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Theoretical Performances of Hypergolic Propellant Dimazine～Chlorine Trifluoride Systems

By

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Summary: The results of calculation for the theoretical performance and various thermodynamic data of Dimazine～chlorine trifluoride propellant system and Dimazine : hydrazine (1 : 1)～chlorine trifluoride propellant system have been presented. The calculation was performed with the OKITAC 5090A at Computation Center, University of Tokyo.

The maximum theoretical specific impulse of Dimazine～chlorine trifluoride propellant system is 199.73 sec. at mixture ratio of 5.75 (P_c=20 atm.), and that of Dimazine : hydrazine (1 : 1)～chlorine trifluoride propellant system is 216.33 sec. at mixture ratio of 3.575 (P_c=20 atm.).

SYMBOLS

a: specific volume of gas per unit weight of propellant [1/kg]
C_p: heat capacity [cal/mole°K]
ΔF^0: free energy [kcal/mole]
g: normal acceleration of gravity [m/sec²]
H^0: enthalpy [kcal/mole]
ΔH_f^0: heat of formation at 298.16°K [kcal/mole]
ΔH_v: heat of vaporization at boiling point [kcal/mole]
I_{sp}: specific impulse [sec]
κ: ratio of specific heat
K: concentration equilibrium constant
K_p: pressure equilibrium constant
$\bar{M}$: mean molecular weight of product gases [g/mole]
m: number of moles on product system
n: number of moles on reactant system
P: combustion pressure [atm]
R: universal gas constant
S^0: entropy [cal/mole°K]
T: temperature [°K]

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c: refers to combustion chamber
e: refers to nozzle exit
i: refers to i-th iteration number to calculate product compositions
o: refers to number of element atoms contained in 100 gr. weight of propellant
x: refers to oxidizer

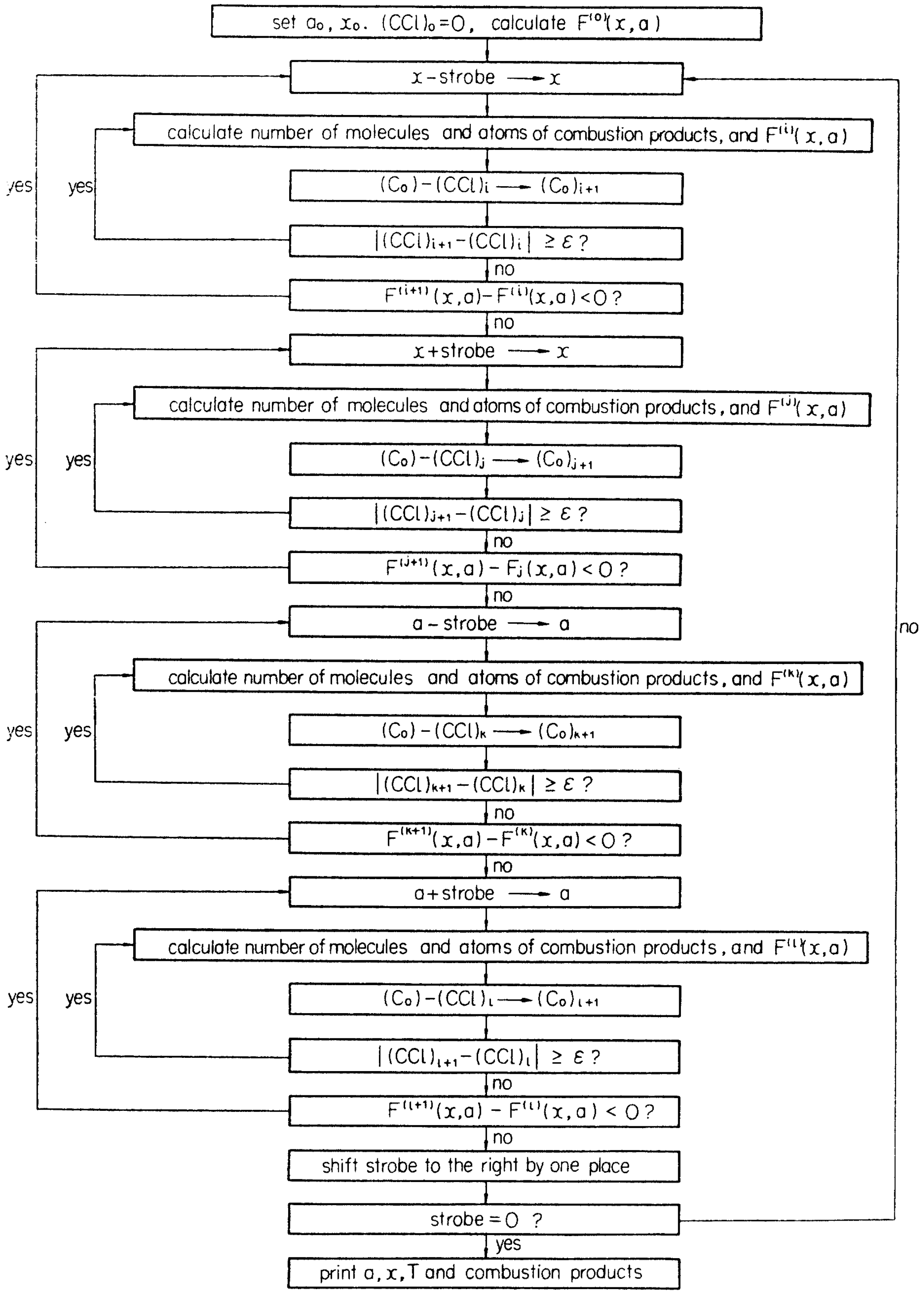

FIG. 1. Flow Chart for Calculation of Combustion Temperature and Composition with Electronic Computer.

