PERFORMANCE CALCULATIONS OF NEW PROPELLANT SYSTEMS

Thesis by

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SUMMARY

The purpose of this thesis is to investigate the effect on performance and chamber temperature of adding hydrogen to a propellant system. The systems investigated are:

(1) RFNA-Aniline

(2) Nitromethane

(3) Anhydrous hydrazene-liquid oxygen

Since a systematic investigation of the performance parameters of the RFNA-Aniline system over a wide range of mixture ratios has never been made, it was decided to make these calculations, in addition to the investigations stated above.

The results of the calculations can best be summarized by a study of the figures at the end of the thesis. A few generalizations can be made. The effect of adding hydrogen in small quantities to a high temperature system is to increase the performance considerably without too much change in the chamber temperature. As more hydrogen is added, the percentage decrease in chamber temperature is greater than the percentage increase in performance. If hydrogen is added in large quantities, both the performance curve (effective exhaust velocity) and the chamber temperature curve flatten out.

The behavior discussed above is characteristic of hot propellant systems such as RFNA-Aniline and anhydrous hydrazene. In a low temperature system, such as nitromethane, the effect is quite different. The addition of hydrogen in small quantities causes a rapid decrease in chamber temperature, but the increase in performance is considerably less on a percentage basis. As more hydrogen is added the changes in performance and chamber temperature are almost linear.

ACKNOWLEDGEMENT

The author is indebted to Dr. David Altman of the Chemistry Section, Jet Propulsion Laboratory, California Institute of Technology, for the use of his development of equations for calculating the composition of products of reaction, for the use of data prepared by him on the anhydrous hydrazine - liquid oxygen system, and for his valuable guidance in the formulation of this thesis.

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INTRODUCTION

One of the major problems in designing a liquid-propellant rocket motor today is high temperature. The problem can be dealt with principally in two ways: (1) by finding materials which can withstand the high temperatures encountered in a rocket motor, or, (2) by finding suitable means of cooling the motor. Progress has been made in solving this problem by both methods. It hardly seems possible, however, that materials will be found that will be able to withstand the temperatures encountered in the hotter propellant systems, and the problem has resolved itself, then, into one of finding better cooling methods.

Sweat and film cooling are both being developed to the point where it can almost be said that no propellant system is "too hot to handle". Hydrogen is perhaps the best gas that can be found to add to a propellant system, from the standpoint of performance, by virtue of its low molecular weight. In an over-all analysis, the extremely low density of hydrogen would be a serious disadvantage, except in very large rockets, where the density of the propellants is overshadowed by the specific impulse. Forgetting for the moment over-all rocket design and considering only the performance of a propellant system in the rocket motor, it is seen that the addition of hydrogen is useful in at least two ways: (1) it lowers the chamber temperature and (2) it increases the performance. It is most gratifying that recent experiments have shown that hydrogen is also one of the best gases for use as a sweat coolant.

It was decided, therefore, to investigate the effect on performance and chamber temperature of adding hydrogen to various propellant systems. The two systems of immediate importance were the RFNA-aniline system and the monopropellant, nitromethane. Since nitromethane is a cool propellant compared to the

RFNA-aniline system, an interesting comparison should be obtained of the effect of adding hydrogen. Both virtues of the hydrogen addition evidently can be exploited to a greater extent in a very hot propellant system; consequently, it was decided to make calculations on the anhydrous hydrazine-liquid oxygen system.*

Since a systematic investigation of the performance parameters of the RFNA-aniline system over a wide range of mixture ratios had never been made, it was decided to make these calculations before starting the analysis of hydrogen addition. The range of mixture ratios included in the analysis extends from 1.500 to 6.000; the stoichiometric mixture ratio is 4.171.

The body of the thesis is divided into four parts: the first part is a discussion of the assumptions that are made in the formulas that are used for the performance calculations, and also introduces the various parameters that are used in evaluating the merits of a propellant system; the second part is a development of the equations used to solve for the composition of the gas mixture, including the minor components, atomic oxygen and hydrogen, nitrous oxide, and hydroxyl ions; the third part is a sample calculation of the composition and of the performance for a stoichiometric mixture of RFNA-aniline with 1½ moles of hydrogen added; the fourth part is a presentation and discussion of the results obtained from an analysis of the three propellant systems, RFNA-aniline, nitromethane, and anhydrous hydrazine-liquid oxygen.

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*Calculated under the direction of Dr. David Altman by members of the Chemistry Section, Jet Propulsion Laboratory, California Institute of Technology, using the "frozen-composition" method of calculation of performance parameters.

EXPLANATION OF SYMBOLS

(The symbols are listed approximately in the order in which they appear in the text.)

a	Number of moles of hydrogen (H_2) in the products of reaction
b	Number of moles of water vapor (H_2O) in the products of reaction
c	Number of moles of carbon monoxide (CO) in the products of reaction
d	Number of moles of carbon dioxide (CO_2) in the products of reaction
e	Number of moles of oxygen (O_2) in the products of reaction
f	Number of moles of nitrogen (N_2) in the products of reaction
g	Number of moles of nitrous oxide (NO) in the products of reaction
h	Number of moles of hydroxyl ions (OH) in the products of reaction
i	Number of moles of atomic hydrogen (H) in the products of reaction
j	Number of moles of atomic oxygen (O) in the products of reaction
C	Number of gram atoms of carbon in the reactants
H	Number of gram atoms of hydrogen in the reactants
N	Number of gram atoms of nitrogen in the reactants
O	Number of gram atoms of oxygen in the reactants
K_n	Equilibrium constant based on the ratios of the number of moles
K_p	Equilibrium constant based on the ratios of partial pressures
K_1, K_2, K_3, etc.	Particular equilibrium constants based on the ratios of the number of moles of component gases in given reactions
A	An arbitrary coefficient defined by the sum $2C - O + H/2$

B	An arbitrary coefficient defined by the sum H + 2C - O
D	An arbitrary coefficient defined by the sum O - C - H/2
$\Delta H_{300}^{T^{o}K}$	Change in enthalpy between temperatures 300°K and T°K
$n^{T^{o}K}$	Number of moles of products of reaction at temperature T°K
$\overline{n}$	Average number of moles of products of reaction between temperatures T_c and T_e
T_c	Equilibrium chamber temperature in degrees Kelvin
T_e	Equilibrium exhaust temperature in degrees Kelvin
$\Delta H_{T_c}^{T_e}$	Enthalpy change between the equilibrium temperatures, T_c and T_e, and equal to $\Delta H_{300}^{T_c} - \Delta H_{300}^{T_e}$
$(\Delta H_{T_c}^{T_e})_T$	Apparent enthalpy change between the equilibrium temperatures, T_c and T_e, and equal to $\Delta H_{300}^{T_c} - \Delta H_{300}^{T_e} + \delta Q_f$
$\overline{\gamma}$	Value of the ratio of the average apparent specific heats between T_c and T_e
$\overline{C_p}$	Value of the average apparent specific heat at constant pressure between T_c and T_e
$\overline{C_v}$	Value of the average apparent specific heat at constant volume between T_c and T_e
R_u	Universal gas constant, equal to 1.986 cal/gram mole-°K
R_{gas}	Gas constant for a particular gas in cal/gram - °K
Q_f(reactants)	Heat of formation of the reactants in kcal, at 300°K
Q_f(products)	Heat of formation of the products of reaction in kcal, at 300°K
$Q_{av}^{T^{o}K}$	Heat available in kcal, at T°K, from the heat of chemical reaction
ΔT	An increment of temperature in °K
$\delta n_{T_c}^{T_e}$	Change in the number of moles of component gases during the adiabatic expansion from T_c to T_e
δQ_f(products)	Change in the value of the heat of formation of the products of reaction due to the change in composition, in kcal

P_e	Exhaust pressure of the nozzle in psia
P_c	Chamber pressure in psia
r	Mixture ratio. The ratio of the weight of oxidizer to the weight of fuel in a propellant system
J	Mechanical equivalent of heat = 4.187×10^7 ergs/cal
c	Effective exhaust velocity in ft/sec
c*	Characteristic velocity in ft/sec
I_{sp}	Specific impulse in lb-sec/lb
g	Acceleration due to gravity (arbitrarily chosen as 32.16)
RFNA	Red fuming nitric acid (in this thesis, nitric acid with 6.3% N_2O_4)
$\bar{M}$	Average molecular weight of chamber gases
C_F	Theoretical thrust coefficient

PART I

DISCUSSION OF ASSUMPTIONS AND INTRODUCTION OF PARAMETERS

Though this thesis is not concerned with the presentation of a derivation of the equations describing the flow through the combustion chamber and nozzle of a liquid-propellant rocket, it is well to recall the assumptions involved in their derivation, in order to keep in mind the limitations of these equations. The velocity of the gases in the chamber is of the order of 50 ft/sec in a rocket of conventional design. The exhaust velocity of the gases is of the order of 7000 ft/sec. Thus, the first assumption that is made is that the velocity of the gases in the chamber is negligible. The gas is further assumed to be non-viscous, which means that the flow is not complicated by frictional effects. By making the additional assumptions that the flow is steady, and that the expansion of the gas in the nozzle is an adiabatic expansion of a perfect gas, the two following equations may be written:

$$T/T_c = (p/p_c)^{\frac{\gamma-1}{\gamma}}$$

$$v = \left\{\frac{2\gamma R_g T_c}{\gamma-1}(1 - T/T_c)\right\}^{\frac{1}{2}}$$

The first equation is simply an expression of an adiabatic expansion process; the second is an expression for the velocity of the gas at any point in the nozzle. If the pressure, p, is atmospheric pressure, and T the exhaust temperature, then the particular value of v is called the effective exhaust velocity, c, which is one of the important parameters used in judging the merit of a propellant. It is assumed, therefore, that the gases are always expanded to atmospheric pressure. The remaining assumption is that there is no change in the gravitational potential energy of the gases.

Several other parameters are found useful in evaluating the merits of propellants. One is the specific impulse, I_{sp}, which may be defined as the pounds of thrust per pound of propellant consumed per second, and may be found from the equation, $I_{sp} = c/g$, the effective exhaust velocity divided by gravity's acceleration. Another parameter is the characteristic velocity, $c*$, which is defined by the equation, $c* = a_c/\Gamma'$ where Γ' is a rather complicated function of γ, the ratio of the specific heats, and a_c is the apparent velocity of sound in the chamber. This parameter will be discussed in greater detail later in the thesis. The ratio of the effective exhaust velocity to the characteristic velocity is equal to the theoretical thrust coefficient, $C_F = c/c*$, which is defined by the equation $F/p_c f_t$.

The assumptions discussed thus far have pertained primarily to the flow process of hot gases through the nozzle without mentioning anything about the chemical composition of these gases. It is assumed that the products of reaction of the propellants reach an equilibrium composition at the chamber temperature and pressure. As the gases expand through the nozzle, the temperature decreases continuously, which causes a change in the composition. It is also assumed that when the gases reach the exhaust temperature, they have the equilibrium composition for that temperature and pressure. The performance calculation of the propellants is based, then, on the average value of the thermodynamic properties of the gases in expanding from the chamber pressure to atmospheric. Performance calculations are sometimes based on the assumption that there is no change in composition during the expansion. In this method the composition at the equilibrium chamber temperature is found and frozen throughout the expansion process. Since the gases move through the combustion chamber and nozzle with considerable velocity, it is doubtful whether there is sufficient time for the equilibrium composition to be achieved; yet it is probably true that the composition is changing during the expansion, so that some kind of average value of the thermodynamic properties of the gas mixture should describe conditions more accurately than the values at the equilibrium chamber temperature. The actual performance probably lies somewhere between the values calculated by the two methods.

PART II

DEVELOPMENT OF THE EQUATIONS FOR SOLVING THE COMPOSITION OF THE PRODUCTS OF REACTION INCLUDING MINOR COMPONENTS

The derivation of these equations was first made by Dr. David Altman and Dr. Sidney Weinbaum of the Jet Propulsion Laboratory, and the development presented here is essentially that developed by them.

The products of reaction at high temperature will be assumed to be:

a = number of moles of hydrogen (H_2)
b = " " " " water (H_2O)
c = " " " " carbon monoxide (CO)
d = " " " " carbon dioxide (CO_2)
e = " " " " oxygen (O_2)
f = " " " " nitrogen (N_2)
g = " " " " nitrous oxide (NO)
h = " " " " hydroxyl ions (OH)
i = " " " " atomic hydrogen (H)
j = " " " " atomic oxygen (O)

The major components are nitrogen and the four gases involved in the water-gas equation, hydrogen, water, carbon monoxide, and carbon dioxide. The other five gases are the minor components. Oxygen may be considered a major component at high mixture ratios.

