EFFECT OF CHEMICAL STRUCTURE ON ROCKET FUEL IMPULSE

by

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ABSTRACT

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Submitted for the degree of Master of Science in the
Department of Chemical Engineering on
August 24, 1951

This thesis offers proof that the specific impulse of an adiabatic rocket motor fitted with an isentropic nozzle is a function only of the number and type of bonds entering the combustion chamber when the motor operates between two fixed pressures P_1 and P_2.

This function is postulated to be:

$$\frac{u_e}{g_c} = \sqrt{\frac{2J}{g_c} \cdot \frac{\sum_i n_i e_i}{\sum_i n_i w_i}}$$

where i = j, k, l, · · · u = bond types

$\frac{u_e}{g_c}$ = specific impulse

J = mechanical equivalent of heat

g_c = unit conversion factor

n_i = number of bonds of type i

e_i = energy contribution of bond type i to total enthalpy change between combustion chamber and nozzle exit

w_i = mass contribution of bond type i to total mass

$_i$ = summation sign over all i's.

This postulated function is shown to fit the facts for various mixtures of fuel and oxidant.

The magnitudes of e_i and w_i for various bonds of interest are calculated at stoichiometric mixtures of fuel and oxidant. The relative magnitudes of $\frac{e_i}{w_i}$ describe the relative effect of chemical bonds on specific impulse and the optimum structure for a propellant is that which contains the maximum possible values of $\frac{e_i}{w_i}$.

The Appendix contains an extension of Hottel, Williams and Satterfield's generalized Thermodynamic Charts from 3200°K to 4000°K. These charts are good for the system C-H-O and stoichiometric and fuel-rich mixtures only. Small amounts of nitrogen ($\frac{N}{O} < .25$) do not introduce appreciable errors.

Department of Chemical Engineering
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August 24, 1951

Professor Joseph S. Newell
Secretary of the Faculty
Massachusetts Institute of Technology
Cambridge 39, Massachusetts

Dear Sir:

The thesis entitled "Effect of Chemical Structure on Rocket Fuel Impulse" is herewith submitted in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering.

Respectfully,

S. T. Demetriades

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I. INTRODUCTION

Generalized thermodynamic charts have been prepared, (1), which greatly reduce the time and effort required to obtain an evaluation of the theoretical performance of high output combustion systems, such as rockets, operating on mixtures of carbon, hydrogen, oxygen and nitrogen.

It is relatively easy to predict from the above charts, with fair accuracy, the performance of a specific fuel-oxidant mixture. However, there is no way of determining directly, without repeated trials, which is the appropriate way of combining a given number of atoms of carbon, hydrogen, oxygen and nitrogen in order to achieve optimum rocket performance.

The object of this paper is to present a method for predicting the effect of chemical structure on rocket fuel theoretical impulse. The method may be used to predict how a change in chemical structure affects the theoretical specific impulse of a given atomic composition which involves the above four elements.

II. LITERATURE SURVEY

The theoretical performance of various chemical propellant systems has been calculated by a number of investigators. A comprehensive survey of this field appears in (17) and (18). However, the contents of the investigations cited in (17) and (18) are classified and therefore unavailable to this author.

There is no unclassified literature on a generalized method for predicting the effect of chemical structure on specific impulse. The existence of such a method in classified literature does not appear probable.

III. Proof That Specific Impulse Is a Unique Function of the Chemical Bonds of the Reactants

The speed of the exhaust of a rocket is obtained from the adiabatic flow energy balance without external work or potential energy changes.

$$\frac{\Delta H}{W} = \sqrt{\frac{\Delta(u^2)}{2g_c J}} \qquad (1)$$

where H = true total enthalpy, chemical plus sensible, of mixture

W = mass of reactants taken as a basis in calculating ΔH

u = speed of W with respect to the rocket

g_c = unit conversion factor

J = mechanical equivalent of heat

Since the speed of the entering fuel and oxidant is negligible in comparison with the exhaust speed, we may write:

$$\frac{\Delta H}{W} = \frac{u_e{}^2}{2g_c J} \qquad (2)$$

where u_e = speed of exhaust gases with respect to the rocket

Then the specific impulse, $\frac{u_e}{g_c}$, is

$$\frac{u_e}{g_c} = \sqrt{\frac{2J}{g_c}\,\frac{\Delta H}{W}} \qquad (3)$$

The units of specific impulse are:

$$\frac{L}{\Theta} \times \frac{F\Theta^2}{ML} = \frac{F\Theta}{M} = \frac{F}{\frac{M}{\Theta}} \qquad (4)$$

where F = force or weight

M = mass

L = length

Θ = time

Therefore, specific impulse is a measure of the force or thrust delivered per unit mass fired per unit time. Obviously, the highest possible specific impulse for any given system is the goal of the rocket engineer.

Since the quantity $\frac{2J}{g_c}$ is constant under all circumstances, specific impulse varies directly as $\sqrt{\frac{\Delta H}{W}}$ and reaches its maximum as $\frac{\Delta H}{W}$ reaches its maximum.

For a fuel and oxidant mixture of given atomic composition, W is constant and therefore specific impulse becomes maximum as ΔH becomes maximum.

ΔH is, ideally speaking, the total enthalpy change of the gaseous mixture of combustion products between the combustion chamber and the nozzle exit. Enthalpy is a point property or point function, (6, 7, 13), i.e. it is dependent only on the initial and final conditions of the system and is independent of the path followed in producing the changes that differentiate between the initial and the final state of the system. In the case of the rocket motor the system is the mass of reactants W. Therefore, the total enthalpy change ΔH which W undergoes is dependent only on the conditions of the initial state (in the combustion chamber) and the final state (at the nozzle exit area). Uniform conditions are assumed throughout the combustion chamber and on all of the exit area.

The intensive reference variables of which H is a function are temperature (T), pressure (P), and composition. Therefore, ΔH depends only on the composition, pressure and temperature in the combustion chamber and at the exit of the nozzle.

Let the pressure in the combustion chamber and the pressure at the exit of the nozzle be fixed at any two values P_2 and P_3, respectively. Then the total enthalpy at these two locations is a function of temperature and composition only. However, for the kind of process defined above, the total enthalpy (over some convenient basis) in the combustion chamber is equal to the total enthalpy entering the combustion chamber (over the same basis).

Thus, if the variables are designated by the subscripts 1, 2, and 3 for the entrance to the combustion chamber, the combustion chamber and the nozzle exit in that order, we have:

$$H_2 = f_1(T_2, C_2) \qquad (5)$$

$$H_3 = f_2(T_3, C_3) \qquad (6)$$

$$H_1 = H_2$$

where T = the temperature variable.

C = the composition variable.

The pressure at the entrance to the combustion chamber is assumed to be equal to that in the combustion chamber.

The composition C is a function of the temperature and the atomic composition A at any point. Thus, when we consider a mass W whose atomic composition does not vary between the entrance to the chamber and the exit, we may write:

$$H_2 = f_3(T_2,A) \tag{8}$$

$$H_3 = f_4(T_3,A) \tag{9}$$

$$H_1 = H_2 \tag{7}$$

The chemical enthalpy entering the combustion chamber is known to be, (14), a unique function of the number and type, N_1, of chemical structural bonds which unite the atoms that comprise the molecules of the reactants at the entrance to the combustion chamber. Heat capacities are also known to be unique functions of the structural characteristics of the molecules, (13), i.e., the number and type of bonds N_1. If, therefore, the same convenient temperature basis is picked at the entrance to the combustion chamber for all the types of reactants considered, the total enthalpy entering the combustion chamber is a unique function of the number and type of bonds N_1. Then:

$$H_1 = f_5(N_1) \tag{10}$$

The atomic composition A at any point in the combustion chamber and the nozzle is completely and uniquely described by the number and type of bonds N_1, i.e., for every N_1 we have one and only one A. Therefore:

$$A = f_6(N_1) \tag{11}$$

Note, however, that A does not uniquely define N_1, i.e., N_1 is not a unique function of A since we may have different N_1's for the same A.

Thus the total enthalpy in the combustion chamber also, H_2, is a unique function of the number and type of bonds N_1 at the entrance, or

$$H_1 = f_5(N_1) = H_2 \tag{12}$$

Since A is a unique function of N_1,

$$H_2 = f_7(T_2, N_1) \tag{13}$$

and T_2, the temperature in the combustion chamber, is a unique function of N_1, or

$$T_2 = f_8(N_1) \tag{14}$$

If we assume that the expansion from the combustion chamber to the exit of the nozzle is reversible and adiabatic, there is no change in entropy between the combustion chamber and the nozzle exit. Therefore:

$$S_2 = S_3 \tag{15}$$

The entropy in the combustion chamber, S_2, at a fixed pressure P_2, is a unique function of the temperature, T_2, at that location and the atomic composition. But the temperature in the chamber is a unique function of N_1, the number and types of bonds at the entrance. Therefore, S_2 is a unique function of the number and type of bonds at the entrance, or

$$S_2 = f_9(T_2,A) = f_{10}(N_1) = S_3 \qquad (16)$$

The entropy at the nozzle exit, S_3, at a fixed pressure P_3, is a unique function of the temperature at that location, T_3, and the atomic composition only, or.

$$S_3 = f_{11}(T_3,A). \qquad (17)$$

And since S_3 and A are unique functions of N_1, T_3 is a unique function of N_1, or

$$T_3 = f_{12}(N_1). \qquad (18)$$

The enthalpy at the exit of the nozzle, H_3, is a unique function of T_3 and A. Therefore:

$$H_3 = f_4(T_3,A) = f_{13}(N_1). \qquad (19)$$

And since $\Delta H = H_2 - H_3 = f_5(N_1) - f_{13}(N_1)$

$$\Delta H = f_{14}(N_1). \qquad (20)$$

ΔH, the change in total enthalpy between the combustion chamber and the nozzle exit, is proven to be (for an adiabatic reversible expansion from a fixed pressure P_2 to a fixed pressure P_3) a unique function of the type and number of chemical bonds which enter the combustion chamber in a mass W, i.e., for every number and type of bonds N_1 at the entrance, we have one and only one ΔH. Even though N_1 is a function of ΔH, it is not a unique function of the total enthalpy change. The same ΔH may result from a variety of combinations of bond types.

The mass taken as a basis, W, is a unique function of the atomic composition A and therefore a unique function of the number and type of chemical bonds at the entrance, N_1, or

$$W = f_{15}(N_1). \tag{21}$$

Then specific impulse is a unique function of the number and type of bonds at the entrance to the combustion chamber, N_1, or

$$\frac{u_e}{g_c} = \frac{2J}{g_c} \cdot f_{16}(N_1). \tag{22}$$

This result is generally applicable and limited only by the character of the function $f_{15}(N_1)$.

To summarize, for any W with P_2 and P_3 fixed,

$$H_2 = f_1(T_2, C_2)$$

$$H_3 = f_2(T_3, C_3)$$

$$\text{and } H_1 = H_2.$$

$$\text{But } C = g(A),$$

$$\text{therefore } H_2 = f_3(T_2, A),$$

$H_3 = f_4(T_3, A)$,

therefore $H_2 = f_5(N_1) = f_3(T_2, A)$.

But $A = f_6(N_1)$, unique; $N_1 = h(A)$, non-unique,

therefore $f_5(N_1) = f_3(T_2, f_6(N_1)) = f_7(T_2, N_1)$,

or $T_2 = f_8(N_1)$.

Also $S_2 = S_3$,

and $S_2 = f_9(T_2, A) = f_{10}(N_1) = S_3$,

but $S_3 = f_{11}(T_3, A) = f_{11}(T_3, f_6(N_1)) = f_{10}(N_1)$,

therefore $T_3 = f_{12}(N_1)$.

Then $H_3 = f_4(T_3, A) = f_{13}(N_1)$,

therefore $\Delta H = H_2 - H_3 = f_{14}(N_1)$,

and $W = f_{15}(N_1)$,

therefore $\frac{u_e}{g_c} = \sqrt{\frac{2J}{g_c} \cdot \frac{\Delta H}{W}} = \sqrt{\frac{2J}{g_c}} \cdot f_{16}(N_1)$.

IV. Postulation of the Character of the Function $f_{16}(N_1)$ and Discussion

Although proof has been offered above that specific impulse is a function, under the above-stated conditions, of the chemical structure of the reactants entering the combustion chamber, no evidence has been offered as to the character of this function.

The ratio $f_{16}(N_1) = \sqrt{\frac{f_{14}(N_1)}{f_{15}(N_1)}} = \sqrt{\frac{g_c}{2J}} \cdot \frac{u_e}{g_c}$ has the dimensions of $\sqrt{\frac{F \cdot L}{M}}$ where F = force dimension, L = length dimension, M = mass dimension. The variable N, is dimensionless. Therefore, since for a given mass basis the dimensions of $\Delta H = f_{14}(N_1)$ are those of energy and the dimensions of $W = f_{15}(N_1)$ are those of mass, the function f_{14} must have the dimensions of energy, i.e., FL, and the function f_{15} must have the dimensions of mass, i.e., M.

Since each type i of bond contributes a certain amount of energy e_i specific to the bond to the total enthalpy H_1, (14), and since the amount of energy contributed is a unique function of the bond type variable and furthermore since that energy is proportional to the number of bonds of that type, it appears expedient to postulate that, under the conditions stated above, ΔH is the sum of the products of the number n_i of each type of bonds times the corresponding energy contributions of each bond to ΔH.