There are a few references [*1*], [*2*] in regard to theoretical performances of hypergolic propellant, Dimazine~chlorine trifluoride systems, but unfortunately these can not be compared strictly with values of other propellants, since the assumptions for calculation are different. Published results illustrate mainly on

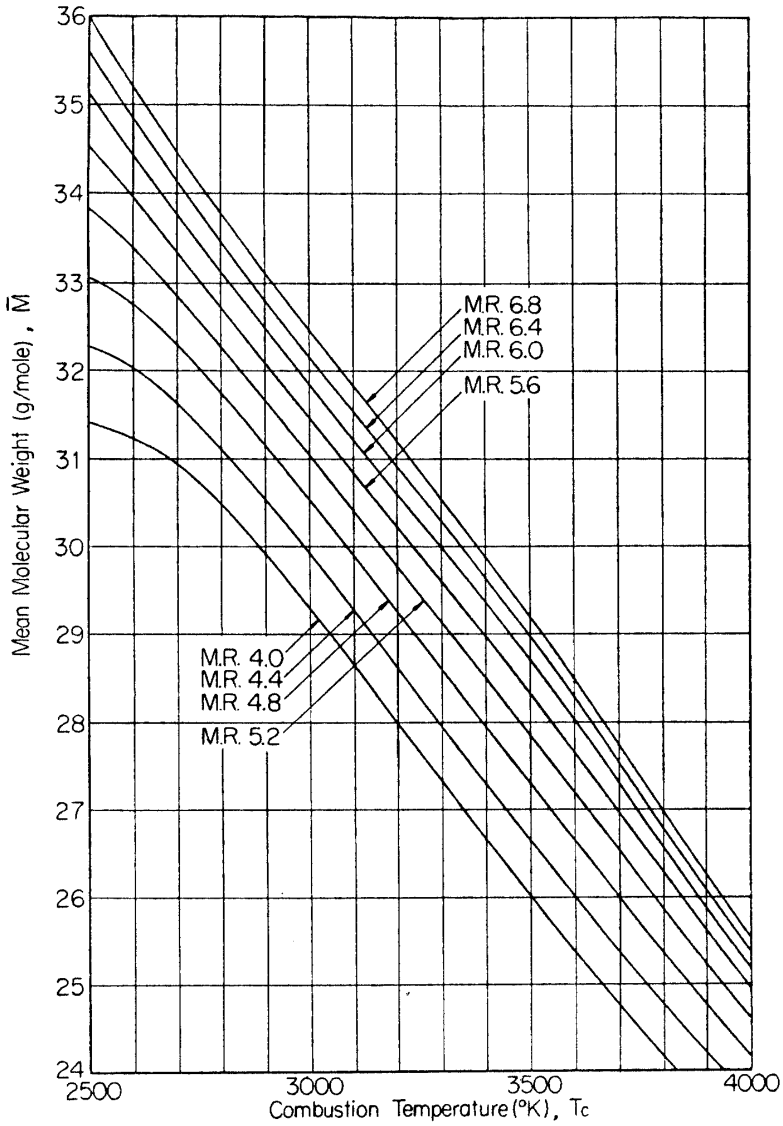

FIG. 2. Mean Molecular Weight of $(CH_3)_2\ NNH_2 \sim ClF_3$ System vs. Combustion Temperature and Mixture Ratio (P_c=20 atm.)

specific impulse, combustion temperature versus mixture ratio. Practically, these are not sufficient to design the rocket engine, and necessitate the other constants as thermodynamic data. So these constants were calculated with OKITAC 5090A of Calculation Center, University of Tokyo.

CALCULATION METHOD

As to the calculation of the equivalent compositions in combustion gas, the two methods are available; the iteration method using matrix or the algolism of transcendental matrix and the approximate solution of algebraic equations. The calculation method applied in this paper belongs to the latter, finding the minimum values of the functions within the capacity of the accumulator of the computer, without looking for extremely accurate results on referring to our published methods [*3*], [*4*].