The problem involves, then, ten unknown quantities; in order to solve, ten equations must be found. It should be pointed out that if the propellant system being investigated contains hydrogen, carbon, oxygen, and nitrogen, we will have ten unknown gases for which to solve. If the system contains no nitrogen, however, the number is reduced to seven, and the problem is considerably simplified. Again, if the system contains no carbon, there are only eight unknown quantities.

Four equations can be obtained immediately by making a balance of atoms on each side of the reaction equation. If we let C, H, N, and O, denote the atoms of carbon, hydrogen, nitrogen, and oxygen, respectively, in the reactants, the reaction equation involving the ten unknown gases becomes,

$$C + H + N + O = aH_2 + bH_2O + cCO + dCO_2 + eO_2 + fN_2 + gNO + hOH + iH + jO$$

from which four equations can immediately be written,

$$c + d = C \tag{1}$$

$$2a + 2b + h + i = H \tag{2}$$

$$2f + g = N \tag{3}$$

$$b + c + 2d + 2e + g + h + j = O \tag{4}$$

The other six equations required can be obtained from six equations involving reactions and dissociations among the ten products:

$$CO_2 + H_2 = CO + H_2O \qquad (K_1) \tag{5}$$

$$\tfrac{1}{2}N_2 + H_2O = NO + H_2 \qquad (K_3) \tag{6}$$

$$2H_2O = 2H_2 + O_2 \qquad (K_6) \tag{7}$$

$$H_2O = H_2 + O \qquad (K_7) \qquad (8)$$

$$\tfrac{1}{2}H_2 = H \qquad (K_9) \qquad (9)$$

$$H_2O = OH + \tfrac{1}{2}H_2 \qquad (K_{10}) \qquad (10)$$

Table III is a list of equilibrium constants over a wide range of temperatures. The data were collected by Hirschfelder, Curtis, McClure, and Osborne and presented in O.S.R.D. Report No. 547. The designations used for the equilibrium constants are those given in Table III. Denoting by K_1, then, the equilibrium constant for the fifth equation, K_3 for the sixth, K_6 for the seventh, K_7 for the eighth, K_9 for the ninth, and K_{10} for the tenth, the remaining six equations are readily obtained. It should be noted, however, that the equilibrium constants given in Table III express the ratios of the partial pressures of the gases. Since we are working with moles of gases, it is necessary to convert the constants given to a form in terms of moles. This can be accomplished by the following formula. For instance, if K_p is the equilibrium constant for the reaction

$$aA + bB = cC + dD$$

then,

$$Kn = K_p \ (n/p)^{c+d-a-b} \quad .$$

Then the relations involving these six equilibrium constants are:

$$K_1 = bc/ad$$

$$K_3 = ga/f^{\frac{1}{2}}b$$

$$K_6 = a^2e/b^2$$

$$K_7 = aj/b$$

$$K_9 = i/a^{\frac{1}{2}}$$

$$K_{10} = ha^{\frac{1}{2}}/b$$

A scrutiny of the ten equations shows that six of the unknown quantities can be expressed in terms of a and b:

$$\left.\begin{array}{ll} c = \dfrac{C}{1 + b/K_1 a} & d = \dfrac{bC}{b + K_1 a} \\[2ex] e = b^2\ K_6/a^2 & h = b\ K_{10}/a^{\frac{1}{2}} \\[2ex] j = b\ K_7/\ a & i = a^{\frac{1}{2}}\ K_9 \end{array}\right\} \qquad (11)$$

The two other unknown quantities, f and g, are expressed as a function of each other.

$$f = \tfrac{1}{2}\ (N-g) \qquad (12)$$

Using these relations, equation (4) becomes

$$b + \frac{C}{1 + b/K_1 a} + \frac{2bC}{b + K_1 a} + 2b^2\ K_6/a^2 + g + b\ K_{10}/a^{\frac{1}{2}} + b\ K_7/a = O$$

and (2) becomes

$$2a + 2b + b\ K_{10}/a^{\frac{1}{2}} + a^{\frac{1}{2}}\ K_9 = H$$

or, solving for b

$$b = \frac{H - 2a - a^{\frac{1}{2}}\ K_9}{2 + K_{10}/\ a^{\frac{1}{2}}} \qquad (I)$$

and solving (4) above for g,

$$g = O - C\,\frac{(K_1 a + 2b)}{K_1 a + b} - b\ (1 + K_{10}/a^{\frac{1}{2}} + K_7/a) - 2K_6\ b^2/a^2 \qquad (II)$$

The remaining independent relations are

$$f = \tfrac{1}{2}(N-g)$$

and

$$f = g^2 a^2/g^2 K_3^2$$

or eliminating f,

$$2g^2a^2/b^2K_3^2 + g - N = 0 \qquad \text{(III)}$$

Now it can be seen that all of the unknown quantities can be found if the proper values of "a" and "b" can be found. The procedure, then, to be followed is outlined below:

(1) Estimate the chamber temperature to the nearest 100°K.

(2) Estimate the total number of moles (using water-gas relation, for instance) and find the values of K_1, K_3, etc., for the pressure in which interested.

(3) Estimate the number of moles of hydrogen, "a".

(4) Calculate the corresponding value of "b" from equation (I).

(5) Calculate the corresponding value of "g" from equation (II).

(6) Substitute these values of "a", "b", and "g" into equation (III).

(7) Repeat the calculations, based on a new value of "a", so chosen that equation (III) will equal zero. If equation (III) is greater than zero, "g" is too large (if positive) and a lower value of "a" should be chosen. If "g" is negative, "a" is too small and a larger value should be chosen.

PART III

SAMPLE CALCULATION FOR A STOICHIOMETRIC MIXTURE OF RFNA AND ANILINE WITH ONE AND A HALF MOLES OF HYDROGEN ADDED

In order to illustrate this method of calculating minor components, and also to show how the performance parameters are calculated, a sample calculation is presented below. The calculation is made on a stoichiometric mixture of the RFNA-Aniline system with three halves moles of hydrogen added.

The reactants are given in the following proportions:

$$HNO_3 + .050\ N_2O_4 + .174\ C_6H_5NH_2 + 3/2H_2 \longrightarrow \text{ten gaseous products}$$

Since the values of the heats of formation and the values of the equilibrium constants are known in three and at best four significant figures, the accuracy of our calculations is limited by these values. Working with four significant figures, permits, in general, the number of moles of a constituent to be calculated to the nearest thousandths of a mole.

The reactants above represent a combined weight of 86.85 grams and the number of atoms can be found to be,

$C = 1.045 \qquad N = 1.274 \qquad O = 3.200 \qquad H = 5.219$

The heat of formation of these reactants is $Q_f = 39.99$ kcal.

Assume the chamber temperature to be $T_c = 3000^\circ K$, the total number of moles to be 4.2, and the chamber pressure to be 300 psi, or 20.41 atmospheres. A reasonable estimate of the total number of moles can be made either by the use of the water-gas equilibrium, or by finding the number of moles of N_2, H_2O, CO, and H_2 that can be formed from the number of atoms of C, N, H, and O available. Estimates obtained in this manner are very close to the actual number of moles. Then the values of the equilibrium constants are found from Table III.

	K_1	K_3	K_6	K_7	K_9	K_{10}	n/p	$(n/p)^{\frac{1}{2}}$
K from Table III	7.582	0.005479	0.001983	0.005336	0.1579	0.05290	0.2058	0.4537
K_n in terms of moles	7.582	0.002436	0.0004031	0.001098	0.07164	0.02400		

Now assume "a" to be 0.723; then, from equation (I), "b" can be found to be 1.830, and solving equation (II) yields $g = 0.004$. Putting these values into equation (III) yields $F(III) = -0.462$. Since equation (III) is less than zero, "a" is too low, so try "a" = 0.724. If this is carried out, $F(III) = +0.558$, which is not as near to zero as the value for $a = 0.723$. Thus it is seen that within our limits of accuracy, $a = 0.723$ is the correct solution.

Now all the other components can be found from the equations previously derived (see page 11, equations (11) and (12)):

$c = 0.783$ $d = 0.261$ $e = 0.003$ $f = 0.635$

$h = 0.052$ $i = 0.061$ $j = 0.003$

The values of the change in enthalpy from 300°K to 3000°K, ΔH_{300}^{3000}, can now be found by use of Table IV, as well as the heat of formation of the products of reaction, Q_f(products), and a table of values constructed. The value of ΔH_{300}^{3000} is given by,

$$\Delta H_{300}^{3000} = \sum_i n_i \Delta H_i$$

and, the value of the heat of formation of the products and of the reactants, by,

$$Q_f = \sum_i n_i Q_{f_i}$$

TABLE I

	n^{3000}	ΔH_{300}^{3000}	Q_f(products)	n^{2900}	ΔH_{300}^{2900}	Q_f(products)
a	0.723	15.30		0.725	14.70	
b	1.830	55.48	105.77	1.844	53.44	106.58
c	0.783	17.50	21.02	0.777	16.68	20.86
d	0.261	9.58	24.65	0.268	9.44	25.31
e	0.003	0.07		0.001	0.02	
f	0.635	14.08		0.636	13.54	
g	0.004	0.09	-0.09	0.003	0.06	-0.06
h	0.052	1.12	-0.48	0.035	0.72	-0.33
i	0.061	0.82	-3.17	0.045	0.58	-2.34
j	0.003	0.04	-0.18	0.001	0.01	-0.06
	4.355	114.08	147.52	4.335	109.19	149.96
			-39.99			-39.99

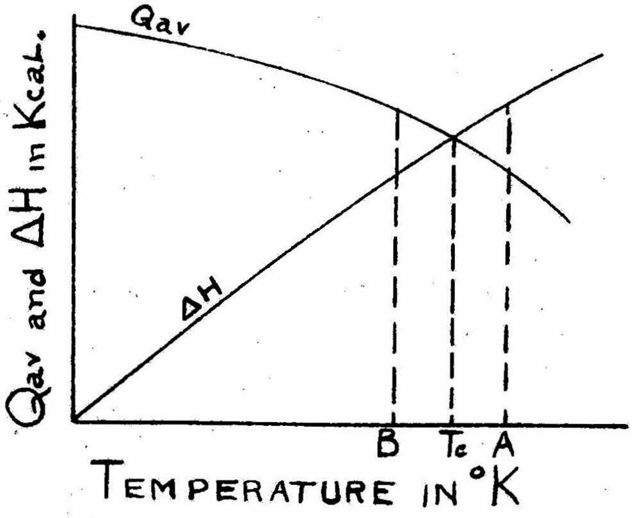
Q_{av} = 107.53 kcal $\qquad$ Q_{av} = 109.97 kcal

where the value of Q_{av}^{3000} has been computed from the relation:

$$Q_{av}^{3000} = Q_f(\text{products}) - Q_f(\text{reactants}) = 107.53 \text{ kcal.}$$

Now, in order to determine whether the next estimate of the chamber temperature should be higher or lower than the original estimate, refer to Figure 1.

FIGURE 1.



Since the value of Q_{av}^{3000} is less than the value of ΔH_{300}^{3000}, a point on Figure 1 corresponding to "A" has been assumed, and the next estimate should be lower than 3000°K.

Now, assuming the chamber temperature, T_c, to be 2900°K, and carrying out a procedure exactly similar to the one just carried out for 3000°K, a table of values can be prepared for the assumed value of 2900°K. Tabulating the values of the number of moles of each gaseous component, the change in enthalpy, and the heat of formation of the products of reaction, it is seen that the value of Q_{av}^{2900} is found to be 109.97 kcal (see Table I).

The actual chamber temperature is found by determining where the heat available is exactly equal to the total change of enthalpy. Thus T_c is found by a linear interpolation,

$$Q_{av}^{2900} + \Delta T/100\,(Q_{av}^{3000} - Q_{av}^{2900}) = \Delta H_{300}^{2900} + \Delta T/100\,(\Delta H_{300}^{3000} - \Delta H_{300}^{2900})$$

solving, $\Delta T = 11^\circ$ and $T_c = 2911^\circ K$.

Having found the equilibrium chamber temperature, the object now is to find what the temperature will be after the gas has expanded through a nozzle. Considering the expansion process to be adiabatic, the exhaust temperature can be expressed as a function of the chamber temperature, the chamber pressure, the exit pressure, and the average value of the ratio of the specific heats, $\bar{\gamma}$. Then, assuming that the exit pressure is atmospheric, the equation can be written,

$$T_e = T_c\,(p_e/p_c)^{\frac{\bar{\gamma}-1}{\bar{\gamma}}} = T_c\,(14.70/300.0)^{\frac{\bar{\gamma}-1}{\bar{\gamma}}}$$

During the expansion process the temperature decreases continuously and therefore, assuming that equilibrium is always achieved, the gas composition is constantly changing. If the exit temperature is estimated, and the equilibrium gas composition computed for this assumed temperature, an average value of the ratio of specific heats, $\overline{\gamma}$, can be found, with which the exit temperature can be computed. Thus, by a process of successive approximation, the exact exhaust temperature can be found.