Thus it is postulated that:

$$\Delta H = \sum_i n_i e_i \qquad (23)$$

where $i = j, k, l, \cdots u,$ = types of bonds.

n_i = the number of bonds of type i, dimensionless.

e_i = the energy contribution of each bond of the type i with dimensions FL.

$\sum_i$ = summation over all the types of bonds present.

For any reactant mixture, the only unknowns in the above general expression for ΔH are the e_i's. These can be easily derived from the generalized thermodynamic charts, (1), in the following manner:

Using the same notation as in the generalized charts

$$\Delta H = \Delta H^r (H_{f,2400} - H_{f,0}) = H_2 - H_3 \qquad (24)$$

$$\text{since } \Delta H^r = \frac{H_2 - H_{f,0}}{H_{f,2400} - H_{f,0}} - \frac{H_3 - H_f}{H_{f,2400} - H_{f,0}}.$$

For any reactant mixture, ΔH can be calculated from the charts. Then, if that mixture contains more than one type of bonds, the ΔH of a sufficient number of other mixtures containing the same type of bonds (and possibly other types) is calculated so that the final number of mixtures chosen is equal to the total number of types of bonds present in all mixtures. Thus, given x types of bonds j, k, l, $\cdots$ u present each n_j, n_k, n_l, $\cdots$ n_u times, x mixtures are chosen which taken all together contain among themselves the types of bonds j, k, l, $\cdots$ u. The corresponding ΔH's are then calculated and the resulting system of x simultaneous linear equations

$$\begin{aligned} \Delta H_1 &= \sum_i n_i e_i \\ \Delta H_2 &= \sum_i n_i e_i \\ &\vdots \\ \Delta H_x &= \sum_i n_i e_i ; \; i = j, k, l, \cdots u. \end{aligned} \tag{25}$$

is solved for e_j, e_k, $e_l \cdots e_u$. Then these e_i's are the energy contributions to the change in total enthalpy of the bonds of type j, k, l, $\cdots$ u in that order.

Note that even though these energy contributions are unique functions of the type of bond (i.e., there is one and only one e for a given bond) when P_2 and P_3 are fixed, the type of bond is not a unique function of the energy contributions (i.e., for a given e there exist many different bonds). It is perfectly legitimate to have two different kinds of bonds of the same energy contribution. In that case ΔH may be equal for two systems of different structure and therefore, in some cases, of different composition. This in no way jeoparadizes the proof leading to (20) or the derivation of the bond contributions e since the resulting system (25) is still algebraically consistent and may yield, at worst, the same e's for two different kinds of bonds.

Summarizing: ΔH is a unique function, with dimensions FL, of N_1. N_1 is a non-unique function of the e_i's. Therefore, e_i is a non-unique function of ΔH (there may be different e_i's for a given ΔH, which is equivalent to saying that ΔH may be the same for different e_i's) and ΔH is a unique function of the e_i's which is postulated to be $\Delta H = \sum_i n_i e_i$.

Other criteria for postulating this form of the function f_{14} are:

1) Ease of prediction of e_i's.
2) Accuracy of predicted e_i's.
3) General applicability of predicted e_i's.

The ease of prediction of e_i's from the linear aggregate (25) is apparent.

The accuracy of predicted e_i's is dependent on the degree of elaboration exercised in choosing the types of bonds for which e_i's are computed. The greater the number of types of bonds employed, i.e., the greater the degree of distinction between types, the more difficult it becomes to use the bond contribution concept. The degree of distinction between bonds, however, is not entirely arbitrary. The tables of bond energies of formation, (14, 15), provide a basis of choice since the differences between energies of formation are, in an indefinite way, a measure of the expected differences between the energy contributions e_i. Thus no distinction will be made between the C-H bonds encountered in CH_4 and those found in C_2H_6. In most cases no distinction will be made between the bond connecting two atoms, say A-B, when one set of atoms C, D, • • • etc. fill the remaining bonds of atoms A and B, and the same bond connecting the same two atoms when a different set of atoms, R, S • • • etc. fill the remaining bonds of atoms A and B, and the same e_i's will be assigned to each bond.

The accuracy of predicted e_i's is within the accuracy inherent to the generalized thermodynamic charts. In this investigation the relative rather than the absolute magnitudes of specific impulse are considered. Since, therefore, it was found that for a series of reactants whose atomic composition does not vary greatly, the error introduced by the charts is relative, in the same direction and equal in magnitude for each reactant mixture, and since for most nitrogen-free stoichiometric mixtures of fuel and oxidant the atomic composition interpolation numbers vary only between 0.75 and 0.95, i.e., the range where the charts are most accurate, there is ample justification for retaining at least four significant figures in the evaluation of specific impulse. In the range of the fuel-oxidant ratios studied the ΔH's predicted from the charts are in the range of 10^5-10^6 B.T.U./lb. mole of fuel and the computed e_i's are in the range of 10^4 B.T.U./bond type. This means that at least the first two or three figures of the five-figure bond energy contributions to ΔH are significant. With the basis for calculation of e_i's assumed on page 22, it was found that all the above statements are supported by evidence accumulated by extensive use of the generalized thermodynamic charts. For example, the ΔH computed from the charts for

$C_6H_{14} + 9.5O_2$ is 534,580 B.T.U./lb. mole of fuel and the ΔH predicted by use of the e_i's for the same reactants is 534,450 B.T.U./lb. mole of fuel.

With the basis chosen here, (see page 22), there is a wide applicability of the e_i's. The computed e_i's can be used to predict the exact ΔH, within the limitations always of the charts, for stoichiometric mixtures, and give the relative magnitude of the energy contribution to ΔH at every other fuel-oxidant ratio even when large quantities of nitrogen are present (i.e., at stoichiometric air).

Each bond also contributes a certain amount to the mass W of the reactants taken as a basis. This amount can be derived in a fashion similar to that used in the derivation of the energy contributions. Thus, given a total of x types of bonds j, k, $\cdots$ u, present, each n_j, n_k, $n_l \cdots n_u$ times, x mixtures are chosen which together contain the types of bonds j, k, l $\cdots$ u. The corresponding total W's are calculated and the resulting system of x simultaneous linear equations

$$\begin{aligned} W_1 &= \sum_i n_i w_i \qquad (26) \\ W_2 &= \sum_i n_i w_i \\ &\vdots \\ W_x &= \sum_i n_i w_i ; \quad i = j, k, l, \cdots u. \end{aligned}$$

is solved for w_j, w_k, $w_l \cdot \cdot \cdot w_u$. Then these w's are the mass contributions to the total mass that is chosen as a basis, of the bonds of type j, k, l, $\cdot \cdot \cdot$ u in that order.

The ease of prediction of w_i's from the linear aggregate (26) is apparent.

The accuracy of predicted w_i's is dependent on the degree of elaboration exercised in choosing the types of bonds for which w_i's are computed. Weight contributions are computed for the bonds and groups for which e_i's are calculated. The accuracy of w_i's also depends on the accuracy of atomic weight data. In general, the predicted weight contributions are more accurate than the predicted e_i's since the function (21) is more justifiable and since the accuracy of the weight data is greater than that of the thermodynamic data.

There are no limits on the applicability of w_i's.

Therefore the quotient $\frac{\Delta H}{W}$ is seen to be the ratio of two sums of bond contributions to the change in total enthalpy and to the mass basis of the system, or

$$\frac{\Delta H}{W} = \frac{n_j e_j + n_k e_k + n_l e_l + \cdot \cdot \cdot n_u e_u}{n_j w_j + n_k w_k + n_l w_l + \cdot \cdot \cdot n_u w_u} . \qquad (2a)$$

A quotient of this nature is maximized when the individual quotients $\frac{n_i e_i}{n_i w_i}$ are maximized, since in order that every individual $\frac{n_i e_i}{n_i w_i}$ may become maximum every $n_i e_i$ must become maximum and every $n_i w_i$ must become minimum. Then, also, the sums $\sum n_i e_i$ and $\sum n_i w_i$ become maximum and minimum respectively.

For a fuel and oxidant mixture of given atomic composition, W is fixed when the mass basis is chosen and therefore there is no need to compute the individual w_i's. Then, in order to have a maximum impulse the appropriate types of bonds must be selected which will contribute maximum e_i's per bond and which will yield the optimum reactant structure within the limitations imposed by valence numbers, possibility of existence of compound, etc.

When a choice must be made from a wide variety of possible atomic compositions, W is not fixed and the bond contributions to the total mass must be calculated for all atomic compositions. All possible quotients $\frac{n_i e_i}{n_i w_i} = \frac{e_i}{w_i}$ must then be formed and by picking the maximum quotients the appropriate bonds must be selected which will yield the optimum reactant structure within the limitations imposed by valence numbers, possibility of existence of compound, etc.

This paper provides tables of the contributions e_i of various types of bonds to the total ΔH and of the quotients $\frac{e_i}{w_i}$ for the most important structural bonds and groups.

In both the fixed atomic composition case and the case where a choice must be made from a variety of possible atomic compositions, a general method for the selection of the optimum structure of any atomic composition is introduced so that the work of selecting the optimum structure becomes systematic and less effort- and time-consuming.

V. Derivation of Bond Contributions to Total Enthalpy Change and to Total Weight

The bonds of various fuels and oxidants used in rocket propulsion were studied extensively and the results appear below. Attention is called to the fact that various assumptions were made and different bases were selected in an attempt to reduce the computational effort where such assumptions and bases would not affect the consistency of the final results. All assumptions and choices of bases are stated at the proper places in the text.

A. Stoichiometric liquid oxygen as oxidant

When pure oxygen is used as oxidant, it was found that, in general, an increase of the oxygen beyond the stoichiometric ratio, makes the specific impulse decrease, mainly because of the increase in W. ΔH increases too, because oxygen dilution lowers the temperature and suppresses dissociation, but the corresponding increase of ΔH is small. As the oxygen is decreased below the stoichiometric ratio and down to a certain critical value, ΔH again increases, because incomplete combustion lowers the temperature, and the specific impulse becomes greater since W becomes smaller. As the oxygen is decreased below the critical point, specific impulse drops sharply. No study of this critical point is made here but its existence is worth noting.

The relative magnitudes of the energy contributions of the various bonds were not found to be greatly affected by the change in the amount of oxygen.

TABLE 1

HEATS OF COMBUSTION(a)

Hydrogen, Carbon, Carbon Monoxide and Hydrocarbons

Note:

The following values are taken from the tables of the American Petroleum Institute Research Project 44, of the National Bureau of Standards on the Collection, Calculation and Compilation of data on the Properties of Hydrocarbons.

Compound	Formula	State	Heat of combustion ΔH_c° at 25°C and constant pressure to form H_2O(gas) and CO_2(gas) K cal/mole
Hydrogen	H_2	gas	57.7979
Carbon	C	solid gr.	94.0518
Carbon Monoxide	CO	gas	67.6361
PARAFFINS			
Methane	CH_4	gas	191.759
Ethane	C_2H_6	g	341.261
Propane	C_3H_8	g	488.527
n-Butane	C_4H_{10}	g	635.384
2Methylpropane (Isobutane)	C_4H_{10}	g	633.744
n-Pentane	C_5H_{12}	g	782.040
2-Methylpentane (Isopentane)	C_5H_{12}	g	780.120
2,2-Dimethyl propane (Neopentane)	C_5H_{11}	g	777.370
n Hexane	C_6H_{14}	g	928.930
3-Methylpentane	C_6H_{14}	g	927.870
2,2-Dimethylbutane	C_6H_{14}	g	924.530
2,3-Dimethylbutane	C_6H_{14}	g	926.400
n-Heptane	C_7H_{16}	g	1,075.850
2,3-Dimethylpentane	C_7H_{16}	g	1,073.120
n-Octane	C_8H_{18}	g	1,222.770
n-Nonane	C_9H_{20}	g	1,369.700
n-Decane	$C_{10}H_{22}$	g	1,516.630

(a) All other heats of combustion used in this text were taken from (1), (6), (8) and (20).

TABLE 1, CONT'D

Compound	Formula	State	Heat of combustion ΔH_c° at 25°C and constant pressure to form H_2O(gas) and CO_2(gas) K cal/mole
MONOOLEFINS			
Ethene (ethylene)	C_2H_4	g	316.195
Propene (propylene)	C_3H_6	g	460.428
1-Butene	C_4H_8	g	607.679
cis-2-Butene	C_4H_8	g	606.037
trans-2-Butene	C_4H_8	g	604.994
2-Methylpropene (isobutene)	C_4H_8	g	604.056
2-Methyl-1-Butene	C_5H_{10}	g	750.570
3-Methyl-1-Butene	C_5H_{10}	g	752.330
2-Methyl-2-Butene	C_5H_{10}	g	749.080
ACETYLENES			
Ethyne (acetylene)	C_2H_2	g	300.096
Propyne(Methylacetylene)	C_3H_4	g	442.070
1-Butyne(ethylacetylene)	C_4H_6	g	589.302
2-Butyne (dimethylacetylene)	C_4H_6	g	584.974
3-Methyl-1-butyne	C_5H_8	g	734.050
ALKYL BENZENES			
Benzene	C_6H_6	g	757.52
Toluene	C_7H_8	g	901.50
Ethylbenzene	C_8H_{10}	g	1048.53
1,2-Dimethylbenzene	C_8H_{10}	g	1045.94
1,3-Dimethylbenzene	C_8H_{10}	g	1045.52
1,4-Dimethylbenzene	C_8H_{10}	g	1045.69
1-Methyl-4-ethylbenzene	C_9H_{12}	g	1192.47
ALCOHOLS(b)			
Methyl alcohol	CH_4O	liquid	149.80
Ethyl alcohol	C_2H_6O	l	296.35
n-Propylalcohol	C_3H_8O	l	439.80
isopropylalcohol	C_3H_8O	l	432.60
n-Butyl alcohol	$C_4H_{10}O$	l	586.25
Amyl alcohol	$C_3H_{12}O$	l	723.70
Methyl-diethyl corbinol	$C_6H_{14}O$	l	853.15

(b) From (6)

The bond O-O connecting the two oxygen atoms in the oxygen molecules entering the combustion chamber was assumed to make a contribution of zero to the change in total enthalpy and to the total weight. The e's and w's of all other bonds were computed on this basis.