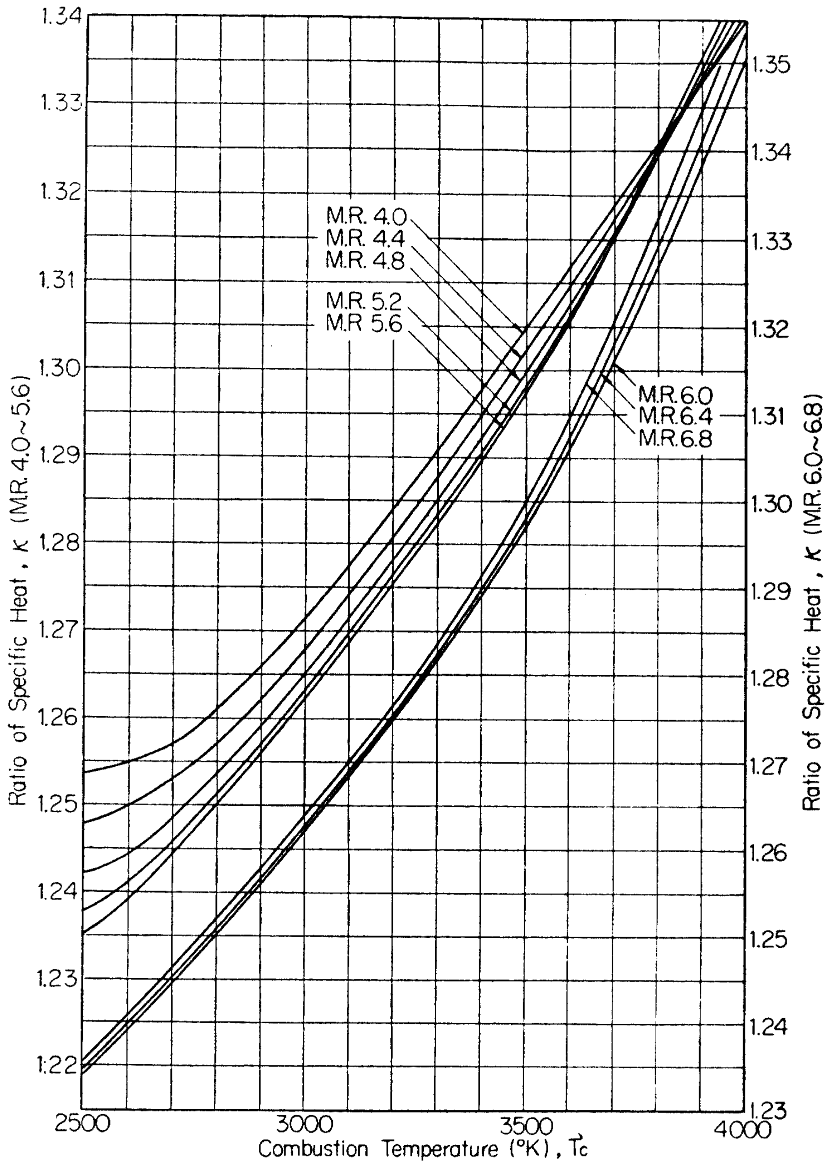

FIG. 3. Ratio of Specific Heat of $(CH_3)_2NNH_2$~ClF_3 System vs. Combustion Temperature and Mixture Ratio (P_c=20 atm.).

Assumption.—The following terms are assumed;

(1) Ideal gas.

(2) The law of conservation of mass for reaction system.

(3) The adiabatic chemical reaction.

(4) Frozen equilibrium at the nozzle.

(5) The combustion conditions;

standard temperature	298.16°K
combustion pressure	20 atm.

(6) The atmospheric pressure is 1 atm.

(7) The static pressure of combustion gas at the exit of the nozzle is 1 atm.

Equilibrium constants and conservation of mass.—The combustion products on $(CH_3)_2NNH_2$~ClF_3 and $(CH_3)_2NNH_2 : N_2H_4(1:1)$~$ClF_3$ system are con-

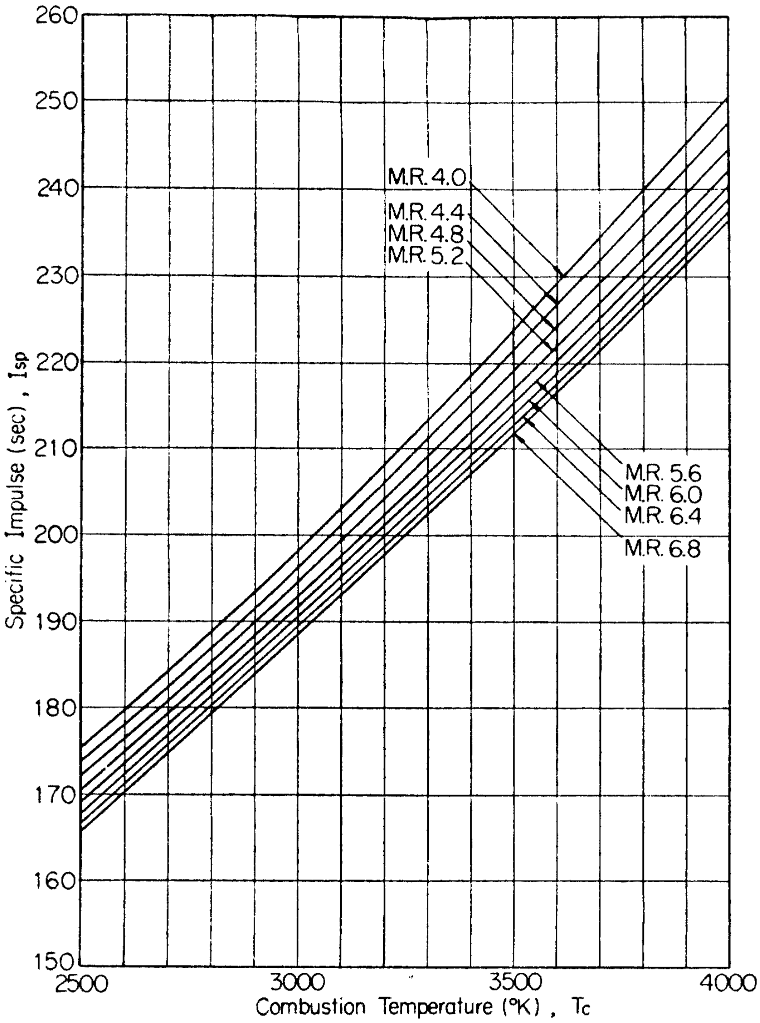

FIG. 4. Specific Impulse of $(CH_3)_2NNH_2 \sim ClF_3$ System vs. Combustion Temperature and Mixture Ratio (P_c=20 atm.).

sidered to be HF, F, CF_4, CF_3, CF_2, CF, C (gas), H_2, H, Cl, HCl, Cl_2, CCl, N_2 and N. The other gaseous species are omitted, since their quantity are negligible.

The following equations for conservation of mass are described;