Assume, then, the exhaust temperature, T_e, to be 1700°K. Since there are no minor components below 2000°K, within the limits of our accuracy, the components of the gas mixture can be computed by means of equation (5), the water-gas equilibrium. A general solution of this equation can be written,

$$(K-1)\ a^2 + (KD + B) - H/2 = 0$$

where $A = 2C - O + H/2$, $B = H + 2C - O$, and $D = O - C - H/2$. For the temperature assumed and for the reactants under consideration,

$A = 1.500 \quad B = 4.109 \quad D = -0.455$ and $K_1 = 3.555$

and the solution to the simple quadratic equation is,

$a = 0.843 \quad b = H/2 - a = 1.767 \quad c = A - a = 0.657$

$d = D + a = 0.388$ and $f = N/2 = 0.637.$

A table of values can then be formed:

TABLE II

	n^{2911}	n^{1700}	ΔH_{300}^{1700}	δn_{2911}^{1700}	δQ_f(prod)	n^{1800}	ΔH_{300}^{1800}	δn_{2900}^{1800}	δQ_f(prod)
a	0.725	0.843	8.62	-	-	0.824	9.08	-	-
b	1.842	1.767	24.42	-0.075	-4.34	1.786	26.80	-0.056	-3.24
c	0.778	0.657	7.21	-0.121	8.18	0.676	8.00	-0.102	6.90
d	0.267	0.388	6.82	0.121		0.369	7.02	-0.102	
e	0.001	-	—	-	-	-	-	-	-
f	0.636	0.637	6.91	-	-	0.637	7.46	-	-
g	0.003	-	-	-0.003	0.06	-	-	-0.003	0.06
h	0.037	-	-	-0.037	0.34	-	-	-0.037	0.34
i	0.047	-	-	-0.047	2.44	-	-	-0.047	2.44
j	0.001	-	-	-0.001	0.06	-	-	-0.001	0.06
	4.337	4.292	53.98		6.740	4.292	58.36		6.56

The various columns are computed as follows:

n^{2911}	The number of moles of each component at 2911°K, the computed chamber temperature, is found by interpolation between the values found for 2900°K and 3000°K.
n^{1700}	The number of moles of each component at 1700°K, the estimated exhaust temperature, is found by use of the water-gas equilibrium.
ΔH^{1700}_{3000}	The change in enthalpy from 300°K to 1700°K for each component is found by multiplying the number of moles by the ΔH^{1700}_{300} per mole given in Table IV.
δn^{1700}_{2911}	The change in the number of moles of each component in going from 2911°K to 1700°K.
δQ_f(prod)	The heat which appears during the expansion process as a result of the disappearance of minor components is found by multiplying the change in the number of moles, δn^{1700}_{2900}, by the heat of formation of the component.

Having all of these values, it is now possible to calculate the apparent enthalpy change during the process of expansion. This apparent enthalpy change represents the change in energy available to produce an effective exhaust velocity. It can be found from the following relation:

$$\left(\Delta H^{1700}_{2900}\right)_T = \Delta H^{2911}_{300} + \delta Q_f(\text{prod}) - \Delta H^{1700}_{300}$$

where ΔH^{2911}_{300} can be found by a linear interpolation between the values found for 2900°K and 3000°K,

$$\Delta H^{2911}_{300} = \Delta H^{2900}_{300} + \Delta T \left(\Delta H^{3000}_{2900} \right) = 109.73 \text{ kcal}$$

then solving,

$$\left(\Delta H^{1700}_{2911}\right)_T = 62.500 \text{ kcal}$$

The average apparent value of the specific heat at constant pressure, $\bar{C}_p$, can then be found by dividing the apparent enthalpy change by the average number of moles, $\bar{N}$, and by the temperature change from T_c to T_e ,

$$\bar{C}_p = (\Delta H^{1700}_{2911})_T \Big/ \bar{N}\,(T_c - T_e) = 11.962$$

and the average apparent value of the specific heat at constant volume, $\bar{C}_v$, from

$$\bar{C}_v = \bar{C}_p - R_u = 9.976$$

where R_u is the Universal Gas Constant equal to 1.986 cal/gram mole degree Kelvin. The average value of gamma is simply the ratio of these two,

$$\bar{\gamma} = \bar{C}_p/\bar{C}_v = 1.199 \quad \text{and} \quad \frac{\bar{\gamma}-1}{\bar{\gamma}} = 0.1660.$$

Then the exhaust temperature, T_e, is found from the equation,

$$T_e = T_c\,(p_e/p_c)^{\frac{\bar{\gamma}-1}{\bar{\gamma}}} = 1764°K$$

Now assume the value of the exhaust temperature to be 1800°K and make precisely the same calculations that have just been made for T_e = 1700°K. By a process of linear interpolation for values of $\Delta H^{2911}_{T_e}$ and δQ_f(prod), then, the exact exhaust temperature can be found using successive approximations. Ordinarily only three approximations are necessary, since the value of the ratio of the specific heats does not vary much in a one-hundred-degree temperature interval. It should be noted here that this method of approximation is not unduly long if the chamber temperature is less than 2000°K, since only the water-gas equation must then be solved. If, however, the exhaust temperature is appreciably higher, and minor components still appear, the calculations are extremely long and tedious.

The object of the preceding calculations have been to obtain two important values, the apparent enthalpy change between chamber temperature and exhaust, $(\Delta H_{T_c}^{T_e})_T$, and the average value of the ratio of the specific heats, $\overline{\gamma}$, for it is now possible to calculate the following important parameters of the propellants: the effective exhaust velocity, c; the specific impulse, I_{sp}; the characteristic velocity, c*; and the theoretical thrust coefficient, C_F.

$$c = 0.03281 \left[2J(\Delta H_{T_c}^{T_e})_T / M\right]^{\frac{1}{2}} = 7841 \text{ ft/sec}$$

$$I_{sp} = c/g = 243.8 \text{ sec}$$

$$c^* = a_c/\Gamma' = 5546 \text{ ft/sec}$$

where J is the mechanical equivalent of heat, a conversion factor to convert from kcal to ergs, equal to 4.186×10^{10} and 0.03281 converts cm/sec to ft/sec; g is the acceleration due to gravity taken as 32.16 ft/sec^2; M is the mass of the reactants; a_c is the apparent velocity of sound in the chamber; Γ' is a function of the average ratio of specific heats,

$$\Gamma' = \overline{\gamma} \left(\frac{2}{\overline{\gamma} + 1} \right)^{\frac{\overline{\gamma} + 1}{2(\overline{\gamma} - 1)}} = 0.7090.$$

The apparent velocity of sound in the chamber may be found from the following expression:

$$a_c = (\overline{\gamma} R_{gas} T_c)^{\frac{1}{2}} = (\overline{\gamma} R_u T_c / \overline{M})^{\frac{1}{2}} = 3932 \text{ ft/sec}$$

where $\overline{M}$ is the average molecular weight of the products of reaction. The expression "apparent velocity of sound in the chamber" is used, for want of a better term, to distinguish this quantity from the actual velocity of sound at the chamber temperature, which would be found from the expression:

$$a = (\gamma_c R_{gas} T_c)^{\frac{1}{2}}$$

where γ_c is the ratio of the specific heats at the chamber temperature. Since $\gamma_c \neq \bar{\gamma}$, the velocity required for the calculation of c* is rather difficult to give a name, but varies with the actual velocity of sound at the equilibrium chamber temperature as the ratio, $(\gamma_c / \bar{\gamma})^{\frac{1}{2}}$.

PART IV

DISCUSSION OF RESULTS

A. RFNA-Aniline System

The analysis of the RFNA-aniline system, by the method discussed in Part II, over a range of mixture ratios from 1.5 to 6.0, yields several interesting features. The acid used in the analysis is red fuming nitric acid with 6.8% N_2O_4 by weight. The aniline is presumed to be pure. The value of the heat of formation of aniline used in this analysis is -6.11 kcal per gram mole. A more accurate value would have been -4.55, based on the value of the heat of combustion of aniline reported by C. M. Anderson and E. C. Gilbert.* The effect on performance and chamber temperature of an error in the value of the heat of formation of aniline is shown by the data presented in Table X. The error in chamber temperature due to an error of 5.89 kcal/gram mole in the heat of formation of aniline is found to be only one half of one percent at a mixture ratio of 2.8. At higher mixture ratios the error will be even less, since less aniline enters the reaction at higher mixture ratios. The error in performance is less than the error in chamber temperature. Assuming, then, that the value used was in error by 34% (1.56 kcal/gram mole), the error in chamber temperature may be assumed to be less than two tenths of one percent, at mixture ratios above 2.8, which is certainly negligible.

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*Journal of the American Chemical Society, Volume 64 (1942) page 2371.

Table V is a tabulation of the results obtained, and Figures 2, 3, and 4 are a graphical presentation of these results. Figure 2 shows how the average value of the specific heat at constant pressure, $\overline{C}_p$, increases as stoichiometric is approached from either side. This is due to the increase in the triatomic components, principally CO_2 and H_2O, which have a higher value of C_p than the other components. Since the next highest value of C_p is that of O_2, the curve drops more slowly for mixture ratios above stoichiometric, where O_2 is in excess. Since $\overline{\gamma}$ is simply the ratio of the specific heats, it reaches a minimum where the $\overline{C}_p$ is a maximum. The average molecular weight of the gas mixture, $\overline{M}$, increases with mixture ratio, as would be expected, since the heavier components predominate as the mixture ratio increases.

Shifting attention to Figure 3, now, it is seen that the chamber temperature does not reach a maximum value at stoichiometric, as one might expect. The maximum occurs on the under-oxidized side, somewhere in the vicinity of a mixture ratio of 3.7. The highest temperature will be reached in the chamber when a certain composition of gases exists such that the Q_{av} and the C_p have the optimum value. Another way of saying this is that as the mixture ratio decreases from stoichiometric to that at maximum T_c, the value of C_p decreases faster than the value of Q_{av} decreases, and the optimum values occur at a mixture ratio lower than stoichiometric. The same result was obtained in a subsequent calculation; when $\frac{1}{2}$ mole of H_2 was added to a stoichiometric mixture of RFNA-aniline, the temperature was found to increase again, showing that the maximum temperature occurs on the under-oxidized side.

Figure 4 shows the effect of mixture ratio on performance. The maximum effective exhaust velocity, c, occurs at a mixture ratio of about 3.6, a ratio slightly less than the ratio for maximum T_c. Since the average molecular weight of the products, $\overline{M}$, decreases more rapidly than T_c with decreasing mixture ratio in this region, $(T_c/\overline{M})^{\frac{1}{2}}$, which varies directly as c, should reach a maximum at a ratio slightly less than the maximum for T_c. It must be remembered that c also varies with the ratio of specific heats, $\widetilde{\gamma}$, in a rather complicated manner. This dependence will be discussed later in the thesis. Since the curve is very flat in this region, the behavior discussed above is probably only of academic interest. As a matter of fact, probably the most interesting feature of this particular analysis is that the curves c versus r, and T_c versus r, are very flat in the region between 3.0 and 4.5.

B. Addition of H_2 to a Stoichiometric Mixture of RFNA-Aniline

Figure 5 shows the effect on c and T_c of adding H_2 to the RFNA-aniline system at stoichiometric mixture ratio. As previously alluded to, the value of T_c is higher on the slightly under-oxidized side, as evidenced by the maximum in the T_c curve at about ½ mole of H_2 added. It is interesting to note the scales, liquid H_2 added by weight, and liquid H_2 added by volume. If ½ mole of H_2 is added, for instance, the performance is increased 4.1% and T_c is increased 0.9%. If one mole of H_2 is added, the performance is increased 6.5% and T_c is decreased about 1.2%. It should be noted that 1 mole of H_2 amounts to almost 50% of the total volume of propellants, and 4½% of the total weight. Since T_c is not decreased appreciably, even by this much addition of H_2, it might seem that this procedure is of little help toward solving the high temperature problem in rocket motor design. However, it is assumed that H_2 is added by sweat or film cooling through a porous wall; then the magnitude of T_c is no longer of primary importance, for, if the cooling system functions properly, the chamber walls are protected by the film of coolant, through which the temperature gradient is extremely high, and the wall temperature is reduced to a range well within the present-day design limits. It is conceivable that an effective propellant system can be designed using the RFNA-aniline system simply as a means of heating hydrogen to a high temperature. For instance, if three fourths of the volume of propellants carried were hydrogen, a theoretical c of 8223 ft/sec could be realized, which is a 13.4% increase in performance over the acid-aniline system at stoichiometric. Since the theoretical T_c would be only 1607°C, it would no longer be necessary to use the expedient of cooling the chamber at all, if suitable means could be devised to mix the propellants thoroughly to prevent the possibility of local hot spots in the chamber. It seems that such a propellant scheme would be admirably suited to the liquid oxygen-liquid hydrogen propellant system if the technical skill in handling liquid oxygen and particularly liquid hydrogen reaches the stage where such a propellant system becomes feasible.