In order to employ the generalized thermodynamic charts at their maximum accuracy (see Appendix), stoichiometric mixtures of fuel and oxidant were used in the prediction of e_i's and w_i's. However, by employing scattered mixtures in the fuel-lean and fuel-rich regions it was confirmed that even though the magnitudes of the e_i's changed, the relative magnitudes remained substantially the same. The same was found to be true for the weight contributions, w_i.

Thus, an increase in oxygen always increases and a decrease in oxygen always decreases all the weight bond contributions. Therefore, if the $\frac{e_j}{w_j}$ quotient for a certain bond j is the highest of all other quotients at the stoichiometric ratio of oxygen to fuel, the same quotient will still be the highest at all other ratios of oxygen to fuel since all the w_i's will change in the same relative way.

In Table 1 are listed the heats of combustion of various paraffin and olefin hydrocarbons, alcohols, ethers, aldehydes, ketones, amines, aromatics and other organic compounds, which are probable rocket fuels and which provide among them a great number of important bonds. The heats of combustion for the fuels listed are at 25°C and constant pressure and over gaseous H_2O and CO_2. The units employed are B.T.U./lb. mole. The initial state of the fuels is gaseous (unless otherwise noted) since methane, the critical temperature of which is -83°C, was used to derive the important C-H bond and since a change of basis for other fuels would needlessly complicate all calculations.

The ΔH calculated for liquid hydrocarbon fuels is in general less by 1 per cent than that calculated for gaseous hydrocarbons. The latest heat of combustion data were used in all cases, (5, 6, 8, 15).

These heats of combustion are converted to the basis used in the generalized thermodynamic charts, (1, page 46), i.e., to heat evolved on cooling given compound from 300°K to 0°K, plus heat released by burning with O_2 at 0°K to give CO_2, H_2O (vapor), O_2 and N_2. This is equivalent to burning the compound at 300°K (or 25°C, approximately) to give CO_2, H_2O (vapor), O_2 and N_2, adding the heat released by cooling the products to 0°K and subtracting the heat necessary to heat the stoichiometric oxygen used from 0°K to 300°K. Then the enthalpy of the liquid oxygen used is added and the result is H_1.

As an example, consider the calculation of H_1 for methane.

$$CH_4 + 2O_2 = CO_2 + 2H_2O + \Delta H_c$$

ΔH_c = heat of combustion of CH_4, gaseous, at 25°C, over CO_2, H_2O (vapor) = 345,166 B.T.U./lb. mole.

in general, for a gas,

$$\Delta H^2_{1,sensible} = (c_{p,av.})_2 (t_2 - t_{base}) - (c_{p,av.})_1 \times (t_1 - t_{base}). \qquad (27)$$

or, approximately,

$$\Delta H^2_{1,sensible} = (c_{p,av.})_2 (t_2 - t_1). \qquad (28)$$

then from Figure 27, reference (1),

$c_{p,av.,CO_2}$ = 7.45 B.T.U./lb. mole.

$c_{p,av.,H_2O}$ = 7.95 B.T.U./lb. mole.

$c_{p,av.,O_2}$ = 6.94 B.T.U./lb. mole.

therefore,

$$\Delta H_{sensible} = (1 \times 7.45 + 2 \times 7.95 - 2 \times 6.94)\ 1.8 \times 298 = 5{,}080 \text{ B.T.U./lb. mole.}$$

And since the enthalpy of the liquid oxygen used is -1818 B.T.U./lb. mole,

$$H_1 = 345{,}166 + 5{,}080 - 3{,}636 = 346{,}610 \text{ B.T.U./lb. mole.}$$

Since for stoichiometric mixtures of hydrocarbons and oxygen the flame temperature is beyond the range of the generalized thermodynamic charts in (1) the charts were extended to 4000°K. The extensions appear in the Appendix with an appropriate discussion.

Figures A1, A2, and A3 are the extensions of and correspond to Figures 29, 31, and 32 of reference (1) in that order. It was not found necessary to extend Figure 30 of reference (1). Use must be made of Figure 33 of reference (1) for the prediction of $(\alpha - \beta)$.

The composition interpolation number plots as well as Figure 33 of (1) apply to and should be used concurrently with the corresponding extended charts in the Appendix.

The interpolation numbers used have only three significant figures the last of which is doubtful. However, it was found that a change in the interpolation number by 0.005 in either direction does not affect the results as long as the change is in the same direction for all compounds studied and as long as a change in the composition of the system in one direction produces a relative change in the interpolation number. Thus it was found that if the Figure 29, (1), interpolation number for $C_4H_{10} + 6.5O_2$ is assumed to be 0.894 and that of $C_5H_{12} + 8O_2$ is assumed to be 0.896, the resulting ΔH's are consistent and they are the same in the first three significant figures as when the interpolation numbers are assumed to be 0.899 and 0.901 for $C_4H_{10} + 6.5O_2$ and $C_5H_{12} + 8O_2$ respectively. Even if there were a change to the third significant figure of ΔH, that change would be kept consistent in a homologous series of compounds if the interpolation numbers were kept consistent and the relative magnitude of the ΔH's and the e_1's would not change.

It must be emphasized that the relative magnitudes of the bond energy contributions are not appreciably affected by any of the factors contributing to the errors inherent to the charts if those errors are kept in the same direction.

(1.) Bonds encountered in normal paraffins

In general, the formula for paraffin hydrocarbons is C_nH_{2n+2}. Then the basis correction for the heat of combustion and the liquid oxygen correction and reduction of the heat of combustion to H_1 is, in terms of n:

$$298(1.8)\left[7.45n + (n+1)(7.95) - \left(\frac{3n+1}{2}\right)(6.95)\right] - \frac{1818(3n+1)}{2} = (1500 - 55n)\ \text{B.T.U./lb. mole}$$

Table 2 provides the bonds found in various paraffins and the corresponding $H_{f,2400}$, H_1 and H^r for stoichiometric combustion with liquid oxygen. The bonds C-H, C^i-C^i, C^i-C^{ii}, C^{ii}-C^{ii} were found sufficient to describe the ΔH of the normal paraffins. C^i and C^{ii} represent primary and secondary carbons respectively.

The derived e_1's were used to compute the ΔH of various compounds and the results can be checked with the ΔH's, calculated from the charts, in Table 3.

TABLE 2

The bond types C-H, C^{i}-C^{i}, C^{i}-C^{ii}, C^{ii}-C^{ii}, are represented by the letters a, b_1, b_2, and b_3 respectively. C^{i} and C^{ii} represent primary and secondary carbons respectively.

Compound	Bond Types and Numbers	$H_{f,2400}$	H	H^r
CH_4	4a	143,430	346,616	2.4166
C_2H_6	6a, $1b_1$	242,150	615,664	2.5424
C_3H_8	8a, $2b_2$	340,870	880,688	2.5836
C_4H_{10}	10a, $2b_2$, $1b_3$	439,570	1,144,975	2.6047
C_5H_{12}	12a, $2b_2$, $2b_3$	538,290	1,408,902	2.6173
C_6H_{14}	14a, $2b_2$, $3b_3$	637,010	1,673,249	2.6267
C_7H_{16}	16a, $2b_2$, $4b_3$	735,730	1,937,650	2.6336
C_8H_{18}	18a, $2b_2$, $5b_3$	834,450	2,202,051	2.6389
C_9H_{20}	20a, $2b_2$, $6b_3$	933,170	2,466,470	2.6431
$C_{10}H_{22}$	22a, $2b_2$, $7b_3$	1,031,890	2,730,889	2.6464

As an example of the calculation of ΔH, consider the case of CH_4.

$CH_4 + 2O_2 = CO_2 + 2H_2O$, fictitious composition.

$H_1^r = 2.4166$, Fig. 29, ($\underline{1}$), interpolation no. $= 0.840$,

read $T_1 = 3417^\circ K$ from Fig. A1.

$T_1 = 3417^\circ K$, Fig. 31, ($\underline{1}$), interpolation no. $= 0.860$,

read $S^r + \beta = 1.1305$ from Fig. A2.

From Fig. 33, ($\underline{1}$), $\alpha - \beta = 0.0175$.

Therefore, $S^r + \alpha = 1.1480$.

$S^r + \alpha = 1.1480$, Fig. 32, ($\underline{1}$), interpolation no. $= 0.860$,

read $T_2 = 2700$ from Fig. A3.

$T_2 = 2700$, Fig. 30, ($\underline{1}$), interpolation no. $= 0.850$,

read $H_2^r = 1.6020$.

Then $\Delta H^r = 0.8146$,

$\Delta H = (0.8146)(143,430) = 116,840$ B.T.U./lb. mole fuel

Then, the contribution of each C-H bond is $\frac{116,840}{4} = 29,210$ B.T.U./C-H bond.

For $C_2H_6 + 3.5O_2$, $\Delta H = 198,660$ B.T.U./lb. mole fuel.

Therefore, the C^1-C^1 energy contribution is 198,660 - - 6 x 29,210 = 23,400 B.T.U./C^1-C^1 bond.

TABLE 3

Reactants	W	Fg.29	Fg.31	Fg.33	Fg.32	Fg.30	Calc'd ΔH	Pred'd ΔH
CH_4+2O_2	80	.840	.860	.0175	.860	.850	116,840	
$C_2H_6+3.5O_2$	142	.870	.890	.0178	.875	.875	198,660	
$C_3H_8+5O_2$	204	.890	.898	.0195	.890	.880	283,800	
$C_4H_{10}+6.5O_2$	266	.894	.900	.0197	.895	.885	367,350	
$C_5H_{12}+8O_2$	328	.896	.902	.0199	.900	.888	450,980	450,900
$C_6H_{14}+9.5O_2$	390	.898	.904	.0200	.903	.891	534,480	534,450
$C_7H_{16}+11O_2$	452	.90	.906	.0202	.905	.894	618,450	618,000
$C_8H_{18}+12.5O_2$	514	.902	.908	.0203	.907	.897	701,280	701,550
$C_9H_{20}+14O_2$	576	.904	.909	.0204	.909	.899	784,890	785,100
$C_{10}H_{22}+15.5O_2$	638	.906	.910	.0205	.910	.901	869,260	868,650

Heat of combustion data used for the determination of H in Table 2 are from (5), page 244.

Table 3 gives the calculated values of ΔH (in B.T.U./lb. mole fuel) and W (in lbs.) and the predicted values for ΔH. The interpolation numbers used in calculating ΔH are given under the headings Figure 29, Figure 31, Figure 33 (the $\alpha - \beta$ is listed), Figure 32 and Figure 30, for the corresponding figures of (1) and the Appendix (see page 72).

Table 4 gives the energy (e_1) and weight (w_1) contributions as well as the $\frac{e_1}{w_1}$ ratios of the listed bond types. The bond type code letters are explained in Table 2.

TABLE 4

Bond Type	Energy Contributions	Weight Contributions	$\frac{e_1}{w_1}$
a	29,210	20	1460
b_1	23,400	22	1064
b_2	25,060	22	1139
b_3	25,130	22	1142

(2.) Bonds encountered in branched paraffins

In general, the formula for branched paraffin hydrocarbons is C_nH_{2n+2}. Their complete combustion yields n moles CO_2 and n + 1 moles H_2O. Then the basis correction for the heat of combustion, the liquid oxygen correction and the reduction of the heat of combustion to H_1 is, in terms of n:

$$298(1.8)\left[7.45n + (n+1)(7.95) - \frac{3n+1}{2}(6.95)\right] - \frac{1818}{2}(3n+1) = (1500 - 55n) \text{ B.T.U./lb. mole.}$$

Table 5 lists the bonds found in various branched paraffins and the corresponding $H_{f,2400}$, H_1 and H^r for stoichiometric combustion with liquid oxygen. The bonds C^i-C^{iii}, C^{ii}-C^{iii}, C^i-C^{iv}, C^{ii}-C^{iv} and C^{iii}-C^{iii} were found sufficient to predict, in conjunction with the bonds derived from other hydrocarbons, the ΔH of the branched paraffins.

Table 6 gives the values of ΔH (in B.T.U./lb. mole fuel) as calculated from the charts and W (in lbs.), and the predicted values for ΔH. The interpolation numbers used in calculating ΔH are given under the headings Figure 29, Figure 31, Figure 33 (The α - β is listed), Figure 32 and Figure 30, for the corresponding figures of (1) and the Appendix (see page 72).

TABLE 5

The bond types $C^{i}-C^{iii}$, $C^{ii}-C^{iii}$, $C^{i}-C^{iv}$, $C^{ii}-C^{iv}$ and $C^{iii}-C^{iii}$ are represented by the letters b_4, b_5, b_6, b_7 and b_8 in this order. For other bond type code letters see previous tables.