$$(H_0)=(H)+2(H_2)+(HCl)+(HF) \qquad (1)$$

$$(C_0)=(CCl)+(CF)+(CF_2)+(CF_3)+(CF_4)+(C) \qquad (2)$$

$$(N_0)=(N)+2(N_2) \qquad (3)$$

$$(F_0)=(HF)+(F)+(CF)+2(CF_2)+3(CF_3)+4(CF_4) \qquad (4)$$

$$(Cl_0)=(HCl)+(Cl)+2(Cl_2)+(CCl). \qquad (5)$$

Concentration equilibrium constants are expressed as

$$1/2H_2=H \qquad (H)/(H_2)^{\frac{1}{2}}=a^{\frac{1}{2}}K_1 \qquad (6)$$

$$1/2Cl_2=Cl \qquad (Cl)/(Cl_2)^{\frac{1}{2}}=a^{\frac{1}{2}}K_2 \qquad (7)$$

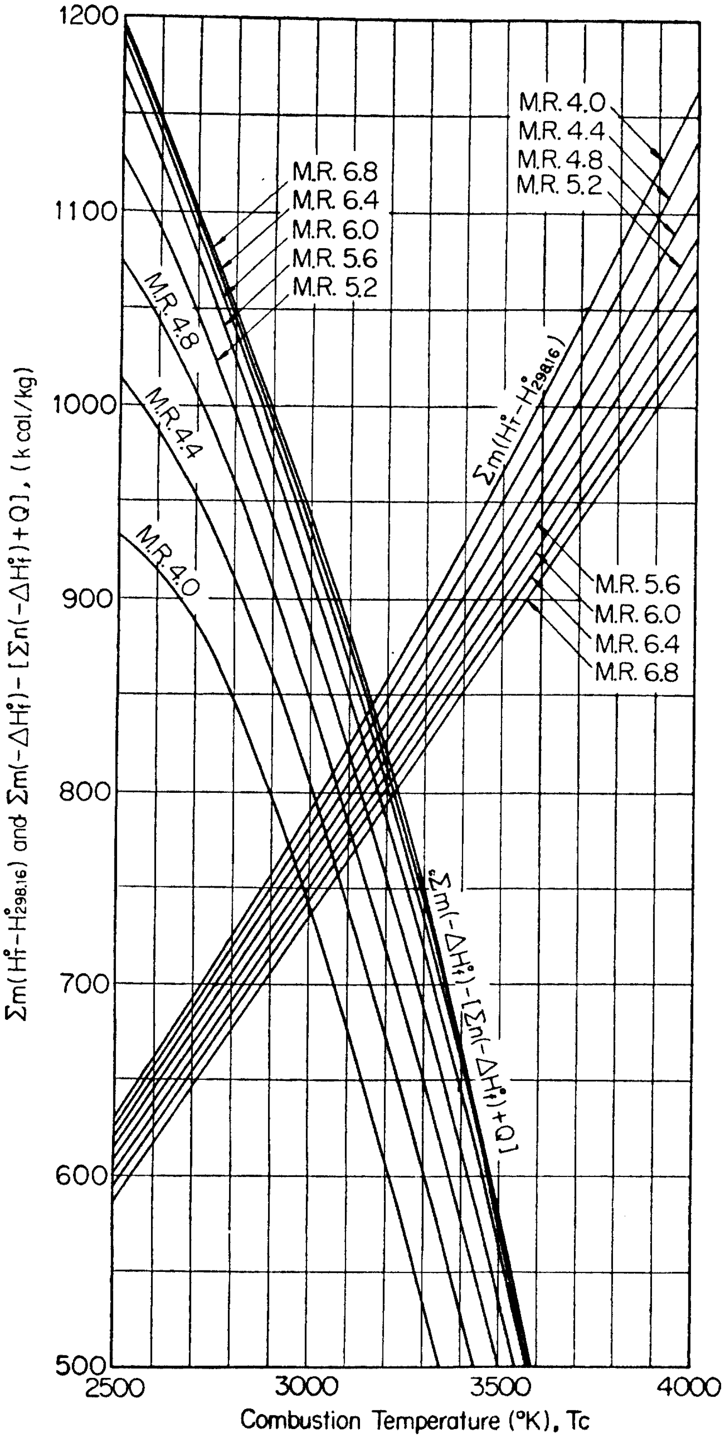

FIG. 5. Chart of Determination of Combustion Temperature on $(CH_3)_2NNH_2 \sim ClF_3$ System.

$$1/2N_2 = N \qquad (N)/(N_2)^{\frac{1}{2}} = a^{\frac{1}{2}}K_3 \qquad (8)$$

$$HF = 1/2H_2 + F \qquad (H_2)^{\frac{1}{2}}(F)/(HF) = a^{\frac{1}{2}}K_4 \qquad (9)$$

$$HCl = 1/2Cl_2 + 1/2H_2 \qquad (Cl_2)^{\frac{1}{2}} \cdot (H_2)^{\frac{1}{2}}/(HCl) = K_5 \qquad (10)$$