C. The Addition of Hydrogen to Nitromethane

Figure 6 shows the effect of adding H_2 to the comparatively cool propellant, nitromethane. The most outstanding feature in the curve is that the sharp increase in performance noticed in the RFNA-aniline system is not present. Both the T_c and the c curve have almost a linear relation with the number of moles of H_2 added. Discussing, as before, the addition of $\frac{1}{2}$ mole of H_2, it is seen that the decrease in T_c is 9.6% while the increase in performance is only 1.2%. For 1 mole of H_2 added the T_c decreases 17.4% while the performance increase is 2.1%. The effect of adding H_2 to a cool propellant system, then, is a great decrease in T_c, but not much increase in performance.

D. The Addition of Hydrogen to the Anhydrous Hydrazine-Liquid Oxygen System

Figure 7 shows the effect on T_c and c of adding H_2 to a stoichiometric mixture of anhydrous hydrazine and liquid oxygen. These curves were drawn from data computed by members of the Chemistry Section of JPL, under the direction of Dr. David Altman. The calculations were made by a "frozen composition" method, that is, by assuming that the composition of the gas mixture does not change during the expansion process. This approximation involves considerable error when comparing results with those obtained by this method, especially at high chamber temperatures, since the additional heat available due to the disappearance of minor components during expansion down the nozzle, which is neglected in the frozen composition method, is appreciable.* Consequently, this difference in assumptions must be borne in mind when making comparisons with this system. Referring to Figure 7, it is seen that the two curves presented there have approximately the same shape as those in Figure 5, drawn for the RFNA-aniline system. This is to be expected since the stoichiometric chamber temperatures are of the same order of magnitude in the two cases. In general, the results obtained from these calculations show better performance than was found in the case of the RFNA-aniline system. This must be taken with a grain of salt, however, even though the hydrazine system has the higher T_c, since it can be deduced from consideration of the average molecular weight of the products of reaction, that the addition of H_2 to RFNA-aniline (average molecular weight of products at stoichiometric is 23.38) should have a greater effect in increasing performance than in the hydrazine system (average molecular

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*In the case of the calculation of T_c and c of the RFNA-aniline system at stoichiometric mixture ratio, the value of the enthalpy change between T_c and T_e was found to be 43.95 kcal while the value of the change in heat due to the disappearance of minor components during expansion was found to be 23.07 kcal.

weight of the products of reaction at stoichiometric is 19.7). The calculations show a 5.1% increase in performance and an 0.8% decrease in T_c, with the addition of $\frac{1}{2}$ mole of H_2, and an 8.5% increase in performance and a 3.6% decrease in T_c, with the addition of 1 mole of H_2.

CONCLUSIONS

Figures 8 and 9 show the comparative results obtained from an analysis of the three systems. Though it is appreciated that generalizations concerning the effects of this treatment of hydrogen addition should not be made without the advantage of considerably more information on a variety of systems, it is believed that the following conclusions are justified by the results at hand. The effect of adding hydrogen in small quantities to a high temperature system is to increase the performance considerably without too much change in the chamber temperature. This change is caused principally by a lowering of the average molecular weights of the products of reaction, without disturbing the equilibrium composition enough to cause a proportionate change in the heat available, Q_{av}. As more hydrogen is added the composition is altered in such a manner as to decrease the Q_{av} sufficiently to cause a greater decrease in T_c than the increase in performance, on a percentage basis. As more hydrogen is added both the T_c and c curves begin to flatten out.

The effect is quite different in a low temperature system such as nitromethane. The addition of hydrogen in small quantities causes a rapid decrease in T_c. This rapid decrease in T_c also tends to counterbalance the effect of the decrease in average molecular weight, resulting in a lesser increase in performance than is found in a hotter system where the decrease in T_c is not so sudden. The effect can be calculated almost entirely from the water-gas equilibrium, since the dissociations into minor components at a temperature below 2500°K are already quite small (T_c for nitromethane is 2452°K). The average molecular weight of the products is 20.3 at T_c, so the addition of hydrogen certainly causes a reduction; however, since the performance varies as the quantity $(T_c / \overline{M})^{\frac{1}{2}}$ (neglecting the effect of $\overline{\gamma}$ for the moment) the decrease in T_c tends to negate the effect of the decrease in $\overline{M}$.

The subject would not be complete without discussing the effects of a change in the average apparent specific heat at constant pressure, $\overline{C}_p$, and the ratio of the specific heats, $\overline{\gamma}$. The equation for c can be expressed in terms of $\overline{\gamma}$, T_c, and T_e ,

$$c = \sqrt{\frac{2\,\overline{\gamma}}{\overline{\gamma}-1} R\, T_c \left(1 - \frac{T_e}{T_c}\right)^1} = \sqrt{\frac{2\,\overline{\gamma}}{\overline{\gamma}-1} R\, T_c \left[1 - (p_e/p_c)^{\frac{\overline{\gamma}-1}{\overline{\gamma}}}\right]}$$

where $\left[1 - (p_e/p_c)^{\frac{\overline{\gamma}-1}{\overline{\gamma}}}\right]$ may be called the ideal thermodynamic efficiency. It is seen that the larger the value of $\overline{\gamma}$, the larger the value of the ideal thermodynamic efficiency. On the other hand, the lower the value of $\overline{\gamma}$, the greater will be the factor $\overline{\gamma}/\overline{\gamma}-1$, so that the highest c can be expected, all other things being held constant, when the value of $\overline{\gamma}$ is least. This is true because the factor $\overline{\gamma}/\overline{\gamma}-1$ increases faster than the ideal thermodynamic efficiency decreases with a decrease in $\overline{\gamma}$. Hydrogen, having the lowest C_p per gram mole of all the major components, decreases the value of the average specific heat of the mixture, when it is added to a propellant system. Thus hydrogen increases the value of $\overline{\gamma}$. It is seen, then, that the addition of hydrogen to a propellant system has three effects on the composition of the gas mixture: (1) it lowers the average molecular weight of the products, (2) it increases the value of $\overline{\gamma}$, and (3) it alters the equilibrium composition in such a way that the chamber temperature is in general decreased, except for the addition of small amounts in which case the temperature may at first increase, as discussed previously.

A further investigation of other propellant systems should be made. The calculations are long and tedious, but it is believed that some valuable information may be obtained by investigating the very hot propellant systems, particularly the liquid oxygen-liquid hydrogen system. Since liquid hydrogen presents such tremendous technical difficulties in preparation, handling, and storage, it is suggested that the addition of other materials, such as ammonia or hydrazine, to a propellant system also be considered. It must be remembered, too, that the arbitrary choice of a chamber pressure of 300 psia was dictated by the fact that it is standard practice to compare propellant systems at this pressure, but this does not mean that 300 psia is the best chamber pressure for any particular propellant system by any means. Investigations of the effect of chamber pressure on chamber temperature and performance are being made.

REFERENCES

1. Weissbluth, M. "Performance of Jet Motors Based on Theoretical Calculations with Special Reference to the Liquid Oxygen-Gasoline Propellant Combination," Air Corps Jet Propulsion Research, GALCIT Project No. 1, Progress Report No. 16, April 28, 1944.

2. Bichowsky and Rossini. "Thermochemistry of Chemical Substances," Reinhold Publishing Corporation, 1933.

3. Johnston, S. A. "Preliminary Investigation of Hydrogen Peroxide as a Rocket Motor Propellant Component," ORDCIT Project No. 4, AIR. LAB., Project MX121, Progress Report 1-24, JPL, GALCIT.

4. Hughes, Corruccini, and Gilbert. J. Am. Chem. Soc. <u>61</u>, 2639 (1939).

5. Blatt, A. H. "Compilation of Data on Organic Explosives," O.S.R.D. Report No. 2041.

6. Hirschfelder, McClure, Curtiss, and Osborne. "Thermodynamic Properties of Propellant Gases," O.S.R.D. Report No. 547.

7. Stosick, A. J. "Performance Calculations for Propellants Using Hydrogen Peroxide and Performance Calculations for Diethyleneglycol Dinitrate as a Monopropellant," AIR LAB. Project No. MX121, April 2, 1945.

Table III Equilibrium constants.*

Temp·(°K)	K_1	K_2	K_3	K_4	K_5	K_6	K_7	K_8	K_9	K_{10}
296.1	1.007×10^{-5}	7.82×10^{24}		7.280×10^{2}	1.58×10^{24}					
700	0.1110	3.637×10^{3}		9.150×10^{-3}	1.06×10^{13}					
800	.2478	31.25		2.909×10^{-3}	9.64×10^{11}					
900	.4546	0.7513		1.177×10^{-3}	1.48×10^{11}					
1000	.7286	.03720		5.638×10^{-4}	3.29×10^{10}					
1100	1.058	3.147×10^{-3}		3.070×10^{-4}	9.55×10^{9}					
1200	1.435	3.994×10^{-4}		1.847×10^{-4}	3.39×10^{9}					
1300	1.844	6.975×10^{-5}		1.196×10^{-4}	1.40×10^{9}					
1400	2.270	1.553×10^{-5}		8.239×10^{-5}	6.56×10^{8}					
1500	2.704	4.218×10^{-6}		5.946×10^{-5}	3.38×10^{8}					
1600	3.135	1.348×10^{-6}		4.460×10^{-5}	1.89×10^{8}					
1700	3.555	4.925×10^{-7}		3.479×10^{-5}	1.13×10^{8}					
1800	3.975	2.029×10^{-7}		2.783×10^{-5}	7.08×10^{7}					
1900	4.393	9.211×10^{-8}		2.293×10^{-5}	4.66×10^{7}					
2000	4.782	4.545×10^{-8}	5.736×10^{-6}	1.923×10^{-5}	3.19×10^{7}	8.13×10^{-8}	2.08×10^{-7}	8.650×10^{-7}	1.629×10^{-3}	1.644×10^{-4}
2100	5.149	2.393×10^{-8}	1.495×10^{-5}	1.641×10^{-5}	2.26×10^{7}	3.45×10^{-7}	8.85×10^{-7}	2.460×10^{-6}	3.119×10^{-3}	3.698×10^{-4}
2200	5.420	1.320×10^{-8}	3.69×10^{-5}	1.421×10^{-5}	1.65×10^{7}	1.308×10^{-6}	3.34×10^{-6}	6.546×10^{-6}	5.610×10^{-3}	8.072×10^{-4}
2300	5.853	7.902×10^{-9}	8.39×10^{-5}	1.247×10^{-5}	1.24×10^{7}	4.19×10^{-6}	1.096×10^{-5}	1.560×10^{-5}	9.683×10^{-3}	1.567×10^{-3}
2400	6.140	4.873×10^{-9}	1.685×10^{-4}	1.107×10^{-5}	9.48×10^{6}	1.260×10^{-5}	3.305×10^{-5}	3.475×10^{-5}	1.592×10^{-2}	2.951×10^{-3}
2500	6.440	3.138×10^{-9}	3.512×10^{-4}	9.95×10^{-6}	7.40×10^{6}	3.452×10^{-5}	9.121×10^{-5}	7.231×10^{-5}	2.514×10^{-2}	5.230×10^{-3}
2600	6.668	2.089×10^{-9}	6.74×10^{-4}	9.00×10^{-6}	5.88×10^{6}	8.85×10^{-5}	2.34×10^{-4}	1.426×10^{-4}	3.837×10^{-2}	8.995×10^{-3}
2700	6.954	1.435×10^{-9}	1.188×10^{-3}	8.21×10^{-6}	4.74×10^{6}	2.06×10^{-4}	5.55×10^{-4}	2.672×10^{-4}	5.675×10^{-2}	1.462×10^{-2}
2800	7.185	1.018×10^{-9}	2.05×10^{-3}	7.56×10^{-6}	3.87×10^{6}	4.64×10^{-4}	1.243×10^{-3}	4.797×10^{-4}	8.185×10^{-2}	2.312×10^{-2}
2900	7.376	7.360 /x 10^{-10}	3.42×10^{-3}	6.98×10^{-6}	3.21×10^{6}	9.90×10^{-4}	2.65×10^{-3}	8.260×10^{-4}	1.148×10^{-1}	3.556×10^{-2}
3000	7.582	5.458×10^{-10}	5.479×10^{-3}	6.49×10^{-6}	2.69×10^{6}	1.983×10^{-3}	5.336×10^{-3}	1.373×10^{-3}	0.1579	5.290×10^{-2}
3100	7.748		8.525×10^{-3}		2.27×10^{6}	3.803×10^{-3}	1.027×10^{-2}	2.210×10^{-3}	.2125	7.677×10^{-2}
3200	7.929		1.294×10^{-2}		1.94×10^{6}	7.055×10^{-3}	1.904×10^{-2}	3.452×10^{-3}	.2813	1.087×10^{-1}
3300	8.078		1.859×10^{-2}		1.66×10^{6}	1.248×10^{-2}	3.389×10^{-2}	5.253×10^{-3}	.3654	1.513×10^{-1}
3400	8.192		2.758×10^{-2}		1.44×10^{6}	2.157×10^{-2}	5.857×10^{-2}	7.798×10^{-3}	.4682	2.060×10^{-1}
3500	8.304	1.621×10^{-10}	3.894×10^{-2}	4.86×10^{-6}	1.26×10^{6}	3.583×10^{-2}	9.778×10^{-2}	1.132×10^{-2}	.5910	2.763×10^{-1}
3600	8.449		5.404×10^{-2}		1.10×10^{6}	5.821×10^{-2}	1.591×10^{-1}	1.611×10^{-2}	.7367	3.814×10^{-1}
3700	8.535		7.355×10^{-2}		9.69×10^{5}	9.166×10^{-2}	2.516×10^{-1}	2.248×10^{-2}	.9084	4.891×10^{-1}
3800	8.664		9.821×10^{-2}		8.59×10^{5}	1.412×10^{-1}	3.876×10^{-1}	3.086×10^{-2}	1.107	5.984×10^{-1}
3900	8.712		1.300×10^{-1}		7.64×10^{5}	2.134×10^{-1}	5.878×10^{-1}	4.166×10^{-2}	1.336	7.569×10^{-1}
4000	8.752	6.88×10^{-11}	1.693×10^{-1}	3.94×10^{-6}	6.83×10^{5}	3.157×10^{-1}	8.711×10^{-1}	5.544×10^{-2}	1.597	9.495×10^{-1}
4100	8.819		2.162×10^{-1}		6.12×10^{5}	4.526×10^{-1}	1.298	7.258×10^{-2}	1.893	1.164
4200	8.884		2.760×10^{-1}		5.52×10^{5}	6.519×10^{-1}	1.806	9.423×10^{-2}	2.228	1.428
4300	8.898		3.463×10^{-1}		5.01×10^{5}	9.139×10^{-1}	2.537	1.206×10^{-1}	2.598	1.730
4400	8.929		4.302×10^{-1}		4.51×10^{5}	1.263	3.508	1.528×10^{-1}	3.012	2.089
4500	8.952	3.38×10^{-11}	5.291×10^{-1}	3.38×10^{-6}	4.10×10^{5}	1.718	4.778	1.916×10^{-1}	3.470	2.478
4600	8.974		6.451×10^{-1}		3.74×10^{5}	2.307	6.431	2.379×10^{-1}	3.969	2.923
4700	8.984		7.799×10^{-1}		3.41×10^{5}	3.068	8.545	2.927×10^{-1}	4.520	3.432
4800	8.994		9.344×10^{-1}		3.12×10^{5}	4.015	11.21	3.570×10^{-1}	5.118	3.992
4900	9.003		1.115		2.86×10^{5}	5.228	14.59	4.321×10^{-1}	5.764	4.637
5000	9.012	2.02×10^{-11}	1.317	3.00×10^{-6}	2.63×10^{5}	6.693	18.77	5.193×10^{-1}	6.461	5.317