<u>Compound</u>	<u>Bond Types and Numbers</u>	$H_{f,2400}$	<u>H</u>	<u>H^r</u>
C_4H_{10} Isobutane	10a, $3b_4$	439,570	1,142,017	2.5980
C_5H_{12} Isopentane	12a, $1b_2$, $2b_4$, $1b_5$	538,290	1,405,446	2.6109
C_5H_{12} 2,2 Dimethyl propane	12a, $4b_6$	538,290	1,400,496	2.6016
C_6H_{14} 3-Methyl pentane	14a, $2b_2$, $1b_4$, $2b_5$	637,010	1,671,341	2.6237
C_6H_{14} 2,2 Dimethyl butane	14a, $1b_2$, $3b_6$, $1b_7$	637,010	1,665,329	2.6142
C_6H_{14} 2,3 Dimethyl butane	14a, $4b_4$, $1b_8$	637,010	1,668,695	2.6195
C_7H_{16} 2,3 Dimethyl pentane	16a, $1b_2$, $3b_4$, $1b_5$, $1b_8$	735,730	1,932,736	2.6269

TABLE 6

Reactants	W	Fg.29	Fg.31	Fg.33	Fg.32	Fg.30	Calc'd ΔH	Pred'd ΔH
$C_4H_{10}+6.5O_2$ Isobutane	266	.894	.900	.0197	.895	.885	367,040	
$C_5H_{12}+8O_2$ Isopentane	328	.896	.902	.0199	.900	.888	449,960	
$C_5H_{12}+8O_2$ 2,2-Dimethyl propane	328	.896	.902	.0199	.900	.888	447,100	
$C_6H_{14}+9.5O_2$ 3-Methyl pentane	390	.898	.904	.0200	.903	.891	532,990	532,820
$C_6H_{14}+9.5O_2$ 2,2-Dimethyl butane	390	.898	.904	.0200	.903	.891	529,800	
$C_6H_{14}+9.5O_2$ 2,3-Dimethyl butane	390	.898	.904	.0200	.903	.891	531,903	
$C_7H_{16}+11O_2$ 2,3-Dimethyl pentane	452	.900	.906	.0202	.905	.894	614,260	614,800

Table 7 gives the energy (e_i) and weight (w_i) contributions as well as the $\frac{e_i}{w_i}$ ratios of the listed bond types. The bond type code letters are explained in Table 5.

TABLE 7

Bond Type	Energy Contributions	Weight Contributions	$\frac{e_i}{w_i}$
b_4	25,000	22	1137
b_5	24,380	22	1108
b_6	24,140	22	1097
b_7	23,480	22	1067
b_8	23,000	22	1045

(3.) Bonds encountered in monoolefins

In general, the formula for monoolefins is C_nH_{2n}. Their complete combustion yields n moles CO_2 and n moles H_2O. Then the basis correction for the heat of combustion, the liquid oxygen correction and the reduction of the heat of combustion to H_1 is, in terms of n:

$$298(1.8)\left[7.45n + 7.95n - \frac{3n}{2}(6.94)\right] -$$

$$- 2727n = -50n \text{ B.T.U./lb. mole.}$$

Table 8 lists the bonds found in various monoolefins and the corresponding $H_{f,2400}$, H_1 and H^r for stoichiometric combustion with liquid oxygen. The bonds $C^i = C^i$, $C^i = C^{ii}$, $C^{ii} = C^{ii}$,cis, $C^{ii} = C^{ii}$ trans, $C^i = C^{iii}$ and $C^{iii} = C^{ii}$ were found sufficient to predict, in conjunction with the bonds derived from other hydrocarbons, the ΔH of the monoolefins.

Table 9 gives the values of ΔH (in B.T.U./lb. mole fuel) as calculated from the charts and W (in lbs.), and the predicted values for ΔH. The interpolation numbers used in calculating ΔH are given under the headings Figure 29, Figure 31, Figure 33 (The α - β is listed), Figure 32 and Figure 30, for the corresponding figures of (1) and the Appendix (see page 72).

TABLE 8

The bond types $C^i = C^i$, $C^i = C^{ii}$, $C^{ii} = C^{ii}$ is, $C^{ii} = C^{ii}$ trans, $C^i = C^{iii}$ and $C^{iii} = C^{iii}$ are represented by the letters c_1, c_2, c_3, c_4, c_5 and c_6 in this order. For other bond type code letters see previous tables.

Compound	Bond Types and Numbers	$H_{f,2400}$	H	H^r
C_2H_4	4a, $1c_1$	197,440	569,050	2.8821
C_3H_6	6a, $1b_2$, 1c2	296,160	828,620	2.7978
C_4H_8 1-Butene	8a, $1b_2$, $1b_3$, $1c_2$	394,880	1,093,620	2.7694
C_4H_8 cis-2-Butene	8a, $2b_2$, $1c_3$	394,880	1,090,660	2.7620
C_4H_8 trans-2-Butene	8a, $2b_2$, $1c_4$	394,880	1,088,780	2.7572
C_4H_8 2-Methyl propene	8a, $2b_4$, $1c_5$	394,880	1,087,100	2.7529
C_5H_{10} 2-Methyl-1-butene	10a, $1b_2$, $1b_4$, $1b_5$, $1c_5$	493,600	1,350,780	2.7365
C_5H_{10} 3-Methyl-1-butene	10a, $2b_4$, $1b_5$, $1c_2$	493,600	1,353,950	2.7430
C_5H_{10} 2-Methyl-2-Butene	10a, $1b_2$, $2b_4$, $1c_6$	493,600	1,348,100	2.7311

TABLE 9

Reactants	W	Fg.29	Fg.31	Fg.33	Fg.32	Fg.30	Calc'd ΔH	Pred'd ΔH
$C_2H_4+3O_2$	124	.910	.915	.0207	.915	.910	178,310	
$C_3H_6+4.5O_2$	186	.910	.915	.0207	.915	.910	255,100	
$C_4H_8+6O_2$	248	.910	.915	.0207	.915	.910	338,570	338,670
$C_4H_8+6O_2$	248	.910	.915	.0207	.915	.910	336,440	
$C_4H_8+6O_2$	248	.910	.915	.0207	.915	.910	336,100	
$C_4H_8+6O_2$	248	.910	.915	.0207	.915	.910	337,580	
$C_5H_{10}+7.5O_2$	310	.910	.915	.0207	.915	.910	419,300	420,300
$C_5H_{10}+7.5O_2$	310	.910	.915	.0207	.915	.910	421,050	421,530
$C_5H_{10}+7.5O_2$	310	.910	.915	.0207	.915	.910	418,620	

Table 10 gives the energy (e_1) and weight (w_1) contributions as well as the $\frac{e_1}{w_1}$ ratios of the listed bond types. The bond type code letters are explained in Table 8.

TABLE 10

Bond Type	Energy Contributions	Weight Contributions	$\frac{e_1}{w_1}$
c_1	61,470	44	1394
c_2	54,800	44	1246
c_3	52,640	44	1198
c_4	52,300	44	1190
c_5	53,902	44	1225
c_6	51,460	44	1169

(4.) Bonds encountered in acetylenes

In general, the formula for acetylenes is C_nH_{2n-2}. Their complete combustion yields n moles CO_2 and (n - 1) moles H_2O. Then the basis correction for the heat of combustion, the liquid oxygen correction and the reduction of the heat of combustion to H_1 is, in terms of n:

$$298(1.8)\left[n(7.45) + (n-1)(7.95) - 6.94\left(\frac{3n-1}{2}\right)\right] - \left(\frac{3n-1}{2}\right)(1818) = -(47n + 1500) \text{ B.T.U./lb. mole.}$$

Table 11 lists the bonds found in various acetylenes and the corresponding $H_{f,2400}$, H_1 and H^r for stoichiometric combustion with liquid oxygen. The bonds $C^i \equiv C^i$, $C^i \equiv C^{ii}$ $C^{ii} \equiv C^{ii}$ were found sufficient to predict, in conjunction with the bonds derived for other hydrocarbons, the ΔH of the acetylenes.

Table 12 gives the values of ΔH (in B.T.U./lb. mole fuel) as calculated from the charts and W (in lbs.) and the predicted values for ΔH. The interpolation numbers used in calculating ΔH are given under the headings Figure 29, Figure 31, Figure 33 (The α - β is listed), Figure 32 and Figure 30, for the corresponding figures of (1) and the Appendix (see page 72).

TABLE 11

The bond types C-H, $C^{i} \equiv C^{i}$, $C^{i} \equiv C^{ii}$ and $C^{ii} \equiv C^{ii}$ are represented by the letters a, d_1, d_2 and d_3 respectively. For other bond type code letters see previous tables.

Compound	Bond Types and Numbers	$H_{f,2400}$	H	H^r
C_2H_2	2a, 1d_1	152,750	538,572	3.5258
C_3H_4	4a, 1b_2, 1d_2	251,470	794,076	3.1577
C_4H_6 1-Butyne	6a, 1b_2, 1b_3, 1d_2	350,190	1,068,043	3.0498
C_4H_6 2-Butyne	6a, 2b_2, 1d_3	350,190	1,051,253	3.0019
C_5H_8 3-Methyl- 1-butyne	8a, 2b_4, 1b_5, 1d_2	448,910	1,319,540	2.9394

TABLE 12

Reactants	W	Fg.29	Fg.31	Fg.33	Fg.32	Fg.30	Calc'd ΔH	Pred'd ΔH
$C_2H_2+2.5O_2$	106	.940	.950	.0230	.940	.940	149,820	
$C_3H_4+4O_2$	168	.930	.942	.0220	.930	.930	230,700	230,150
$C_4H_6+5.5O_2$ 1-Butyne	230	.922	.935	.0218	.922	.922	313,700	
$C_4H_6+5.5O_2$ 2-Butyne	230	.922	.935	.0218	.922	.922	304,280	
$C_5H_8+7O_2$ 3-Methyl-1-butyne	292	.918	.930	.0215	.918	.918	396,110	396,310

Table 13 gives the energy (e_i) and weight (w_i) contributions as well as the $\frac{e_i}{w_i}$ ratios of the listed bond types. The bond type code letters are explained in Table 11.

TABLE 13

Bond Type	Energy Contributions	Weight Contributions	$\frac{e_i}{w_i}$
d_1	91,400	66	1384
d_2	88,250	66	1337
d_3	78,900	66	1194

(5.) Bonds encountered in alcohols

In general, the formula for monohydroxyl hydrocarbons is $C_nH_{2n+2}O$. Their complete combustion yields n moles CO_2 and (n - 1) moles H_2O. Then the basis correction for the heat of combustion, the liquid oxygen correction and the reduction of the heat of combustion to H_1 is, in terms of n:

$$298(1.8)\left[7.45n + (n + 1)(7.95) - \frac{3}{2}n(6.95)\right] -$$

$$- 1818\left(\frac{3n}{2}\right) = 4260 - 50n \text{ B.T.U./lb. mole.}$$

Table 14 lists the bonds found in various alcohols and the corresponding $H_{f,2400}$, H_1 and H^r for stoichiometric combustion with liquid oxygen. The bonds C^o-OH, C^i-OH, C^{ii}-OH and C^{iii}-OH were found sufficient to predict, in conjunction with the bonds derived from other hydrocarbons, the ΔH of the alcohols.

Table 15 gives the values of ΔH (in B.T.U./lb. mole fuel) as calculated from the charts and W (in lbs.), and the predicted values for ΔH. The interpolation numbers used in calculating ΔH are given under the headings Figure 29, Figure 31, Figure 33 (The $\alpha - \beta$ is listed), Figure 32 and Figure 30, for the corresponding figures of (1) and the Appendix (see page 72).

Since the heat of combustion of liquid alcohols was used (because of lack of gaseous state data) the various C-OH bonds include that change of base difference. The C-OH energy contributions should be higher by 2000-5000 B.T.U. and the relative magnitudes should change but should still remain in the same descending order.

TABLE 14

The bond types C^{o}-OH, C^{i}-OH, C^{ii}-OH and C^{iii}-OH are represented by the letters g_1, g_2, g_3 and g_4 in that order. For other bond type code letters see previous tables.

Compound	Bond Types and Numbers	$H_{f,2400}$	H	H^r
CH_3OH	3a, $1g_1$	143,430	265,450	1.8507
C_2H_5OH	5a, $1b_1$, $1g_2$	242,150	529,270	2.1857
n-C_3H_7OH	7a, $2b_2$, $1g_2$	340,870	795,750	2.3344
i-C_3H_7OH	7a, $2b_2$, $1g_3$	340,870	782,790	2.2964
n-C_4H_9OH	9a, $2b_2$, $1b_3$, $1g_2$	439,570	1,059,310	2.4100
n-$C_5H_{11}OH$	11a, $2b_2$, $2b_3$, $1g_2$	538,290	1,306,670	2.4274
$CH_3(C_2H_5)_2C(OH)$	13a, $2b_2$, $1b_4$, $2b_5$, $1g_4$	637,010	1,539,630	2.4170

TABLE 15

Reactants	W	Fg.29	Fg.31	Fg.33	Fg.32	Fg.30	Calc'd ΔH	Pred'd ΔH
$CH_3OH+1.5O_2$	80	.840	.860	.0175	.860	.850	95,340	
$C_2H_5OH+3O_2$	142	.870	.890	.0178	.875	.875	181,500	181,560
n-C_3H_7OH+ $+4.5O_2$	204	.890	.898	.0195	.890	.880	266,700	
i-C_3H_7OH+ $+4.5O_2$	204	.890	.898	.0195	.890	.880	263,970	
n-C_4H_9OH+ $+6O_2$	266	.894	.900	.0197	.895	.885	350,380	350,250
n-$C_5H_{11}OH+$ $+7.5O_2$	328	.896	.902	.0199	.900	.888	434,070	433,800
$CH_3(C_2H_5)_2COH+$ $+9O_2$	390	.898	.904	.0200	.903	.891	509,630	

Table 16 gives the energy (e_i) and weight (w_i) contributions as well as the $\frac{e_i}{w_i}$ ratios of the listed bond types. The bond type code letters are explained in Table 5.

