capacities of Oxygen and Influence of the Δ Level on the Thermodynamic Properties of the Gas. Jour. Am. Chem. Soc., vol. 57, no. 4, April 5, 1935, pp. 682–684.
8. Gordon, A. R.: The Calculation of Thermodynamic Quantities from Spectroscopic Data for Polyatomic Molecules; the Free Energy, Entropy and Heat Capacity of Steam. Jour. Chem. Phys., vol. 2, no. 2, Feb. 1934, pp. 65–72; vol. 2, no. 8, Aug. 1934, p. 549.
9. Stephenson, C. C., and McMahon, H. O.: The Rotational Partition Function of the Water Molecule. Jour. Chem. Phys., vol. 7, no. 8, Aug. 1939, pp. 614–615.
10. Kassel, Louis S.: Thermodynamic Functions of Nitrous Oxide and Carbon Dioxide. Jour. Am. Chem. Soc., vol. 56, no. 9, Sept. 1934, pp. 1838–1842.
11. Bichowsky, F. Russel, and Rossini, Frederick D.: The Thermochemistry of the Chemical Substances. Reinhold Pub. Corp. (New York), 1936.
12. Parks, George S., and Moore, George E.: The Heat of Combustion of Isopropanol. Jour. Chem. Phys., vol. 7, no. 11, Nov. 1936, p. 1066.
13. Dodge, Barnett F.: Chemical Engineering Thermodynamics. McGraw-Hill Book Co., Inc., 1944, diagram facing p. 662.
14. Anon.: Tables of Selected Values of Properties of Hydrocarbons. Am. Pet. Inst. Res. Proj. 44, Nat. Bur. Standards, Sept. 30, 1947.
15. Aston, J. G.: Sources of Thermodynamic Data. Ind. and Eng. Chem., vol. 34, no. 5, May 1942, pp. 514–521.
16. Thompson, H. W.: Thermodynamic Functions and Equilibria of Formaldehyde, Deuteroformaldehyde, Phosgene and Thiophosgene. Trans. Faraday Soc. (London), vol. XXXVII, no. 241, May 1941, pp. 251–260.
17. Justi, E.: Spezifische Wärme Enthalpie, Entropie und Dissoziation technischer Gase. Julius Springer (Berlin), 1938.