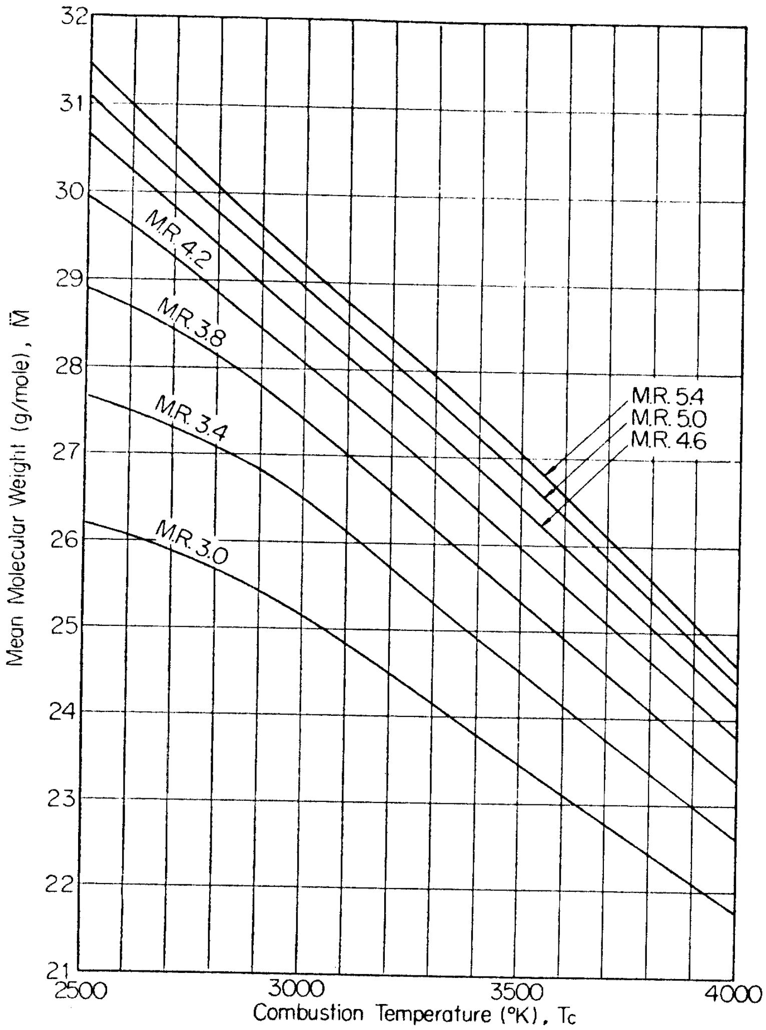

FIG. 6. Mean Molecular Weight of $(CH_3)_2NNH_2:N_2H_4(1:1)\sim ClF_3$ System vs. Combustion Temperature and Mixture Ratio (P_c=20 atm.).

$$CCl=C+Cl \qquad (Cl)\cdot(C)/(CCl)=aK_6 \tag{11}$$

$$CF_4=CF_3+F \qquad (CF_3)\cdot(F)/(CF_4)=aK_7 \tag{12}$$

$$CF_3=CF_2+F \qquad (CF_2)\cdot(F)/(CF_3)=aK_8 \tag{13}$$

$$CF_2=CF+F \qquad (CF)\cdot(F)/(CF_2)=aK_9 \tag{14}$$

$$CF=C+F \qquad (C)\cdot(F)/(CF)=aK_{10}\,. \tag{15}$$

Calculation method and results.—Representing all the reaction products by the function, $x=(H_2)^{\frac{1}{2}}/(HF)$, the following equations are obtained;

$$(F)_i=a^{\frac{1}{2}}K_4/x \tag{16}$$

$$(N_2)=\frac{4(N_0)+aK_3^2-K_3[8a(N_0)]^{\frac{1}{2}}}{8} \tag{17}$$

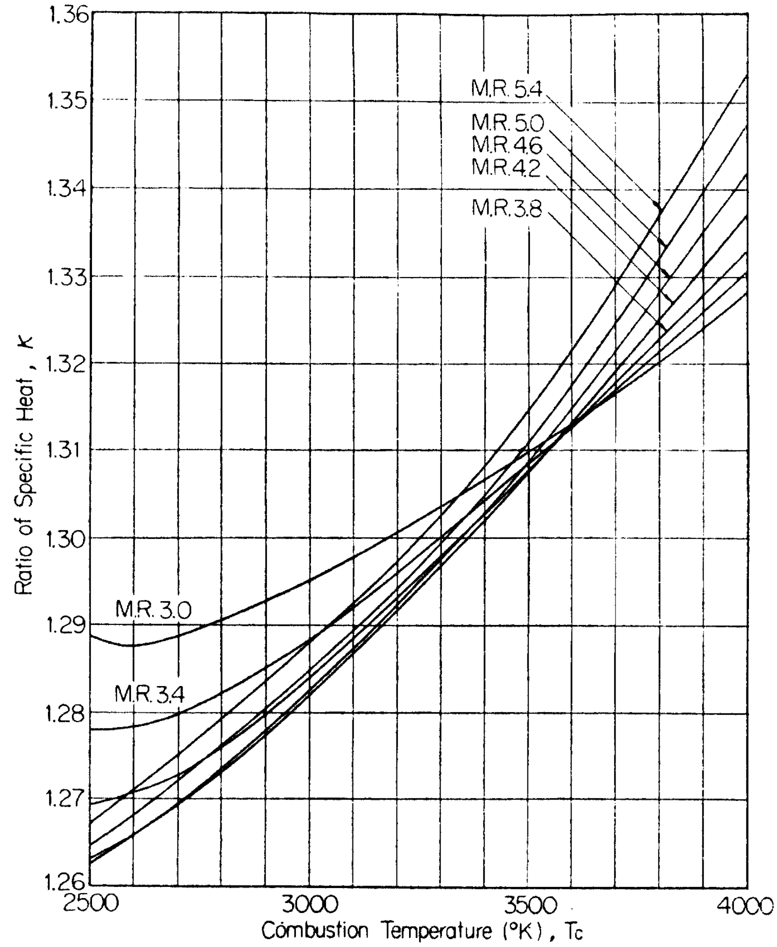

FIG. 7. Ratio of Specific Heat of $(CH_3)_2NNH_2 : N_2H_4(1 : 1) \sim ClF_3$ System vs. Combustion Temperature and Mixture Ratio ($P_c=20$ atm.).

$$(N)=a^{\frac{1}{2}}K_3\cdot(N_2)^{\frac{1}{2}} \tag{18}$$

$$(CF_3)_i=a^{\frac{1}{2}}xK_7(CF_4)_{i-1}/K_4 \tag{19}$$

$$(CF_2)_i=a^{\frac{1}{2}}xK_8(CF_3)_i/K_4 \tag{20}$$

$$(CF)_i=a^{\frac{1}{2}}xK_9(CF_2)_i/K_4 \tag{21}$$

$$(C)_i=a^{\frac{1}{2}}xK_{10}(CF)_i/K_4 \tag{22}$$

$$(CF_4)_i=(C_0)-[(CF_3)_i+(CF_2)_i+(CF)_i+(C)_i+(CCl)_{i-1}] \tag{23}$$

$$(HF)_i=(F_o)-[(F)_i+(CF)_i+2(CF_2)_i+3(CF_3)_i+4(CF_4)_i] \tag{24}$$

$$(H_2)_i=x^2\cdot(HF)_i^2 \tag{25}$$

$$(H)_i=a^{\frac{1}{2}}\cdot x\cdot K_1(HF)_i \tag{26}$$

$$(HCl)_i=\frac{(H_2)_i^{\frac{1}{2}}}{4K_6^2}\{[aK_2^2\cdot K_5^2+2a^{\frac{1}{2}}(H_2)_i^{\frac{1}{2}}\cdot K_2\cdot K_5+(H_2)_i + 8K_5^2\cdot[(Cl_o)-(CCl)_{i-1}]]^{\frac{1}{2}}-[a^{\frac{1}{2}}K_2\cdot K_5+(H_2)_i^{\frac{1}{2}}]\} \tag{27}$$