TABLE 16

Bond Type	Energy* Contributions	Weight Contributions	$\frac{e_i}{w_i}$
g_1	7710	20	385
g_2	12050	20	602
g_3	9380	20	469
g_4	6020	20	301

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* Above liquid basis.

(6.) Bonds encountered in aromatics

A different method of deriving the e_i for bonds encountered in aromatics is employed. The energy contribution e_{Bz} to ΔH of the entire benzene (C_6H_6) molecule is calculated. Then it is assumed that each carbon-hydrogen bond contributes the same amount of energy as in the paraffins, namely $e_a = 29{,}210$ B.T.U. Therefore, the substitution of one hydrogen by, for example, a $-CH_3$ radical will yield:

$$e_{Bz} - e_a + 3e_a + e_{b4} = \Delta H_{C_6H_5CH_3}$$

It was found that it is not necessary to differentiate between ortho-, meta-, and para-substitution since only the fifth or sixth significant figure of the heats of combustion varies in these cases.

In general, the formula for benzene and the alkyl benzenes is C_nH_{2n-6} and their complete combustion products are n moles CO_2 and n - 3 moles H_2O. Then the basis correction for the heat of combustion, the liquid oxygen correction and the reduction of the heat of combustion to H_1 is, in terms of n:

$$298 \times 1.8 \left[n(7.45) + 7.95(n - 3) - \left(\frac{3n - 3}{2}\right] 6.94\right] - \frac{3}{2}(n - 1)1818 = -(4483 + 45n).$$

Table 17 lists the bonds found in various alkyl benzenes and the corresponding $H_{f,2400}$, H_1 and H^r for stoichiometric combustion with liquid oxygen. The group $C_6H_5^-$ was found sufficient to predict, in conjunction with the bonds derived from other hydrocarbons, the ΔH of <u>all</u> monosubstituted benzenes. For polysubstituted benzenes an equivalent basic aromatic group is computed by subtracting sufficient a's from the value e_{Bz}.

Table 18 gives the values of ΔH (in B.T.U./lb. mole fuel) as calculated from the charts and W (in lbs.) and the predicted values for ΔH. The interpolation numbers used in calculating ΔH are given under the headings Figure 29, Figure 31, Figure 33 (The $\alpha - \beta$ is listed), Figure 32 and Figure 30, for the corresponding figures of (<u>1</u>) and the Appendix (see page 72).

TABLE 17

The groups C_6H_5-, $C_6H_4=$ and $C_6H_3\equiv$ represented by the letters k_1, k_2 and k_3 respectively. For other bond type code letters see previous tables.

Compound	Bond Types and Numbers	$H_{f,2400}$	H	H^r
C_6H_6	1a, $1k_1$ or 2a, k_2	458,250	1,358,800	2.9651
$C_6H_5CH_3$	k_1, 3a, $1b_4$	556,970	1,617,900	2.9048
$C_6H_5C_2H_5$	k_1, 5a, $1b_2$, $1b_5$	655,690	1,882,500	2.8710
$CH_3C_6H_4CH_3$	k_2, 6a, $2b_4$	655,690	1,878,200	2.8622
$C_2H_5C_6H_4CH_3$	k_2, 8a, $1b_2$, $1b_4$, $1b_5$	754,410	2,142,450	2.8410

TABLE 18

	W	Fg.29	Fg.31	Fg.33	Fg.32	Fg.30	Calc'd ΔH	Pred'd ΔH
C_6H_6+7.5O_2	318	.940	.945	.0225	.940	.940	412,760	
$C_6H_5CH_3$+9O_2	380	.933	.938	.0220	.933	.933	496,450	496,180
$C_6H_5C_2H_5$+10.5O_2	442	.930	.935	.0215	.930	.930	579,200	579,040
$CH_3C_6H_4CH_3$+ +10.5O_2	442	.930	.935	.0215	.930	.930	579,100	579,600
$C_2H_5C_6H_4CH_3$+ +12O_2	504	.928	.933	.0210	.928	.928	662,950	662,460

Table 19 gives the energy (e_i) and weight (w_i) contributions as well as the $\frac{e_i}{w_i}$ ratios of the listed group types. The group type code letters are explained in Table 17.

TABLE 19

Group Type	Energy Contributions	Weight Contributions	$\frac{e_i}{w_i}$
k_1	383,550	309	1241
k_2	354,340	306	1180
k_3	325,130	291	1119

7. Bonds and groups encountered in amines and other nitrogen containing compounds

In this series of fuels it was found necessary to use the group contribution concept introduced on page 48.

Because of the variety of series studied, no general way of predicting the change of the heats of combustion due to base changes was used.

The number of reactants studied in this table was limited by the availability of reliable thermodynamic data. Thus, interesting monofuels such as hydrazine nitrate were not studied.

Most heats of combustion used in this section were taken from Table 4, page 46 of (<u>1</u>). Then the enthalpy of the liquid oxygen necessary for complete combustion was added to the heat of combustion and the result was H_1, the total enthalpy of the reactants entering the combustion chamber. All fuels studied were in a liquid state and therefore each of the bonds and groups listed here has absorbed the entire change of state error which ranges from 1000 to 5000 B.T.U. per bond (see page 23). This change of basis does not appreciably affect the relative magnitudes of the energy bond contributions.

The limitations of the accuracy of the extended charts for nitrogen containing mixtures have been adequately discussed elsewhere (pages 64 and 76).

Table 20 lists the bonds and groups found in various nitrogen-containing organic compounds and the corresponding $H_{f,2400}$, H_1 and H^r for combustion with stoichiometric liquid oxygen. The groups $C^o\text{-}NH_2$, $C\text{-}\underset{H}{N}\text{-}C$, $C\text{-}\underset{C}{N}\text{-}C$, $C^i\text{-}NH_2$, $C^{ii}\text{-}NH_2$, N-H, $C^o\text{-}NO_2$, $C^i\text{-}NO_2$, C-CN, C-NC and N-H were found sufficient to predict, in conjunction with bonds and groups derived from other hydrocarbons, the ΔH of most nitrogen-organic compounds.

Table 21 gives the values of ΔH (in B.T.U./lb. mole of fuel) as calculated from the charts and W (in lbs.), and the predicted values for ΔH. The interpolation numbers used in calculating ΔH are given under the headings Figure 29, Figure 31, Figure 33 (The $\alpha - \beta$ is listed), Figure 32 and Figure 30, for the corresponding figures of (<u>1</u>) and the Appendix (see page 72).

A more detailed study of the nitrogen-organic compounds is needed and it should be easy to make when more accurate thermodynamic data and charts become available.

TABLE 20

The groups $C^o\text{-}NH_2$, $C\text{-}\underset{H}{N}\text{-}C$, $C\text{-}\underset{C}{N}\text{-}C$, $C^i\text{-}NH_2$, $C^{ii}\text{-}NH_2$, N-N, $C^o\text{-}NO_2$, $C^i\text{-}NO_2$, C-CN, C-NC, N-H are represented by the letters l_1, l_2, l_3, l_4, l_5, l_6, l_7, l_8, l_9, l_{10} and l_{11} in this order. For other bond and group type code letters see previous tables.

Compound	Bond Types and Numbers	$H_{f,2400}$	H	H^r
CH_3NH_2	3a, l_1	182,825	421,680	2.3012
$(CH_3)_2NH$	6a, l_2	281,550	672,140	2.3875
$(CH_3)_3N$	9a, l_3	380,270	960,710	2.5120
$C_2H_5NH_2$	5a, $1b_1$, $1l_4$	281,550	672,320	2.3880
$(CH_2)_2(NH_2)_2$	4a, $1b_1$, $1l_4$	320,970	736,150	2.2375
$C_6H_5NH_2$	k_1, l_5	497,670	1,393,800	2.8010
$C_6H_4(NH_2)CH_3$	k_2, 3a, $1b_4$, $1l_5$	596,390	1,648,450	2.7615
N_2H_4	$4l_{11}$, $1l_6$	123,530	236,550	1.9162
CH_3NO_2	3a, $1l_7$	138,140	284,300	2.0580
$C_2H_5NO_2$	5a, $1b_1$, $1l_8$	236,860	548,150	2.3165
CH_3CN	3a, $1l_9$	192,170	517,710	2.6920
CH_3NC	3a, $1l_{10}$	192,170	536,610	2.7912
NH_3	$3l_{11}$	84,110	131,280	1.5608

TABLE 21

	W	Fg.29	Fg.31	Fg.33	Fg.32	Fg.30	Calc'd ΔH	Pred'd ΔH
$CH_3NH_2+2.25O_2$	103	.800	.790	.0150	.800	.800	150,000	
$(CH_3)_2NH+3.75O_2$	165	.820	.830	.0160	.850	.850	221,000	
$(CH_3)N+5.25O_2$	227	.860	.880	.0170	.870	.860	315,000	
$C_2H_5NH_2+3.75O_2$	165	.830	.840	.0170	.860	.860	227,000	
$(CH_2)_2(NH_2)_2+$ $+4O_2$	188	.815	.830	.0160	.850	.850	256,000	255,840
$C_6H_5NH_2+7.75O_2$	341	.930	.930	.0220	.930	.925	428,400	428,350
$C_6H_4(NH_2)CH_3+$ $+9.25O_2$	403	.932	.932	.0222	.932	.927	511,770	
$N_2H_4+O_2$	64	.560	.590	.0175	.575	.570	85,000	
$CH_3NO_2+0.75O_2$	85	.840	.860	.0160	.850	.840	106,000	
$C_2H_5NO_2+2.25O_2$	147	.875	.880	.0180	.880	.875	185,000	
$CH_3CN+2.75O_2$	129	.910	.910	.0190	.900	.900	162,000	
$CH_3NC+2.75O_2$	129	.910	.910	.0190	.900	.900	168,000	
$NH_3+0.75O_2$	41	.570	.600	.0180	.585	.580	48,900	

Table 22 gives the energy (e_i) and weight (w_i) contributions as well as the $\frac{e_i}{w_i}$ ratios of the listed bond types. The bond and group type code letters are explained in Table 20.

TABLE 22

Bond Type	Energy Contributions	Weight Contributions	$\frac{e_i}{w_i}$
l_1	62,400	43	1450
l_2	45,700	45	1030
l_3	53,100	47	1130
l_4	57,800	43	1345
l_5	44,800	32	1400
l_6	20,300	9.4	2160
l_7	19,400	25	776
l_8	15,550	25	622
l_9	75,400	69	1092
l_{10}	81,400	69	1180
l_{11}	16,300	13.66	1193

B. Accuracy of $\frac{e_1}{w_1}$ ratios

The first two and with some reservations the third figure of the $\frac{e_1}{w_1}$ numbers should be accepted as significant.

The relative magnitudes of $\frac{e_1}{w_1}$ at stoichiometric mixtures are within 1.0 per cent of the relative magnitudes of $\frac{e_1}{w_1}$ at other fuel/oxidant or fuel/(oxidant + diluent) mixtures.

The first two significant figures of atomic weights were used because the relative error thus introduced is negligible.

C. Application of Bond Contributions.

As an illustration of bond contribution uses the following two simple examples: are presented.

Example 1. Which is the best way of introducing oxygen into the fuel structure?

From table 16, p. 47 we see that C^o-OH contributes:

$$e/w)_{g1} = 385.$$

From table 12, p. 57, we see that C^o-NO_2 contributes:

$$e/w)_{17} = 776$$

Therefore the best way of introducing oxygen into a fuel is through a C-NO_2 bond.

Example 2. Which is the best structure for a fuel mixture of composition $C_n H_{2n}$?

By inspection of tables 4, 7, 10, 13 and 19 we see that that fuel is pure nC_2H_4 rather than $n(2/3\ CH_4 + 2/3\ C_2H_2)$ or $n(2/3\ CH_4 + 2/9\ C_6H_6)$.

D. Conclusions

The values of $\frac{e_i}{w_i}$ listed in tables 4, 7, 10, 13, 16, 19 and 22 predict the desirability of inclusion of various chemical bonds in rocket fuel structure. Thus, in order to connect two given atoms in a way which will yield the optimum specific impulse, the bond with the highest possible $\frac{e_i}{w_i}$ must be picked. An inspection of these tables establishes the desirability of bonds such as $C^i = C^i$ over $C^i - C^i$ etc. Usually bonds which contribute maximum values of $\frac{e_i}{w_i}$ also contribute an increase to the flame temperature but this paper did not elaborate on bonds from a temperature point of view.

The calculations of bond contributions assume equilibrium among the chemical species present in the rocket engine. The reactions taking place in it are rapid enough, (17, 18), to justify this assumption even for such a short (10^{-3}-10^{-4} secs) residence time. This paper does not investigate the effect of reactant structure on rates of reaction. It is possible that such an effect may influence, (11), specific impulse by decreasing (or increasing) the rate of reaction so that equilibrium is/not reached within the chamber (or is reached very early in it so that a shorter one could be used). Since, however, a rocket motor is a continuous process and is not dependent on exact timing of detonation (such as is necessary in piston engines) for full efficiency, specific impulse should be insensitive to such "knock" effects.