* See next page for definitions of K_1, K_2 ....

Table III. [Concluded.]

Temp. (°K)	K_{11}	K_{12}	K_{13}	K_{14}	K_{15}	K_{16}	K_{17}
298.1							
400							3.976×10^{-5}
500							1.822×10^{-5}
600							1.026×10^{-5}
700							6.660×10^{-6}
800							4.724×10^{-6}
900							3.603×10^{-6}
1000	2.11×10^{-10}					2.226×10^{-15}	2.888×10^{-6}
1100							2.416×10^{-6}
1200							2.081×10^{-6}
1300							1.835×10^{-6}
1400							1.653×10^{-6}
1500	2.98×10^{-11}				2.77×10^{-6}	9.078×10^{-16}	1.510×10^{-6}
2000	1.13×10^{-11}				2.37×10^{-6}	7.290×10^{-16}	1.136×10^{-6}
2500	6.62×10^{-12}				2.23×10^{-6}	7.446×10^{-16}	9.87×10^{-7}
3000		8.27×10^{-6}	3.55×10^{-7}	1.90×10^{-4}	2.16×10^{-6}		9.93×10^{-7}
3500		3.80×10^{-7}	8.55×10^{-7}	7.61×10^{-4}	2.16×10^{-6}		9.89×10^{-7}
4000		1.20×10^{-6}	1.65×10^{-6}	2.15×10^{-3}	2.17×10^{-6}		9.88×10^{-7}
4500		2.92×10^{-6}	2.62×10^{-6}	4.80×10^{-3}	2.22×10^{-6}		9.87×10^{-7}
5000		5.96×10^{-6}	4.41×10^{-6}	9.09×10^{-3}	2.28×10^{-6}		9.88×10^{-7}

$K_1 = P_{CO}P_{H_2O}/P_{CO_2}P_{H_2}$; $K_2 = P_{CH_4}P_{H_2O}/P^3_{H_2}P_{CO}$; $K_3 = P_{NO}P_{H_2}/P^{1/2}_{N_2}P_{H_2O}$;

$K_4 = P_{NH_3}/P^{1/2}_{N_2}P^{3/2}_{H_2}$; $K_5 = P_{CO}/P^{1/2}_{O_2}$; $K_6 = P_{O_2}P^2_{H_2}/P^2_{H_2O}$;

$K_7 = P_O P_{H_2}/P_{H_2O}$; $K_8 = P_N/P^{1/2}_{H_2}$; $K_9 = P_H/P^{1/2}_{H_2}$; $K_{10} = P_{OH}P^{1/2}_{H_2}/P_{H_2O}$.

$K_{11} = P_{C_2H_2}P^2_{H_2O}/P^2_{CO}P^3_{H_2}$; $K_{12} = P_{CH}P_{H_2O}/P_{CO}P^{3/2}_{H_2}$;

$K_{13} = P_{CN}P_{CO_2}/P^2_{CO}P^{1/2}_{N_2}$; $K_{14} = P_{NH}/P^{1/2}_{N_2}P^{1/2}_{H_2}$;

$K_{15} = P_{HCN}P_{H_2O}/P_{CO}P^{3/2}_{H_2}P^{1/2}_{N_2}$; $K_{16} = P_{C_2N_2}P^2_{CO_2}/P^4_{CO}P_{N_2}$;

$K_{17} = P_{H_2CO}/P_{H_2}P_{CO}$.

TABLE IV

ENTHALPY TABLE

$\Delta H_{300^\circ K}^{T^\circ K}$ kcals/gram mole

T °K	H_2	H_2O	CO	CO_2	O_2	N_2	OH	NO	H,N,O	RΔT
300	0.0	0.0	0.0	0.0	0.0	0.0			0.0	0.0
400	0.695	0.811	0.699	0.942	0.721	0.697			0.497	0.199
500	1.393	1.641	1.404	1.970	1.447	1.399			0.993	0.397
600	2.093	2.496	2.125	3.072	2.203	2.112			1.490	0.596
700	2.796	3.380	2.862	4.232	2.981	2.840			1.987	0.795
800	3.502	4.292	3.615	5.441	3.778	3.582			2.484	0.993
900	4.212	5.234	4.386	6.692	4.594	4.343			2.981	1.192
1000	4.931	6.208	5.171	7.976	5.421	5.118	4.985	5.308	3.477	1.390
1100	5.657	7.211	5.973	9.291	6.278	5.907	5.725	6.133	3.974	1.589
1200	6.393	8.247	6.785	10.629	7.135	6.709	6.465	6.958	4.471	1.788
1300	7.138	9.312	7.606	11.989	7.990	7.520	7.233	7.800	4.967	1.986
1400	7.895	10.399	8.437	13.367	8.847	8.342	8.002	8.643	5.464	2.185
1500	8.664	11.519	9.275	14.760	9.704	9.173	8.783	9.499	5.961	2.384
1600	9.439	12.660	10.120	16.168	10.592	10.009	9.584	10.355	6.457	2.582
1700	10.226	13.821	10.972	17.587	11.481	10.854	10.390	11.221	6.954	2.781
1800	11.023	15.006	11.829	19.017	12.369	11.703	11.197	12.088	7.451	2.980
1900	11.828	16.206	12.689	20.455	13.257	12.558	12.015	12.957	7.947	3.178
2000	12.644	17.424	13.554	21.902	14.146	13.417	12.834	13.827	8.444	3.377
2100	13.466	18.659	14.423	23.358	15.061	14.279	13.643	14.700	8.941	3.576
2200	14.295	19.909	15.294	24.820	15.974	15.143	14.506	15.598	9.438	3.774
2300	15.132	21.171	16.169	26.290	16.889	16.013	15.360	16.480	9.935	3.973
2400	15.975	22.445	17.045	27.760	17.802	16.883	16.213	17.364	10.430	4.171
2500	16.827	23.733	17.923	29.242	18.717	17.758	17.080	18.249	10.928	4.370
2600	17.683	25.031	18.807	30.729	19.659	18.636	17.936	19.143	11.425	4.569
2700	18.542	26.338	19.691	32.218	20.601	19.516	18.807	20.036	11.921	4.767
2800	19.410	27.656	20.576	33.712	21.543	20.399	19.678	20.929	12.418	4.966
2900	20.282	28.980	21.464	35.211	22.486	21.284	20.563	21.823	12.915	5.165
3000	21.160	30.315	22.353	36.712	23.427	22.170	21.447	22.716	13.411	5.363
3100	22.041	31.658	2[illegible].[illegible]42	38.222	24.384	23.058	22.335	23.617	13.908	5.562
3200	22.927	33.006	24.136	39.734	25.344	23.947	23.227	24.519	14.405	5.761
3300	23.818	34.362	25.028	41.244	26.308	24.837	24.121	25.421	14.901	5.959
3400	24.712	35.723	25.923	42.764	27.276	25.729	25.021	26.325	15.398	6.158
3500	25.611	37.092	26.818	44.281	28.247	26.622	25.920	27.229	15.894	6.356
3600	26.512	38.466	27.715	45.808	29.219	27.516	26.822	28.135	16.392	6.555
3700	27.416	39.845	28.513	47.332	30.198	28.412	27.730	29.041	16.889	6.754
3800	28.326	41.231	29.512	48.862	31.178	29.307	28.640	29.948	17.385	6.952
3900	29.236	42.619	30.412	50.394	32.164	30.205	29.552	30.856	17.882	7.151
4000	30.153	44.010	31.313	51.930	33.153	31.104	30.467	31.761	18.379	7.350
4100	31.069	45.413	32.215	53.471	34.139	32.006	31.390	32.682	18.875	7.548

SOURCE OF DATA

THERMODYNAMIC PROPERTIES OF PROPELLANT GASES, HIRSCHFELDER, CURTIS, MCCLURE AND OSBORNE O. S. R. D. REPORT # 547

NOTE: FOR USE OF THIS TABLE IN CALCULATING THEORETICAL PROPELLANT PERFORMANCE
cf: PROGRESS REPORT 1.25

TABLE V

VARIATION OF PERFORMANCE PARAMETERS WITH MIXTURE RATIO IN THE RFNA-ANILINE SYSTEM

Mixture Ratio	1.500	2.300	2.800	3.000	3.500	4.171	5.000	6.000
T_c °K	1570	2622	2974	3042	3111	3082	3003	2814
T_e °K	758	1477	1833	1997	2278	2474	2230	1927
$\bar{M}$	19.12	23.02	25.02	25.70	27.16	28.38	29.00	29.13
$\bar{\gamma}$	1.318	1.235	1.191	1.162	1.115	1.079	1.101	1.144
$\bar{C}_p$	8.235	10.435	12.364	14.239	19.211	27.210	21.717	15.813
c	5614	6340	7129	7224	7287	7255	6988	6538
c*	4040	4868	5040	5071	5064	4993	4840	4610
C_F	1.390	1.405	1.414	1.425	1.439	1.435	1.444	1.429
I_{sp}	174.6	212.7	221.7	224.6	226.6	225.6	217.3	204.8
Γ'	0.7696	0.7280	0.7058	0.6910	0.6671	0.6477	0.6593	0.6815
a_c	3109	3544	3557	3504	3378	3234	3191	3142