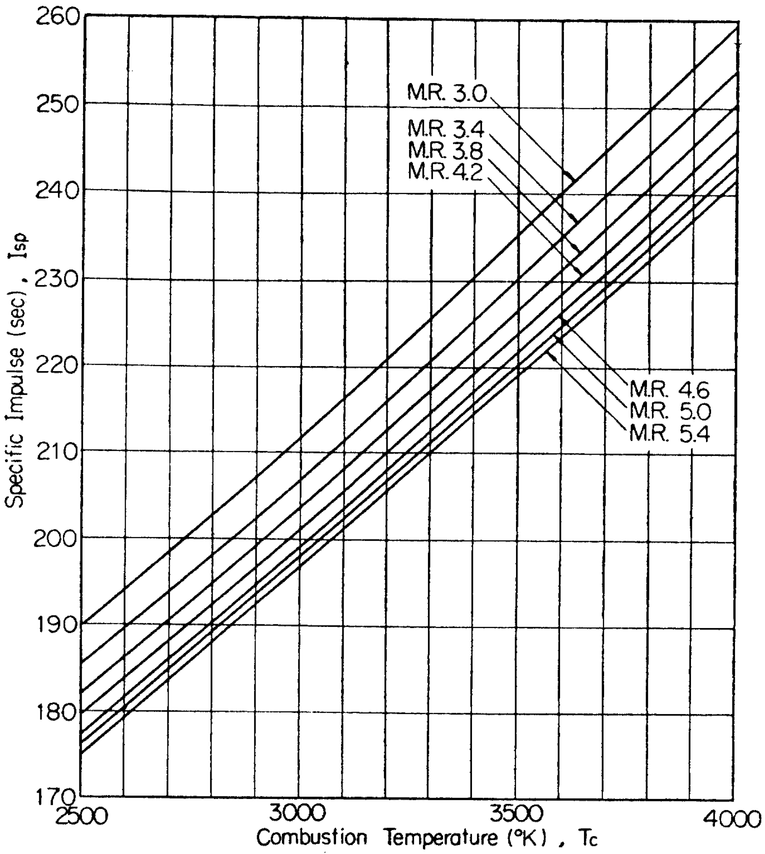

FIG. 8. Specific Impulse of $(CH)_2NNH_2:N_2H_4(1:1)\sim ClF_3$ System vs. Combustion Temperature and Mixture Ratio $P_c=20$ atm.).

$$(Cl)_i = a^{\frac{1}{2}}K_2\cdot K_6\cdot(HCl)_i/(H_2)_i^{\frac{1}{2}} \tag{28}$$

$$(Cl_2)_i = (HCl)_i^2\cdot K_5^2/(H_2)_i^{\frac{1}{2}} \tag{29}$$

$$(CCl)_i = (C)_i\cdot(Cl)_i/aK_6\,. \tag{30}$$

The conformity of results obtained with the following relation is checked for given values of a and x,

$$|1-(CCl)_{i-1}/(CCl)_i| < \epsilon\,. \tag{31}$$

If Eq. (31) is not satisfied, computation is repeated from Eq. (16) using $(CF_4)_i$ and $(CCl)_i$ in place of $(CF_4)_{i-1}$ and $(CCl)_{i-1}$. As the relation of Eq. (31) is fulfilled, then, a and x are revised. Inserting Eq. (16)$\sim$(30) into Eq. (1)$\sim$(5), the following equation is obtained;

$$f_1(a,x) = [(H_o)+4(C_o)+(F)_i+(Cl)_i+2(Cl_2)_i] - [(F_o) + (Cl_o)+(H)_i+2(H_2)_i+3(CCl)_i+3(CF)_i+2(CF_2)_i + (CF_3)_i+4(C)_i] = 0\,. \tag{32}$$