RECOMMENDATIONS

One of the methods for predicting the effect of fuel structure on specific impulse investigated by the author was the quantization of heats of combustion of various fuels on a bond type basis. Thus the contribution h_i of each type of bond i to H_1, the total enthalpy entering the combustion chamber, rather than ΔH was found in a manner similar to that employed in deriving the contributions of each bond to ΔH. The $\frac{h_i}{w_i}$ quotients were then calculated and it was found that their relative magnitudes were not in close agreement with the relative magnitudes of the quotients $\frac{e_i}{w_i}$. No simple correlation could be found between $\frac{h_i}{w_i}$ and $\frac{e_i}{w_i}$. However, the use of $\frac{h_i}{w_i}$ is recommended when only a rough estimate of the effect of structure on specific impulse is necessary. The $\frac{h_i}{w_i}$ can be computed with greater accuracy since no use has to be made of the generalized charts. No table of $\frac{h_i}{w_i}$ is included here since h_i for various bonds can be easily calculated from the tables of H_1 in the text.

It can be seen that in most cases e_i can be predicted to 3 significant figures. This suggests the possibility that tables constructed to give e_i for each bond as a function of the ratio fuel/oxidant at any pressure difference will be accurate enough to use in predicting enthalpy changes of various mixtures used in rockets, gas turbines and jet engines. For example, a plot could be made of e for the bond C-H versus fuel/oxidant at various pressure differences. Given tables for enough bonds, the absolute magnitude of ΔH for any mixture can be predicted.

The critical ratio of fuel/oxidant giving the maximum specific impulse should be further investigated.

The space above the upper (0.9) composition interpolation line of the figures in the Appendix may be used for interpolation numbers between 0.9 and 1.0 by assuming that the "doubled-up" space between 0.9 and 1.0 is equal to the interval between 0.8 and 0.9. The error introduced by this assumption cannot be greater than 1 per cent.

APPENDIX

Early in the investigation of this topic it was found that the generalized charts of Hottel, Williams and Satterfield, (1), do not cover the temperature ranges attained by stoichiometric mixtures of hydrocarbons and liquid oxygen. Because of the general desirability of stoichiometric mixtures (minimum error in reading composition interpolation numbers, ease of computation of H^r, etc.), the charts were extended to cover the region from 3200 to 4000°K.

The bases used in (1), page 44, are employed.

Seven mixtures of carbon, oxygen and hydrogen and one of carbon, oxygen and nitrogen were studied. These mixtures are listed in table A1. Emphasis was placed on the stoichiometric mixtures of CH_4, C_2H_6 and C with oxygen because the composition interpolation numbers, as read from the charts of (1), of the hydrocarbons studied lie between the composition interpolation numbers of these three systems. Then the fuel C_2H_6, with $\frac{C}{H} = 3$, was studied at four different oxygen concentrations.

The oxygen concentrations were picked in the following manner. The $\frac{O}{O + 2C + \frac{H}{2}}$ value of the intersections of the $\frac{C}{C + H} = 0.25$ (corresponding to C_2H_6)

line and the composition interpolation numbers 0.2, 0.4, 0.6, 0.8, in the fuel-rich region, was read from the charts (Figure 29, (1)). Then, since C = 2 and H = 6, the resulting four equations where O is the only unknown were solved and the determined values of O were the oxygen concentrations corresponding to the four fuel-rich mixtures of interpolation numbers 0.2, 0.4, 0.6, 0.8. The atomic ratios of these four mixtures are given in Table A1. Finally, the mixture C + O + 2N was picked because it provides the interpolation number of zero value.

It is worthy of note that the composition C + O, also of composition interpolation number zero, was studied but since its reduced enthalpy and reduced entropy data were within 0.1 per cent of the C + O + 2N line it was not listed in the tables or plotted on the charts.

The absence of nitrogen from the compositions studied does not impair the value of the charts since the flame temperature of mixtures in which an excess of nitrogen is present cannot climb, because of the diluent effect of nitrogen, into the region above 3200°K. Only when a small amount of nitrogen is present does the flame temperature climb above 3200°K, and then the amount of nitrogen is so small ($\frac{N}{O} < 0.25$) that, as revealed by a study of the system $C_2H_4(NH_2)_2 + 4O_2$, (3), the error introduced by ignoring it and reading a composition interpolation number from the $\frac{N}{O} = 0$ table is in the order of 1 per cent. This error is absorbed by the energy contribution of the bonds which link nitrogen with other atoms and therefore it is expected that these bond contributions will all be either higher or lower than the true values. The error will lie in the same direction for all mixtures since the effect of nitrogen within the above-mentioned narrow concentration limits is relatively the same.

It was found that the nitrogen containing bonds' energy contribution values calculated by use of Figures A1, A2, and A3 were less, by 9 per cent, than those calculated by use of the $C_2H_4(NH_2)_2 + 4O_2$ system data. This error should be the same for all mixtures of approximately the same nitrogen content and therefore the relative magnitudes of the energy contributions of various nitrogen containing bonds are true.

For each mixture, the equilibrium gas composition was calculated for values of the temperature at intervals of 200°K between 3200°K and 4000°K, and at 300 psia. It was not found necessary to calculate the equilibrium compositions at 14.7 psia because Figure 30 of reference (1) covers the range of nozzle exit temperatures attained at a pressure of 14.7 psia and Table 14 of Appendix C of reference (1) provides enough data for an extension of the generalized entropy plot at 14.7 psia to cover the ranges of interest. Only the C-H-O mixture data from this table were plotted in Figure 3.

A chemical reaction among a moles of A, b moles of B, etc., to give r moles of R, s moles of S, etc., may be written in the following generalized form:

$$aA + bB + \cdot\cdot\cdot \longleftrightarrow rR + sS + \cdot\cdot\cdot \qquad (A1)$$

At thermodynamic equilibrium the fugacities of the components indicated in Equation (A1) are related by the equation:

$$\frac{(f_R)^r(f_S)^s \cdot\cdot\cdot}{(f_A)^a(f_B)^b \cdot\cdot\cdot} = K \qquad (A2)$$

where f_i ($i = A, B, \cdots R, S \cdots$) is the fugacity of component i, and K, known as the equilibrium constant, is a function only of temperature. If it is assumed that the behavior of the species present is in accordance with the laws of ideal solutions and gases, equation (A2) can be expressed as follows:

$$\frac{(x_R\pi/\Sigma x_i)^r(x_S\pi/\Sigma x_i)^s \cdot\cdot\cdot}{(x_A\pi/\Sigma x_i)^a(x_B\pi/\Sigma x_i)^b \cdot\cdot\cdot} = K \qquad (A3)$$

$i = A, B \cdot\cdot\cdot, R, S \cdot\cdot\cdot$

$$\text{or} \quad \frac{(P_R)^r(P_S)^s \cdot\cdot\cdot}{(P_A)^a(P_B)^b \cdot\cdot\cdot} = K \qquad (A4)$$

Where x_i is the number of moles of component i in the mixture, x_i is the total number of moles of gaseous components, π is the total pressure in atmospheres and P_i is the partial pressure of component i.

From general correlations concerning the compressibility factors and fugacities of gases it is estimated that at pressures below 1000 psia and temperatures above 2000°K the assumption of ideal behavior results in errors of less than 0.2 per cent in calculating volumetric behavior and of less than 0.5 per cent in calculating equilibrium concentrations. Although corrections can be made for variations from ideal behavior, the resulting gain in accuracy is small in comparison with the considerable increase in computational labor.

Allowance was made for the possible presence of the species CO_2, CO, H_2O, H_2, OH, H, O, O_2, NO, and N_2.

The following general expressions for the equilibrium constants were derived by the author from data given in, (1), and, (16).

$$\log K_1 + 9.339 \times 10^2\left(\frac{1}{T}\right) - 1.190 = 0 \qquad (A5)$$

$$\log K_3 + 17.906 \times 10^3\left(\frac{1}{T}\right) - 3.7075 = 0 \qquad (A6)$$

$$\log K_6 + 26.42 \times 10^3\left(\frac{1}{T}\right) - 6.105 = 0 \qquad (A7)$$

$$\log K_7 + 26.51 \times 10^3\left(\frac{1}{T}\right) - 6.564 = 0 \qquad (A8)$$

$$\log K_9 + 12.0 \times 10^3\left(\frac{1}{T}\right) - 3.199 = 0 \qquad (A9)$$

$$\log K_{10} + 15.042 \times 10^3\left(\frac{1}{T}\right) - 3.7368 = 0 \qquad (A10)$$

Where T = °K and K_1, K_3, etc., are the equilibrium constants corresponding to:

$$K_1 = \frac{P_{CO}P_{H_2O}}{P_{CO_2}P_{H_2}} = \frac{x_{CO}x_{H_2O}}{x_{CO_2}x_{H_2}} \qquad (A11)$$

$$K_3 = \frac{P_{NO}P_{H_2}}{P_{N_2}^{1/2}P_{H_2O}} = \frac{x_{NO}x_{H_2}(\pi)^{1/2}}{x_{N_2}^{1/2}x_{H_2O}(\Sigma x)^{1/2}} \qquad (A12)$$

$$K_6 = \frac{P_{O_2}P_{H_2}^2}{P_{H_2O}^2} = \frac{x_{O_2}x_{H_2}(\pi)}{x_{H_2O}^2(\Sigma x)} \qquad (A13)$$

$$K_7 = \frac{P_O P_{H_2}}{P_{H_2O}} = \frac{x_O x_{H_2}(\pi)}{x_{H_2O}(\Sigma x)} \qquad (A14)$$

$$K_9 = \frac{P_H}{P^{1/2}} = \frac{x_H(\pi)^{1/2}}{x_{H_2}^{1/2}(\Sigma x)^{1/2}} \qquad (A15)$$

$$K_{10} = \frac{P_{OH}P_{H_2}^{1/2}}{P_{H_2O}} = \frac{x_{OH}x_{H_2}^{1/2}\pi^{1/2}}{x_{H_2O}(\Sigma x)^{1/2}} \qquad (A16)$$

For a discussion of the accuracy of these equilibrium constants see (17, 19).

These equilibrium relationships combined with the mass balance equations, permit the setting up of a series of simultaneous equations establishing the concentrations of all constituents in the reaction products. These equations can be solved only by trial and error. For the initial trial values the graphical solutions shown in the charts of (3) were used. Hirschfelder's equilibrium constants were used by (3). The equilibrium compositions of the systems $\frac{C}{O} = 0.5$, $\frac{H}{O} = 0$, $\frac{N}{O} = 0$ and $\frac{C}{O} = 0.25$, $\frac{H}{O} = 1$, $\frac{N}{O} = 0$ at 3200°K and 300 psia were calculated from (3) and checked against the data in (1). The results checked in the first four significant figures. The equilibrium data presented here in Table A2 are believed to be accurate up to four significant figures.

As an example of the calculation of equilibrium compositions consider the case of the system $C + O_2$.

There are two elements (C and O) present and four components (CO, CO_2, O_2 and O). Therefore, we need two equilibrium relationships. These are provided by the reactions:

$$2O \rightarrow O_2 \tag{A17}$$

$$CO + \frac{1}{2}O_2 \rightarrow CO_2 \tag{A18}$$

$$\text{Then } K_A = \frac{p_{O_2}}{p_O^2} = \frac{x_{O_2}(\sum x)}{x_O^2 \pi} \tag{A19}$$

$$K_B = \frac{P_{CO_2}}{P_{CO}P_{O_2}^{1/2}} = \frac{x_{CO_2}(\sum x)^{1/2}}{x_{CO}x_{O_2}^{1/2}\pi^{1/2}} \qquad \text{(A20)}$$

where $$K_A = \frac{K_6}{K_7^2} \qquad \text{(A21)}$$

$$K_B = \frac{1}{K_1 K_6^{1/2}} \qquad \text{(A22)}$$

and $$x_{CO_2} + x_{CO} = 1 \qquad \text{(A23)}$$

$$2x_{CO_2} + 2x_{O_2} + x_O + x_{CO} = 2 \qquad \text{(A24)}$$

These yield:

$$\frac{2(1 + x_{CO})(\frac{1}{x_{CO}} - 1)^2}{\pi(K_B)^2 + (\frac{1}{x_{CO}} - 1)^2} + \frac{K_B(1 + x_{CO})(\frac{1}{x_{CO}} - 1)}{K_A^{1/2}(\pi(K_B)^2 + (\frac{1}{x_{CO}} - 1)^2)} - x_{CO} = 0 \qquad \text{(A25)}$$

which can be solved by trial and error, and

$$x_{O_2} = \frac{(1 + x_{CO})(\frac{1}{x_{CO}} - 1)^2}{\pi(K_B)^2 + (\frac{1}{x_{CO}} - 1)^2} \qquad \text{(A26)}$$

Then x_{CO_2} and x_O can be derived from (A23) and (A24) respectively.

In Table A2 the values of $y_i = \frac{x_i}{\sum x}$ are listed.

The method of generalizing enthalpy and entropy employed in (1), page 44, is used here.

The fictitious compositions appearing in Table A3 were determined as outlined on page 59 of (17).

The thermodynamic data appearing in Table A4 were taken from (4) and (16) but were reduced to the basis used in (1). Where necessary corrections were introduced so that they are consistent with the values used in (1), even though those values are not the latest and most accurate, as explained on page 69 of (1).

In general, the enthalpy of a mixture is

$$H_{mix} = \sum_i y_i H_i ,$$

and the entropy is

$$S_{mix} = \sum_i \left(y_i S_i - y_i \, R \ln \frac{P}{1} \right),$$

where i = general component
S = entropy
H = enthalpy
y = mole fraction
R = gas constant
P = partial pressure in atmospheres.