TABLE VI

VARIATION OF PERFORMANCE PARAMETERS WITH MOLES OF HYDROGEN ADDED TO A STOICHIOMETRIC MIXTURE OF RFNA-ANILINE

Moles of H_2 Added	T_c °K	T_e °K	$\bar{C}_p$	$\bar{\gamma}$	$\bar{M}$	c*	c	I_{sp}	C_F
0	3083	2474	27.210	1.0787	38.378	4993	7255	225.6	1.453
½	3110	2252	18.576	1.1200	25.198		7552	234.8	
1	3047	1986	13.987	1.1655	22.403	5430	7726	240.2	1.423
1½	2911	1771	12.051	1.1973	20.132	5546	7841	243.8	1.414
2	2767	1619	11.170	1.2162	18.274	5645	7953	247.3	1.409
2½	2612	1506	10.869	1.2232	16.771	5713	8038	249.9	1.407
3	2468	1368	10.151	1.2432	15.507	5740	8058	250.6	1.404
3½	2344	1265	9.715	1.2570	14.439	5777	8090	251.6	1.400
4	2231	1192	9.552	1.2625	13.525	5813	8120	252.5	1.397
5	2038	1061	9.174	1.2763	12.052	5862	8189	254.6	1.397
6	1880	960	8.908	1.2869	10.909	5904	8228	255.8	1.394
8	1636	814	8.573	1.3015	9.261	5951	8281	257.5	1.392
15	1165	557	8.122	1.3237	6.411		8333	259.1	

TABLE VII

VARIATION OF PERFORMANCE PARAMETERS WITH MOLES OF HYDROGEN ADDED TO NITROMETHANE

Moles of H_2 added	T_c °K	T_e °K	c	I_{sp}	$\bar{M}$
0	2452	1366	7014	218.1	20.330
½	2216	1195	7096	220.6	17.725
1	2026	1069	7159	222.6	15.762
2	1741	891	7257	225.7	13.012
4	1385	677	7398	230.0	9.870
8	1041	500	7533	234.2	7.014

TABLE VIII

VARIATION OF PERFORMANCE PARAMETERS WITH MOLES OF HYDROGEN ADDED TO A STOICHIOMETRIC MIXTURE OF ANHYDROUS HYDRAZINE AND LIQUID OXYGEN*

Moles of H_2 Added	% H_2 by weight	T_c °K	c	I_{sp}
0	0	3283	8291	257.5
½	1.54	3258	8715	270.6
1	3.04	3165	9000	279.5
1½	4.47	3020	9167	284.7
2	5.88	2865	9285	288.3
2½	7.24	2741	9400	291.9
3	8.57	2606	9474	294.2
3½	9.85	2484	9524	295.8
4	11.10	2370	9557	296.8
4½	12.32	2274	9603	298.2
5	13.50	2175	9600	298.1
6	15.78	2005	9593	297.9
7	17.93	1864	9586	297.7
10	23.79	1553	9527	295.8

*Based on the "frozen" composition method of performance calculation.

TABLE IX

HEATS OF FORMATION AT CONSTANT PRESSURE USED IN THIS ANALYSIS

Constituent	Heat of Formation in Kilocalories per Mole
CO_2	94.45
H_2O	57.80
CO	26.84
OH	-9.31
H	-51.90
NO	-21.60
O	-59.10
N	-85.10
N_2O_4	-12.20
HNO_3	41.66
HNO_3 (6.8% N_2O_4)	41.05
*$C_6H_5NH_2$	-6.11
CH_3NO_2	27.60

*A more accurate value is -4.55, based on the value of the heat of combustion of aniline reported by C. M. Anderson and E. C. Gilbert in the Journal of the American Chemical Society, Vol. 64 (1942) page 2371.

TABLE X

DATA SHOWING THE EFFECT OF AN ERROR OF 5.89 KCAL IN THE HEAT OF FORMATION OF ANILINE

Mixture Ratio	3.000	3.500
T_c °K	3042	3111
T_c' °K	3059	3123
% error	00.56	00.39
c	7224	7287
c'	7247	7316
% error	00.32	00.36

T_c	The correct chamber temperature.
T_c'	The chamber temperature computed from an erroneous value of the heat of formation of aniline.

TABLE XI

THE VARIATION OF THE GAS COMPOSITION WITH MIXTURE RATIO AT THE EQUILIBRIUM CHAMBER TEMPERATURE

Mixture Ratio		1.500	2.300	2.800	3.000	3.500	4.171	5.000	6.000
Chamber Temperature in °K		1570	2622	2974	3042	3111	3082	3003	2814
Component Gases									
a	H_2	0.3385	0.1515	0.0799	0.0626	0.0363	0.0197	0.0101	0.0040
b	H_2O	0.0339	0.2264	0.2914	0.3039	0.3181	0.3230	0.3221	0.3184
c	CO	0.4772	0.3674	0.2841	0.2511	0.1783	0.1097	0.0579	0.0226
d	CO_2	0.0160	0.0818	0.1365	0.1589	0.2021	0.2334	0.2461	0.2423
e	O_2			0.0011	0.0034	0.0162	0.0460	0.0924	0.1483
f	N_2	0.1344	0.1678	0.1834	0.1879	0.1954	0.2016	0.2098	0.2135
g	NO			0.0016	0.0031	0.0085	0.0148	0.0146	0.0175
h	OH		0.0014	0.0108	0.0172	0.0302	0.0374	0.0359	0.0270
i	H		0.0038	0.0092	0.0102	0.0098	0.0066	0.0031	0.0011
j	O			0.0008	0.0017	0.0052	0.0079	0.0080	0.0055

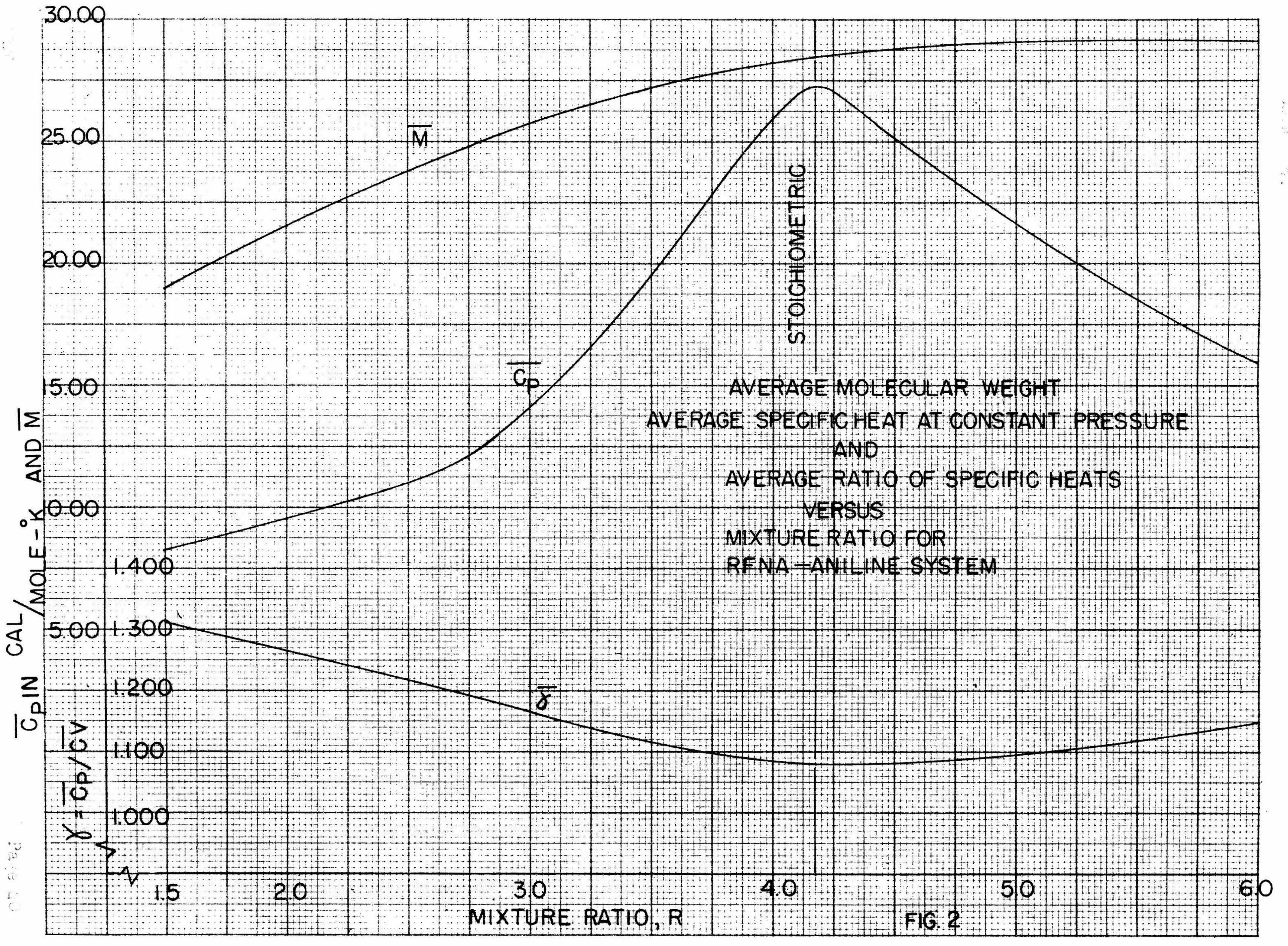
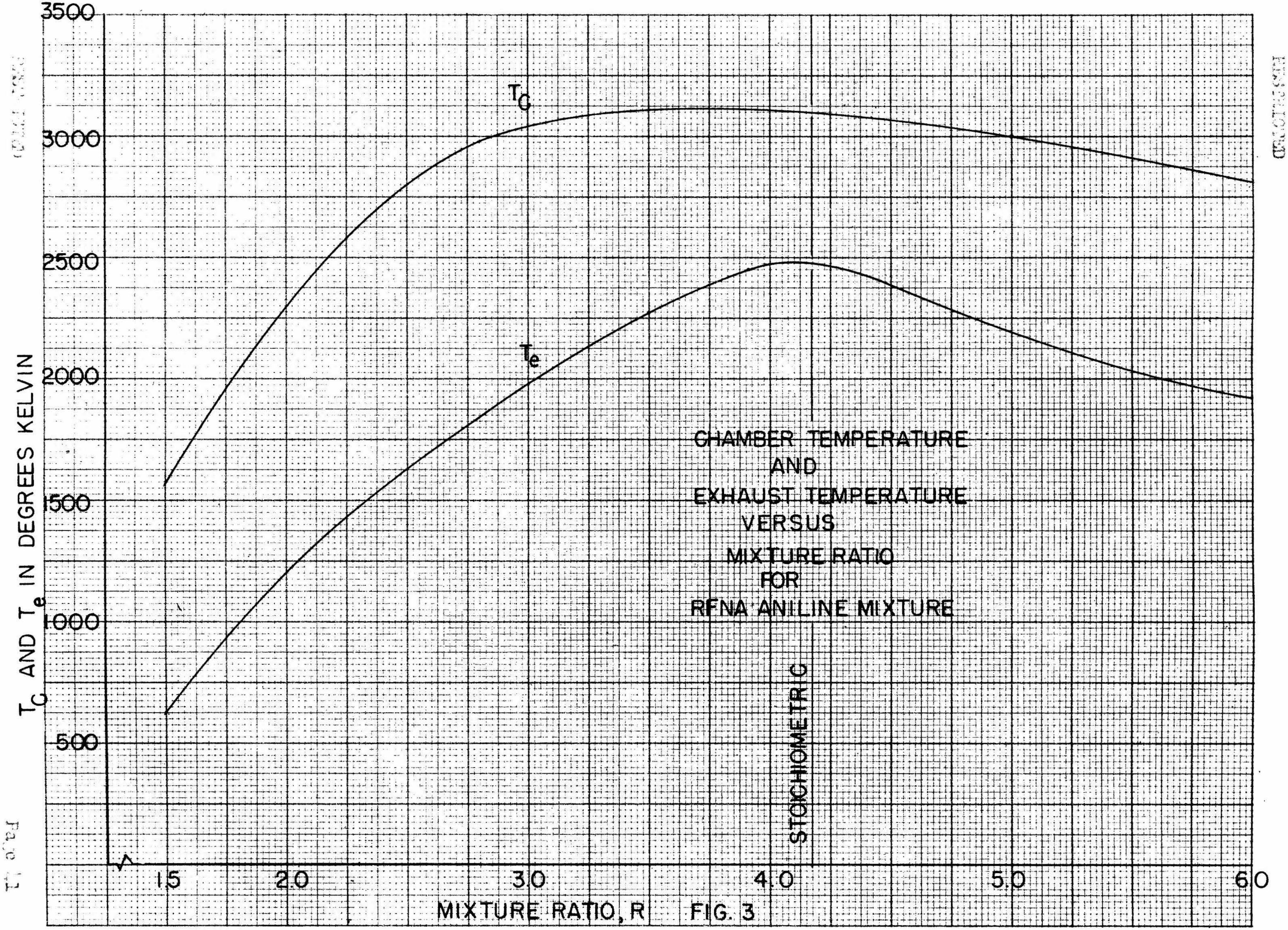