According to the assumption, product gases obey the ideal gas equation,

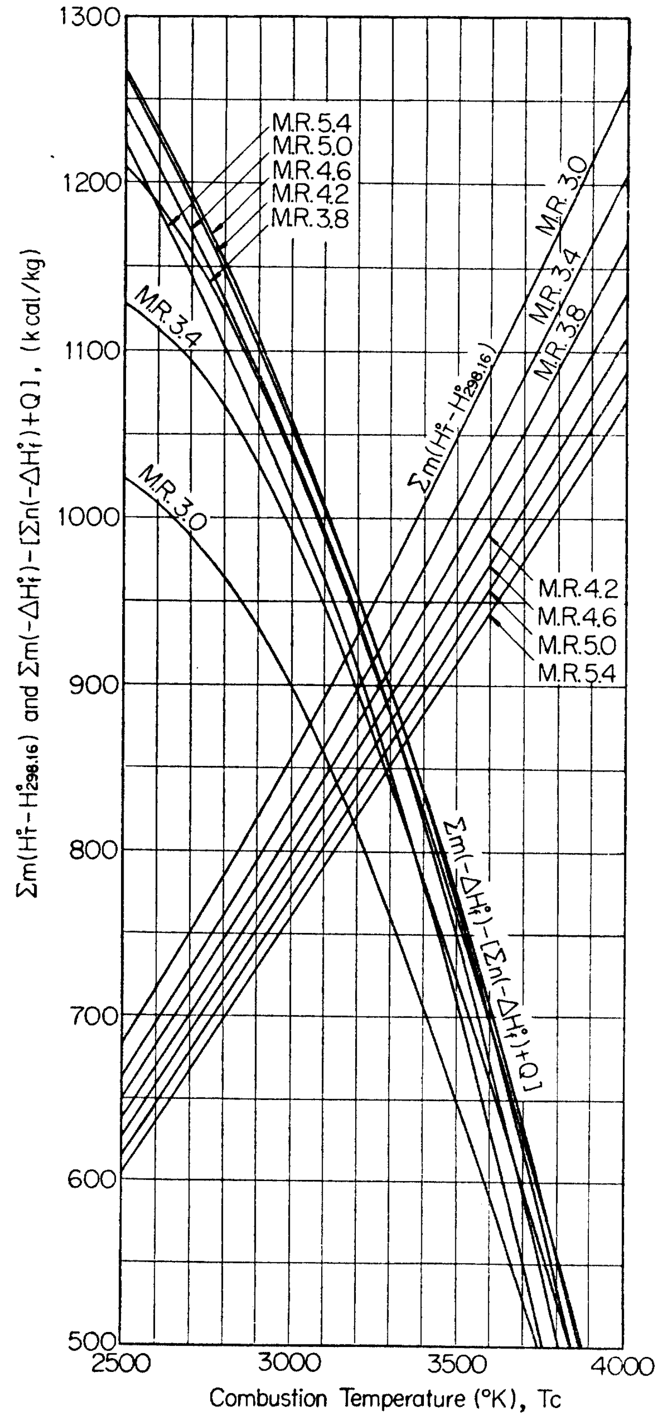

Fig. 9. Chart for Determination of Combustion Temperature on $(CH_3)_2NNH_2 : N_2H_4(1:1) \sim ClF_3$ System.

$$f_2(a,x) = a - \frac{T_c}{273.16}(22.414)(1/P_c)\sum m = 0\,, \tag{33}$$

where a and x must satisfy Eq. (32) and (33), if solved strictly.

Giving $(H_2)^{\frac{1}{2}}/(HF)$ and specific volume, then the number of moles of all

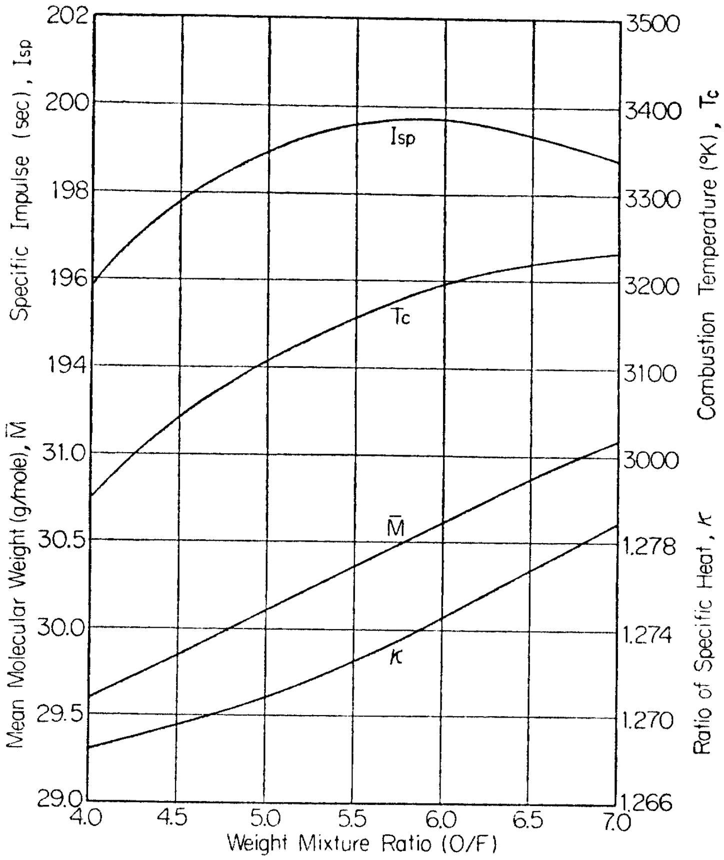

Fig. 10. **Theoretical Performance of $(CH_3)NNH_3 \sim ClF_3$ System ($P_c=20$ atm.).**

products can be calculated.

Namely,

$$\sum m=(HF)_i+(F)_i+(CF_4)_i+(CF_3)_i+(CF_2)_i+(CF)_i +(C)_i+(H_2)_i+(H)_i+(Cl)_i+(HCl)_i+(Cl_2)_i +(CCl)_i+(N_2)+(N)\,. \tag{34}$$

Now, as the strict solution of Eq. (32) and (33) of the simultaneous type, is not simple, the programing is chosen as the computer could find values for given value of a and x which satisfy Eq. (35) within the limits of the accuracy of the computer's accumulator,

$$F(a,x)<\epsilon\ , \tag{35}$$

$$\text{where}\quad F(a,x)=|f_1|+|f_2|\ . \tag{36}$$

Flow chart is shown in Fig. 1 which explains the procedure for computing by the method stated above.