The vertical shift β of the entropy lines at 300 psia was derived, for each interpolation number, from the data in Table 13 of (1). Thus, the tie point of all interpolation numbers is seen to be at T = 2400°K and $S^r_{300} + \beta = 0.9550$, or $\beta = 0.9550 - S^r_{300}$ for any composition.

A plot of atomic composition versus β was made and the β's for the compositions studied here were derived from it and appear on Table A7.

The reduced data of Tables A5 and A6 appear graphically in Figures A1 and A2. The data for the 3000°K to 3200°K region of both figures were taken from (1).

The interpolation lines 0.1, 0.3, 0.5, 0.7 and 0.9 in both figures were fixed by interpolation. The region between 0.8 and 1.0 is most accurate in both charts.

The composition interpolation number plots as well as Figure 33 of (1), apply to and should be used concurrently with the corresponding extended charts in the Appendix.

It can be seen that the interpolation lines for atomic compositions containing hydrogen slope upwards more sharply at higher temperatures than the interpolation line 1.0 (for $C + O_2$) and therefore they intersect this line. This is a true representation of fact since it is much easier to raise the temperature of a carbon and oxygen system than it is to raise the temperature of a carbon, hydrogen and oxygen mixture because the latter system absorbs more energy by dissociation (i.e., there is more dissociation in the C-H-O mixture and that keeps the temperature down).

In Figure A1, the line which begins at the intersection of the T = 3850°K and H^r = 3.50 lines and which is given an atomic composition interpolation number of 0.87, is arbitrarily assumed to be the upper interpolation line in the range from 3850°K to 4000°K since the data for all the other mixtures studied fall below that line. Following this assumption, the 0.9 line is easily located by interpolation between the 0.87 and 1.0 lines.

In Figure A2, the line which begins at $T = 3710°K$ and $S^r + \beta = 1.212$ approximately and which is given an atomic composition interpolation number of 0.88, is arbitrarily assumed to be the upper interpolation line in the range from 3710°K to 4000°K, since the data for all the other mixtures studied fall below that line. Following this assumption, the 0.9 line is easily located by interpolation between the 0.88 and 1.0 lines.

Thus in both figures it was assumed that mixtures with atomic composition interpolation numbers above 0.87 (for H^r) and above 0.88 (for $S^r + \beta$) lie in the space between these lines and the 1.0 lines.

Since H^r_1 is calculated from heat of combustion data with an accuracy of five significant figures, a contraction of the H^r_{300} scale will not impair the accuracy of the determination of ΔH^r. For this reason and in order to make Figure 1 smaller the H^r_{300} scale was contracted by twofold. Thus the unit of the H^r_{300} scale is 0.02 and has a unit scale/(mean scale range) quotient, Q, of $\frac{0.02}{2.00} = 0.01$ whereas the unit of the temperature scale is 10°K, or $Q = \frac{10}{3500} \cong 0.003$. The same temperature scale was retained in all three Figures. In Figure A2 the $S^r_{300} + \beta$ scale has a unit of 0.002 and $Q = \frac{0.002}{1.150} \cong 0.002$, and in Figure A3 the $S^r_{300} + \alpha$ scale has a unit of 0.002 and $Q = \frac{0.002}{1.200} \cong 0.002$. Since each scale unit is large enough to permit reading a value of $\frac{1}{10}$ of it, and since all the scales except that of H^r_{300} have approximately the same Q, the same number of significant figures, namely four, can be read from each of the three scales. A fifth significant figure may be added in some cases without actually sinking into inordinate use of poetic license.

Figure 30, (1), yields $H^r_{14.7}$ to at least four significant figures and although the temperature scale of that plot is such that each scale unit represents 20°K, so that $Q = \frac{20}{2000} = 0.01$, the temperature can be read to four significant figures when use is made of a magnifying lens.

Although it is contrary to the theory of errors to derive results of more significant figures than justifiable by the least accurate data used, when there exist grounds for assuming that the error in the data (or in reading a plot) is in the same direction in all cases and when the relative rather than absolute magnitudes are sought, it is legitimate to vest with significance the first "doubtful" figure.

Suggestions for Improving the Accuracy of the Charts

The accuracy of the charts at the higher temperature ranges can be improved by making separate plots for the fuel-rich, stoichiometric and fuel-lean mixtures so that there would be only one mixture for each interpolation number. As the charts are constructed now, there exists a fuel-lean and a fuel-rich mixture for every interpolation number.

More compositions should be investigated and more accurate values for the thermodynamic functions and the equilibrium constants should be used.

Tie-points should be picked at higher temperatures even if that would mean providing more elaborate equilibrium composition data with the charts and postulating a more elaborate fictitious composition.

Analytical expressions for the atomic composition interpolation numbers should be developed or more accurate plots of the interpolation numbers should be constructed.

A continuous and unique function of the variables C-, H-, O-, and N-content should be developed <u>first</u> and that function should then be plotted on a Temperature-Enthalpy and Temperature-Entropy plane.

Accuracy of Extended Generalized Thermodynamic Charts

The extended charts presented here, although sufficient and accurate for the investigation of stoichiometric and fuel-rich mixtures of hydrocarbons or carbon and oxygen, are not based on a great enough wealth of equilibrium data to satisfy the author of their accuracy in the fuel-lean region, although random calculations have shown that they are certainly within 10 per cent of the truth in that region.

For mixtures containing nitrogen in a ratio of nitrogen to oxygen greater than 0.50, the charts are within 5 per cent of the truth in the 3200°K to 3600°K range and within from 5 to 10 per cent of the truth for the range from 3600°K to 4000°K.

TABLE A1

Compositions Corresponding to Interpolation Numbers Derived from the Graphs in Ref. 1

Reduced Enthalpy at 300 psia. Interpolation No.	Composition	Reduced Entropy at 300 psia. Interpolation No.
0	$C + O + 2N$	0
.2	$C_2H_6 + 4.120(O)$	.26
.4	$C_2H_6 + 5.990(O)$	.46
.6	$C_2H_6 + 6.500(O)$	.60
.8	$C_2H_6 + 6.775(O)$	.76
.84	$CH_4 + 4.0(O)$	.86
.87	$C_2H_6 + 7.0(O)$	.89
1.0	$C + 2O$	1.0

TABLE A2

Equilibrium Gas Compositions at 300 psia

	$C + O + 2N$				$C_2H_6 + 4.12(O)$			
	3400	3600	3800	4000	3400	3600	3800	4000
Y_{O_2}					.00196	.00475	.00843	.01225
Y_O					.00392	.00980	.02073	.03824
Y_{H_2}					.22598	.21569	.20907	.20000
Y_H					.04917	.07475	.11323	.15637
Y_{OH}					.02975	.04804	.06520	.08431
Y_{H_2O}					.30760	.27736	.22441	.17745
Y_{CO}	.5	.5	.5	.5	.32647	.32010	.31226	.30000
Y_{CO_2}					.05515	.04951	.04167	.03138
$Y_{CO}+Y_{CO_2}$					.38162	.36961	.35393	.33138
Y_{N_2}	.5	.5	.5	.5				

TABLE A2, CONT'D

	C_2H_6 + 5.99(0)				C_2H_6 + 6.5(0)			
	3400	3600	3800	4000	3400	3600	3800	4000
Y_{O_2}	.0333	.04534	.05319	.05392	.05343	.06372	.07304	.07157
Y_O	.01593	.03064	.05269	.07990	.02010	.03652	.06103	.09118
Y_{H_2}	.07451	.08971	.10049	.10980	.05858	.07402	.08456	.09510
Y_H	.02843	.04951	.07868	.11593	.02515	.04461	.07255	.10980
Y_{OH}	.06863	.09313	.11691	.12598	.07696	.10245	.12696	.14265
Y_{H_2O}	.41741	.35049	.27893	.20907	.41530	.34927	.27500	.20490
Y_{CO}	.21127	.22941	.23872	.25099	.18382	.20784	.22402	.22745
Y_{CO_2}	.15049	.11177	.08039	.05441	.16666	.12157	.08284	.05735
$CO+CO_2$	.36176	.34118	.31911	.30540	.35048	.32941	.30686	.28480

TABLE A2, CONT'D

	$C_2H_6 + 6.775(O)$				$CH_4 + 4(O)$			
	3400	3600	3800	4000	3400	3600	3800	4000
Y_{O_2}	.06520	.07745	.08309	.07990	.06995	.07966	.08333	.08039
Y_O	.02254	.03995	.06495	.09681	.02319	.04118	.06520	.09745
Y_{H_2}	.05250	.06627	.07819	.08873	.05588	.07255	.08799	.09926
Y_H	.02377	.04191	.06985	.10490	.02451	.04387	.07359	.11029
Y_{OH}	.08039	.10735	.12892	.14510	.08700	.11372	.13602	.15393
Y_{H_2O}	.41246	.34403	.27402	.20540	.45493	.38235	.30487	.22869
Y_{CO}	.17304	.20000	.21373	.22034	.14118	.16250	.17547	.18073
Y_{CO_2}	.17010	.12304	.08725	.05882	.14338	.10417	.07353	.04926
$CO+CO_2$	.34314	.32304	.30098	.27916	.28456	.26667	.24900	.22999

TABLE A2, CONT'D

	$C_2 + H_6 + 3.5O_2$				$C + O_2$			
	3400	3600	3800	4000	3400	3600	3800	4000
Y_{O_2}	.07931	.08701	.08897	.08725	.14755	.17010	.17990	.17500
Y_O	.02456	.04279	.06863	.10122	.03392	.05858	.09534	.14314
Y_{H_2}	.04652	.06172	.07549	.08407				
Y_H	.02245	.04005	.06814	.10270				
Y_{OH}	.08402	.10956	.12990	.14755				
Y_{H_2O}	.40354	.34137	.26961	.20294				
Y_{CO}	.16230	.18980	.21078	.21300	.32892	.39877	.45515	.49314
Y_{CO_2}	.17730	.12770	.08848	.06127	.48961	.37255	.26961	.18872
$CO+CO_2$	.33960	.31750	.29926	.27427	.81853	.77132	.72476	.68186

TABLE A3

Fictitious Compositions Corresponding to The Real Compositions Investigated

300 psia.

(Based on C-H-O-N-content of real compositions at corresponding temperatures.)

T, °K	3400	3600	3800	4000
$C + O + 2N$				
N_2	.5000	.5000	.5000	.5000
CO	.5000	.5000	.5000	.5000
$C_2H_6 + 4.120(O)$				
H_2	.25400	.24600	.23176	.22057
H_2O	.31843	.30841	.29913	.27650
CO	.29553	.28623	.27408	.25662
CO_2	.08609	.08338	.07985	.07476
$C_2H_6 + 5.990(O)$				
H_2	.05875	.05541	.05183	.04960
H_2O	.48389	.45636	.42683	.40850
CO	.12394	.11689	.10932	.10463
CO_2	.23782	.22429	.20979	.20077
$C_2H_6 + 6.50(O)$				
H_2	.02278	.02142	.01995	.01809
H_2O	.50294	.47270	.44034	.40911
CO	.06484	.06094	.05677	.05269
CO_2	.28564	.26847	.25009	.23190
$C_2H_6 + 6.775(O)$				
H_2	.01301	.01224	.01141	.01059
H_2O	.50170	.47232	.44006	.40815
CO	.02560	.02410	.02245	.02082
CO_2	.31754	.29894	.27853	.25334
$CH_4 + 4.0(O)$				
H_2O	.56912	.5334	.49800	.45998
CO_2	.28456	.26667	.24900	.22999

T, °K	3400	3600	3800	4000
$C_2H_6 + 7.0(O)$				
H_2O	.50940	.47625	.44889	.41140
CO_2	.33960	.31750	.29926	.27427
$C + 2.0(O)$				
CO_2	.81853	.77132	.72476	.68186

TABLE A4

The values of total enthalpy H and entropy S for the chemical species H, H_2, O, OH, H_2O, CO, N_2, O_2, and CO_2 are given below. These values are from references (1) and (4). The units of enthalpy are calories/g-mole and of entropy calories/g-mole °K, which equals BTU/16 mole °R. The values are based on a "dead" state of 0°K and products of complete combustion as described in Chapter 4 of reference (1). The thermodynamic functions are for the ideal gaseous state commonly used in physicochemical calculations. To convert calories/g-mole °K to BTU/lb-mole, multiply the former by 1.8000.

ENTHALPY

Temp., °K	3400	3600	3800	4000
H	97002	97934	98865	99796
H_2	83839	85627	87427	89235
O	75428	76360	77291	78222
OH	64940	66735	68535	70339
H_2O	38106	40851	43620	46409
CO	94776	96563	98360	100140
O_2	29358	31312	33282	35267
CO_2	45038	48116	51230	54382
N_2	27807	29580	31355	33130

ENTROPY

Temp., °K	3400	3600	3800	4000
H	39.50	39.81	40.11	40.41
H_2	49.584	50.105	50.609	51.102
O	50.580	50.89	51.19	51.49
OH	62.49	62.98	63.53	63.94
H_2O	70.20	70.96	71.67	72.32
CO	66.658	67.228	67.784	68.326
O_2	69.215	69.805	70.385	70.955
CO_2	81.904	82.834	83.744	84.634
N_2	64.895	65.390	65.865	66.305

TABLE A5

Reduced Enthalpy, H^r, versus Temperature, °K, at 300 psia.