AVERAGE MOLECULAR WEIGHT
AVERAGE SPECIFIC HEAT AT CONSTANT PRESSURE
AND
AVERAGE RATIO OF SPECIFIC HEATS
VERSUS
MIXTURE RATIO FOR
RFNA – ANILINE SYSTEM

FIG. 2



CHAMBER TEMPERATURE
AND
EXHAUST TEMPERATURE
VERSUS
MIXTURE RATIO
FOR
RFNA ANILINE MIXTURE

FIG. 3

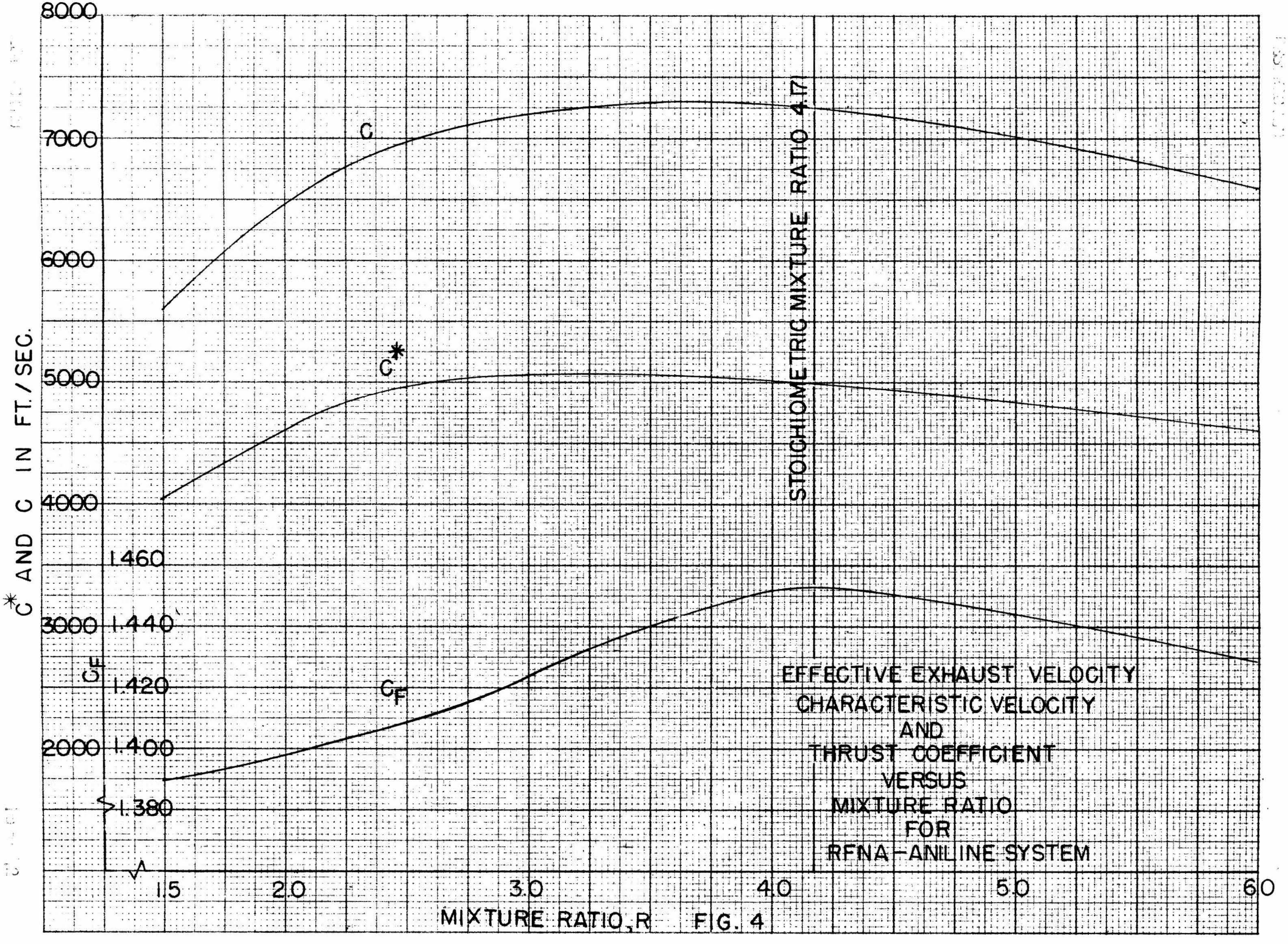
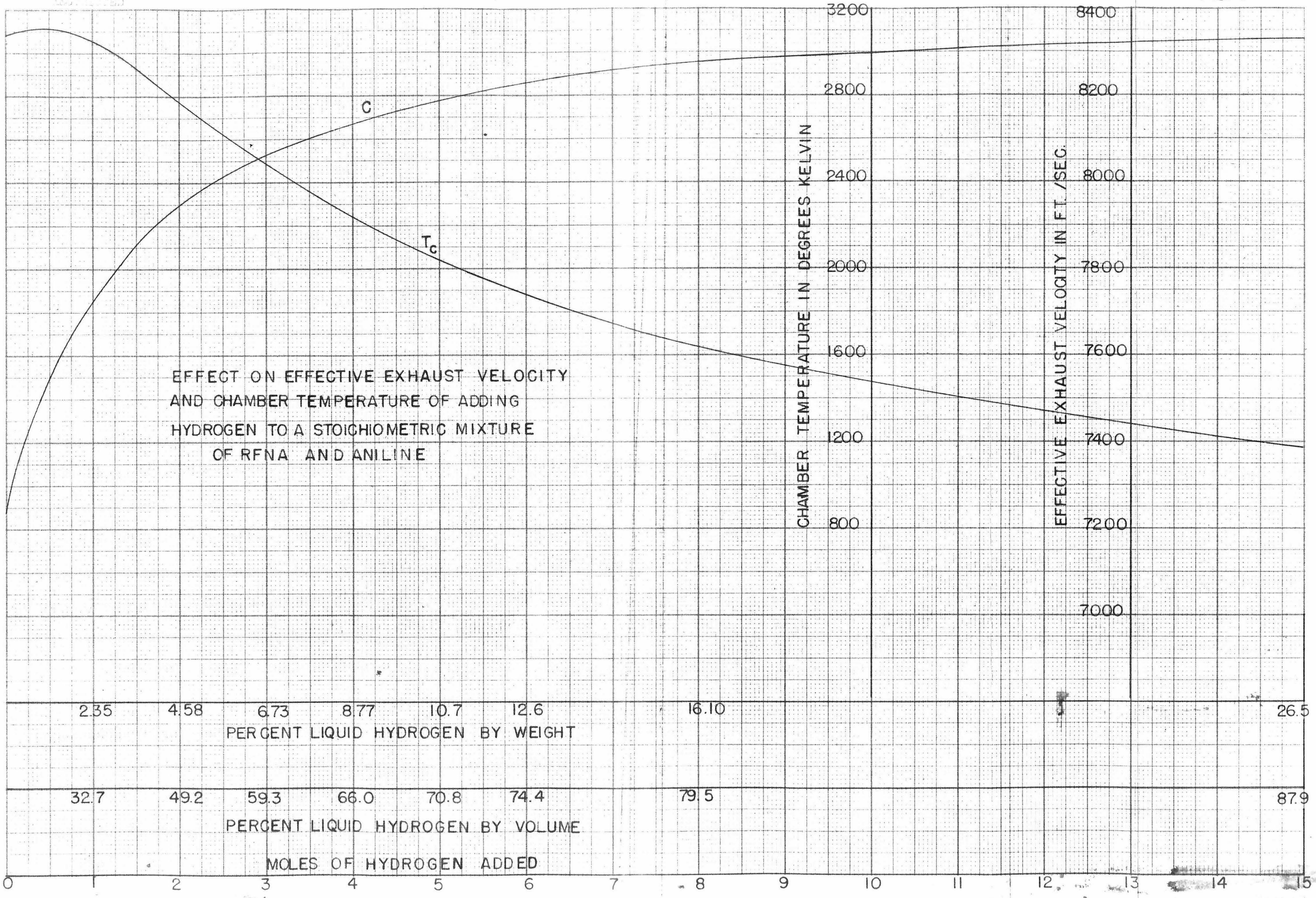
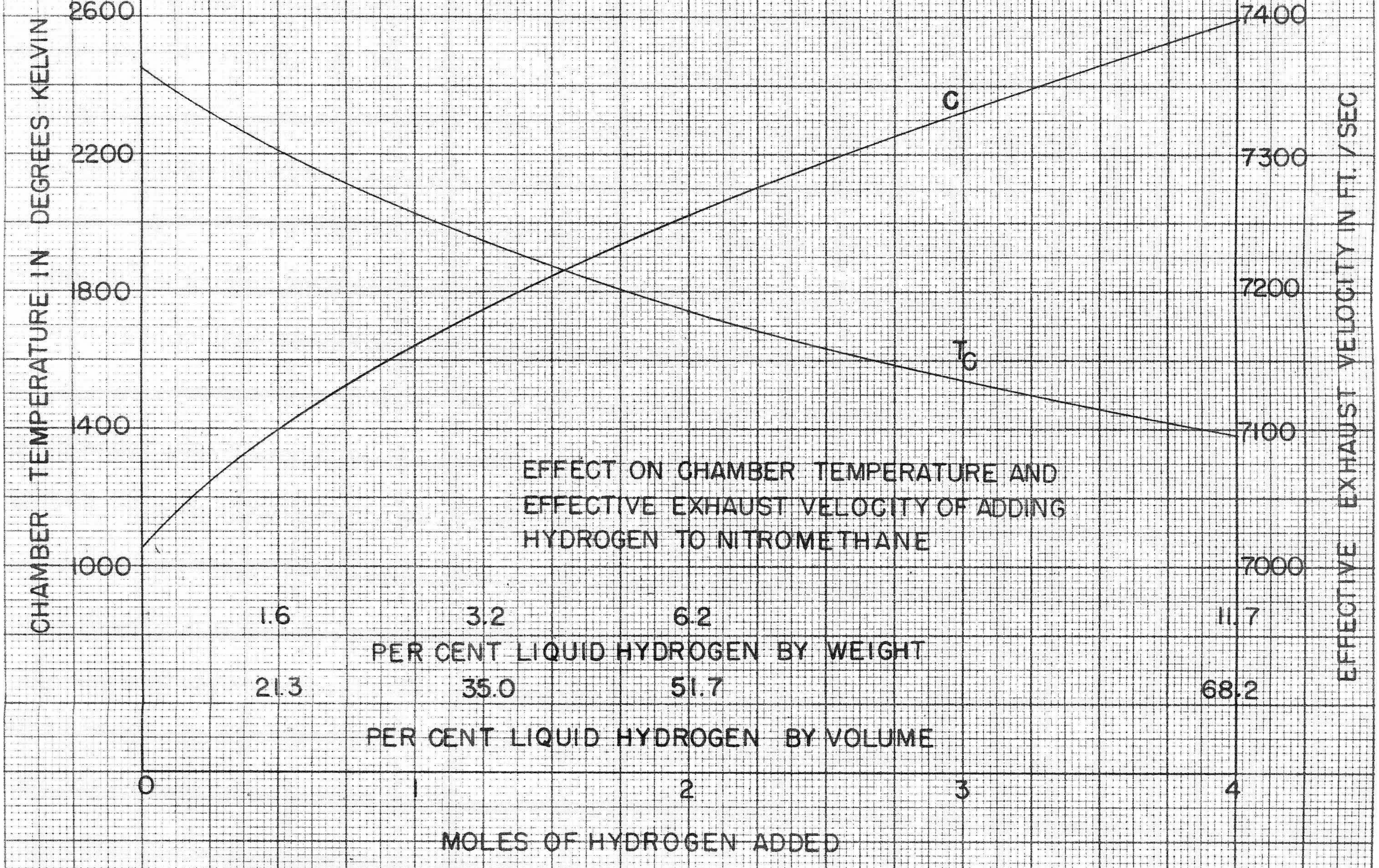

8000
7000
6000
5000
4000
3000
2000
1.460
1.440
1.420
1.400
1.380
C^* AND C IN FT./SEC.
C_F
C
C^*
C_F
STOICHIOMETRIC MIXTURE RATIO 4.17
1.5
2.0
3.0
4.0
5.0
6.0
MIXTURE RATIO, R
EFFECTIVE EXHAUST VELOCITY
CHARACTERISTIC VELOCITY
AND
THRUST COEFFICIENT
VERSUS
MIXTURE RATIO
FOR
RFNA-ANILINE SYSTEM