Between the concentration equilibrium constant K and the pressure equilibrium constant K_p, the following relation exists for 100 g of propellant;

$$K=\left(\frac{1.2181}{T}\right)^{m_1+m_2+m_3+\dots-n_1-n_2-n_3-\dots}\cdot\ e^{-\Delta F_T^0 R/T}\,. \tag{37}$$

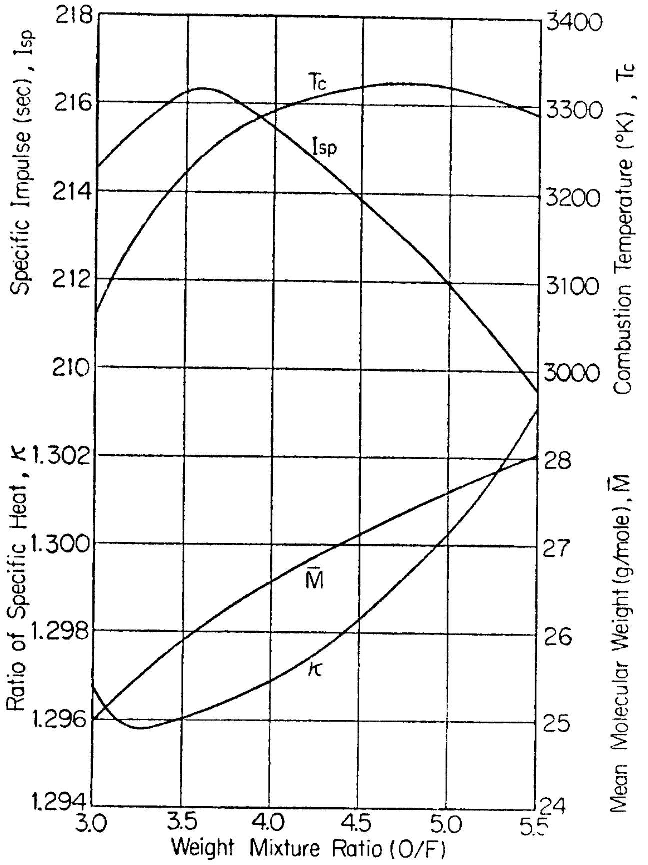

FIG. 11. Theoretical Performances of $(CH_3)_2NNH_2:N_2H_4(1:1)\sim ClF_3$ System (P_c=20 atm.).

For the chemical relation,

$$n_1A_1+n_2A_2+n_3A_3+\cdots=m_1B_1+m_2B_2+m_3B_3+\cdots, \tag{38}$$

the concentration equilibrium constant K is given by

$$K(a)^{m_1+m_2+m_3+\cdots-n_1-n_2-n_3-\cdots}=\frac{(B_1)^{m_1}\cdot(B_2)^{m_2}\cdot(B_3)^{m_3}\cdots}{(A_1)^{n_1}\cdot(A_2)^{n_2}\cdot(A_3)^{n_3}\cdots}. \tag{39}$$

As the pressure equilibrium constant K_p has the following relation,

$$K_p=e^{-\Delta F_T^0/RT}, \tag{40}$$

the concentration equilibrium constant K is given by

$$K=\left(\frac{1.2181}{T}\right)^{m_1+m_2+m_3+\cdots-n_1-n_2-n_3-\cdots}\times K_p. \tag{41}$$

Since, the following relation should be held,

$$\sum m(H^0_{T_c}-H^0_{298.16})=\sum m(-\Delta H^0_f)-[\sum n(-\Delta H^0_f)+Q]. \tag{42}$$

The intercepted point of two lines, $\sum n(H^0_{T_c}-H^0_{298.16})$ and $\sum m(-\Delta H^0_f)-[\sum n(-\Delta H^0_f)+Q]$ versus temperature, gives the combustion temperature. Mean molecular weight and ratio of specific heat given by gas composition is shown in Fig. 2, 3, 6 and 7.

Because the boiling point of chlorine trifluoride is lower than standard temperature, convections for the heat of vaporization and the heat capacity of vapor given by Eq. (43) is required,

$$Q=n_x\int_{T_{b.p.}}^{298.16} C_p dT+n_x(\Delta H_v)\,. \tag{43}$$

As the combustion temperature is determined, specific impulse is given by the conventional energy equation;

$$I_{sp}=\sqrt{\frac{2\kappa RT_c}{g(\kappa-1)\bar{M}}\left[1-\left(\frac{P_e}{P_c}\right)^{\kappa-1/\kappa}\right]}\,. \tag{44}$$

Fig. 3 and 4 show the results of specific impulse calculated by Eq. (44) versus weight mixture ratio and temperature of propellant. Fig. 9 and 10 represent the relation of specific impulse, combustion temperature, mean molecular weight and ratio of specific heat versus weight mixture ratio.

Heat capacity and ratio of specific heat are derived from Eq. (45) and (46).

$$C_p=\frac{\sum(m\cdot C_p^0)}{\sum m} \tag{45}$$

and

$$\kappa=\frac{1}{1-R/C_p}\,. \tag{46}$$

Since thermodynamic data for the carbon fluoride systems are not easily available, entropy, enthalpy and heat capacity are estimated by additivity rule developed by S. Benson and J. Buss [5] and the pressure equilibrium constants of these are calculated by Eq. (47),

$$\ln K_p=\frac{\sum m(S_T^0)-\sum n(S_T^0)}{R}-\frac{\sum m(H_T^0)-\sum n(H_T^0)}{RT}\,. \tag{47}$$

For the other thermodynamic data those presented in Ref. 6–10 are used.

CONCLUSION

The results of computation are shown in Fig. 9 and 10 and the following maximum performances are obtained:

(1) For $(CH_3)_2NNH_2$~ClF_3 propellant system at weight mixture ratio 5.75, the maximum specific impulse 199.73 sec., combustion temperature 3,176°K, mean molecular weight 30.55, and ratio of specific heat 1.2740 are obtained.

(2) For $(CH_3)_2NNH_2 : N_2H_4$ (1 : 1)~ClF_3 propellant system at weight mixture ratio 3.575, maximum specific impulse 216.33 sec., combustion tempera-

ture 3,235°K, mean molecular weight 26.02, and ratio of specific heat 1.2961 are obtained.

These performances are rather poor in comparison with performances given in Ref. 1 and 2. The lower combustion temperatures should be attributed to the fact neglecting the effect of graphite and C_2F_2 as combustion products. This in turn depreciate the final performance values. However, according to the results of Ref. 11, graphite and C_2F_2 are produced in large quantity especially at fuel rich side.

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