Interpolation line*	H^r			
	3400	3600	3800	4000
0	1.4647	1.5582	1.6517	1.7452
.2	1.7885	2.0607	2.4303	2.9489
.4	2.0840	2.5077	2.9991	3.4807
.6	2.2430	2.6808	3.1986	3.7930
.8	2.3455	2.7779	3.2886	3.8851
.84	2.3872	2.8252	3.3402	3.9586
.87	2.4026	2.8530	3.3530	3.9684
1.0	2.4467	2.8607	3.3065	3.7629

---

*See Table A1 for corresponding compositions.

TABLE A6

Reduced Entropy, $S^r+\beta$, versus Temperature, °K, at 300 psia.

Interpolation Line*	3400	3600	3800	4000
0	1.0049	1.0134	1.0216	1.0294
.26	1.0522	1.0800	1.1123	1.1663
.46	1.0863	1.1331	1.1851	1.2426
.60	1.1065	1.1567	1.2123	1.2680
.76	1.1209	1.1701	1.2268	1.2833
.85	1.1217	1.1764	1.2299	1.2913
.88	1.1244	1.1810	1.2359	1.2940
1.00	1.1380	1.1853	1.2338	1.2813

---

*See Table A1 for corresponding compositions.

TABLE A7

Vertical Shift (β) of S_{300} lines versus Atomic Composition and Entropy Interpolation Numbers at 300 psia.

Atomic Comp.	$\frac{C}{O}$,	$\frac{H}{O}$,	$\frac{N}{O}$,	Interpolation No.	β
C + O + 2N	1	0	2	0	.0289
C_2H_6 + 4.120(O)	.485	1.456	0	.26	.0107
C_2H_6 +5.990(O)	.338	1.001	0	.46	.0100
C_2H_6 +6.500(O)	.3077	.923	0	.60	.0110
C_2H_6 +6.775(O)	.2952	.885	0	.76	.0115
CH_4 + 4(O)	.25	1.0	0	.86	.0130
C_2H_6 + 7(O)	.2857	.857	0	.89	.0104
C + 2(O)	.50	0	0	1.0	.0193

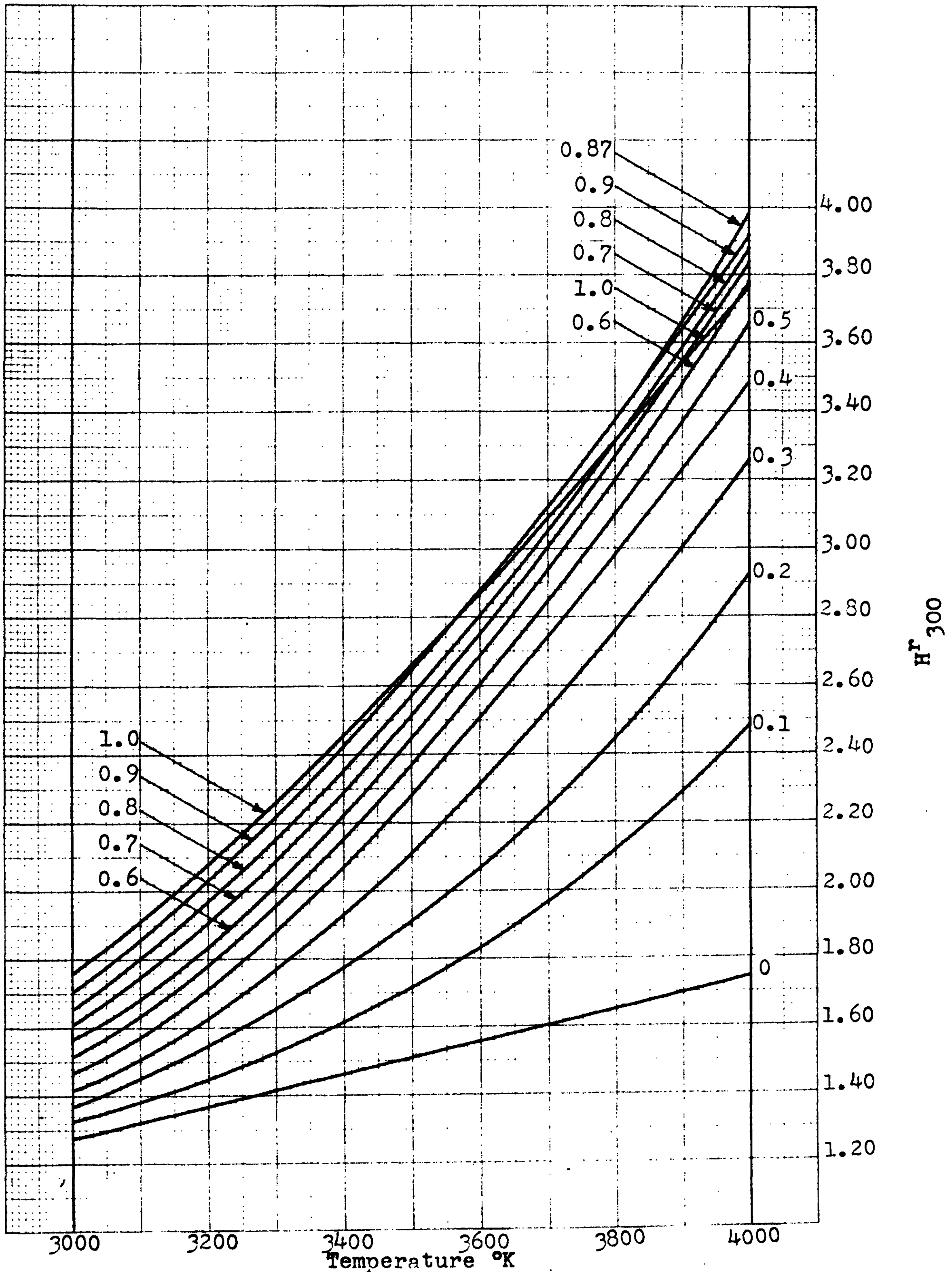

Figure A1. Generalized Temperature-Enthalpy Relation at 300 psia.

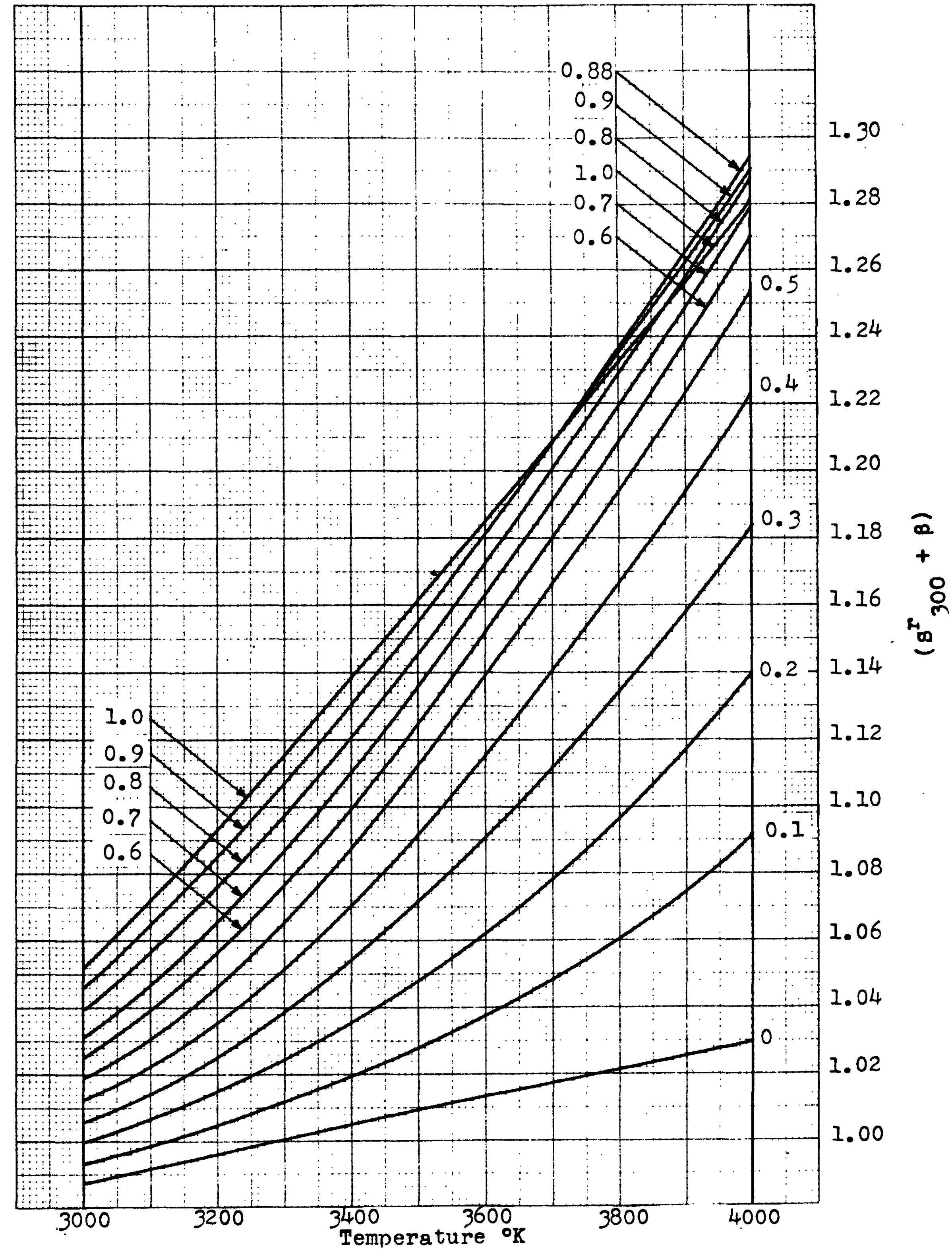

Figure A2. Generalized Temperature-Entropy Relation at 300 psia.

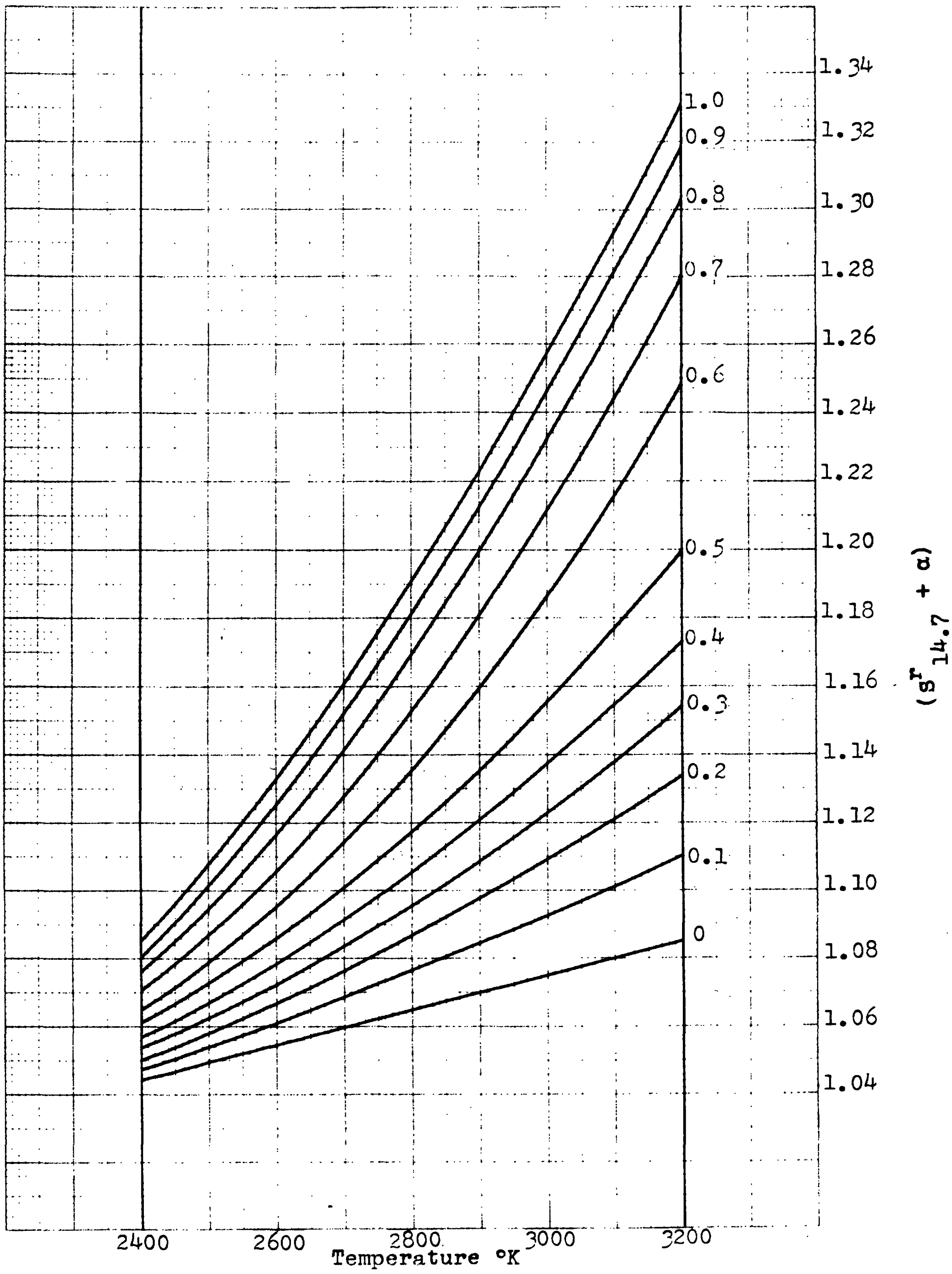

Figure A3. Generalized Temperature-Entropy Relation at 14.7 psia.

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