FIG. 4

FIG. 5

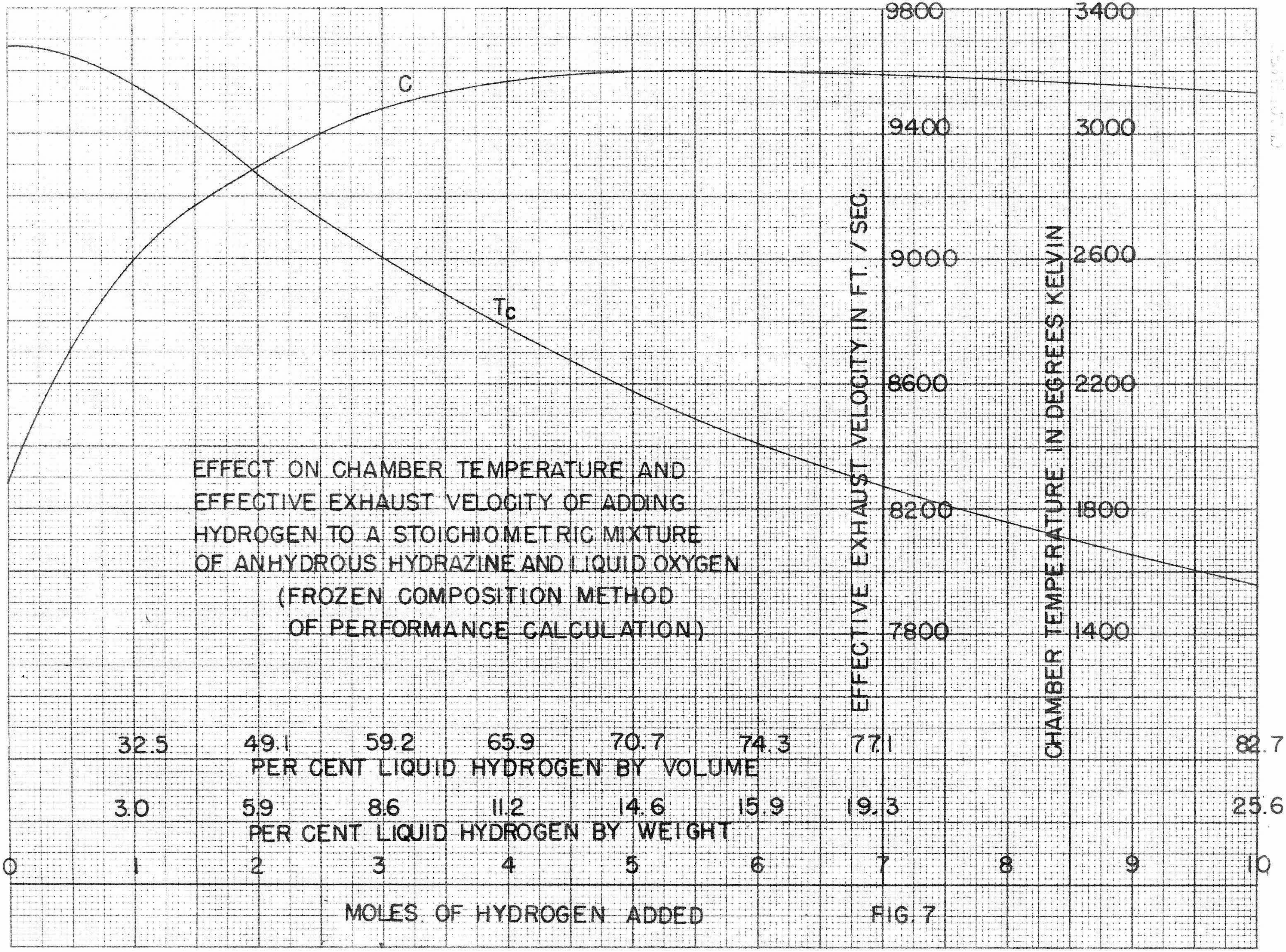


EFFECT ON EFFECTIVE EXHAUST VELOCITY AND CHAMBER TEMPERATURE OF ADDING HYDROGEN TO A STOICHIOMETRIC MIXTURE OF RFNA AND ANILINE



EFFECT ON CHAMBER TEMPERATURE AND EFFECTIVE EXHAUST VELOCITY OF ADDING HYDROGEN TO NITROMETHANE

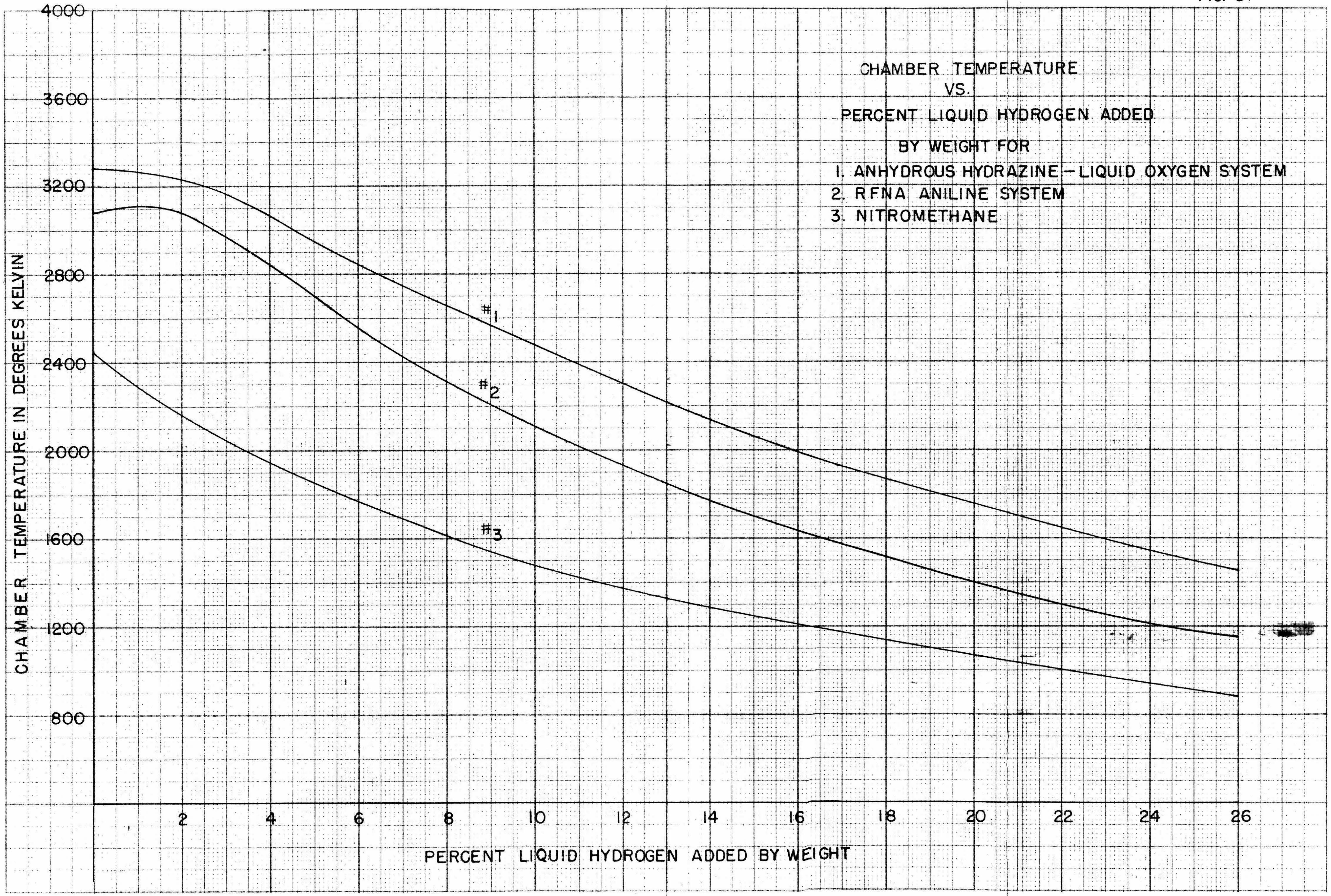
FIG. 6



EFFECT ON CHAMBER TEMPERATURE AND EFFECTIVE EXHAUST VELOCITY OF ADDING HYDROGEN TO A STOICHIOMETRIC MIXTURE OF ANHYDROUS HYDRAZINE AND LIQUID OXYGEN (FROZEN COMPOSITION METHOD OF PERFORMANCE CALCULATION)

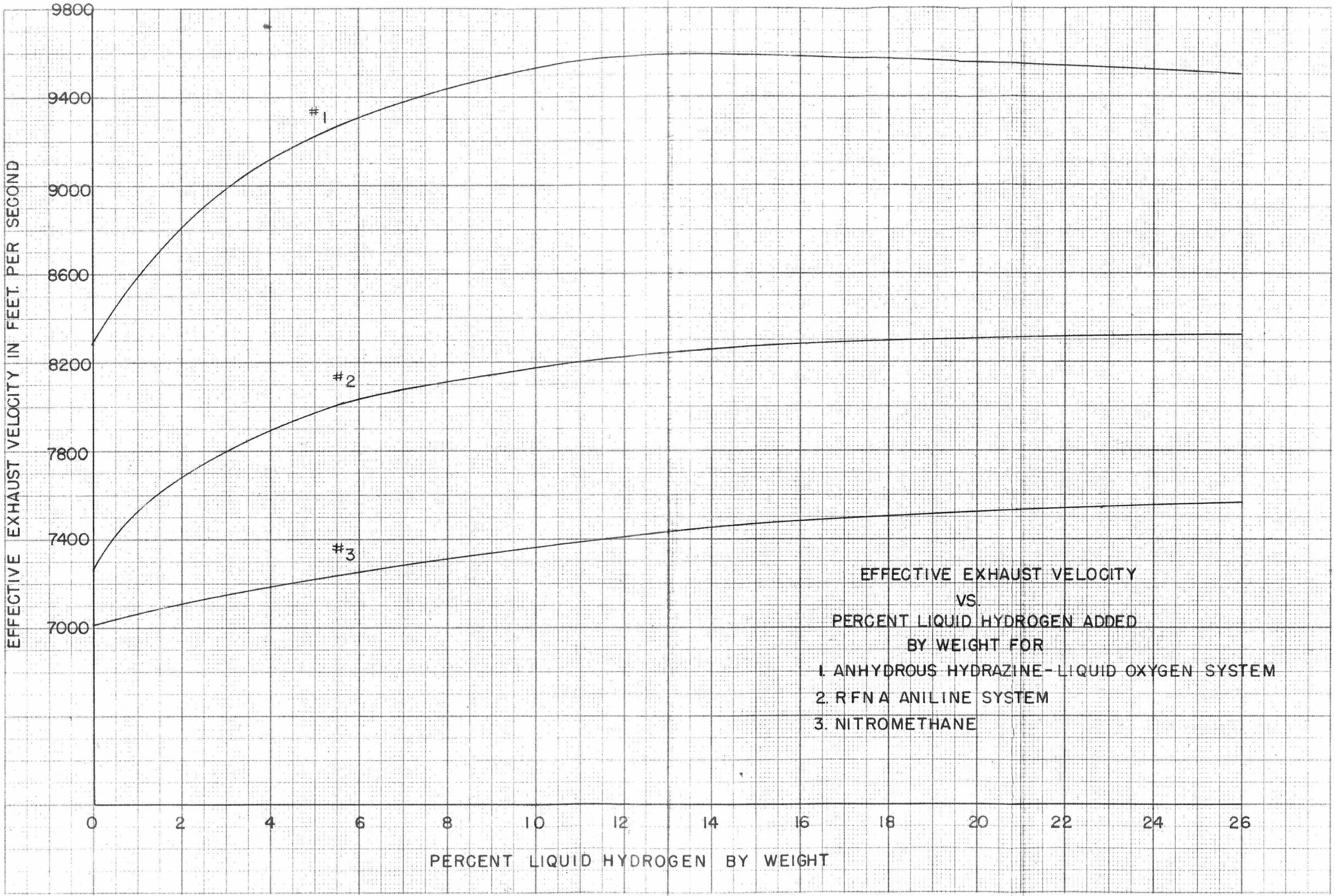
FIG. 7

FIG. 8



CHAMBER TEMPERATURE
VS.
PERCENT LIQUID HYDROGEN ADDED
BY WEIGHT FOR
1. ANHYDROUS HYDRAZINE – LIQUID OXYGEN SYSTEM
2. RFNA ANILINE SYSTEM
3. NITROMETHANE

FIG. 9



EFFECTIVE EXHAUST VELOCITY
VS.
PERCENT LIQUID HYDROGEN ADDED
BY WEIGHT FOR
1. ANHYDROUS HYDRAZINE-LIQUID OXYGEN SYSTEM
2. RFNA ANILINE SYSTEM
3. NITROMETHANE