RESEARCH MEMORANDUM

THEORETICAL PERFORMANCE OF LITHIUM AND FLUORINE AS A ROCKET PROPELLANT

By Sanford Gordon and Vearl N. Huff

Lewis Flight Propulsion Laboratory
Cleveland, Ohio

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

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SUMMARY

Theoretical values of performance parameters for liquid lithium and liquid fluorine as a rocket propellant were calculated with the assumptions both of equilibrium composition and of frozen composition during the expansion process for a wide range of fuel-oxidant ratios, combustion pressures, and expansion ratios. The parameters included were specific impulse, combustion-chamber temperature, nozzle-exit temperature, composition, mean molecular weight, characteristic velocity, coefficient of thrust, and ratio of nozzle-exit area to throat area.

For a chamber pressure of 300 pounds per square inch absolute and an exit pressure of 1 atmosphere, the maximum equilibrium specific impulse value calculated was 335.5 pound-seconds per pound at a weight percent of fuel in mixture of 31.35.

The effect of ionization on the calculated performance was shown to be negligible by a comparison of values of various parameters calculated both with and without ionized substances as products of combustion.

INTRODUCTION

Liquid lithium and liquid fluorine are of interest as a rocket propellant because the thrust per unit flow rate is the highest known except for some propellants having liquid hydrogen as a fuel. A compendium of information concerning lithium is given in reference 1 and information concerning fluorine is presented in reference 2. Availability of raw materials for the production of lithium and fluorine as well as additional information concerning these substances is presented in reference 3. Values of specific impulse and combustion-chamber temperature for the lithium-fluorine combination for three fuel-oxidant ratios are presented in references 4 and 5. The values of reference 4 appear to be too high. The difference between the values presented herein and those of reference 5 is primarily due to the selection of a lower value for the dissociation energy of F_2 for the present report.

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Further calculations were made at the NACA Lewis laboratory during 1950 to determine a larger number of performance parameters over a wider range of conditions than previously published and to determine the effect of ionization on performance of lithium and fluorine as a rocket propellant; the results are presented herein. The data, which were computed with the assumptions both of equilibrium composition and of frozen composition during the expansion process, cover a wide range of mixture ratios and include values of specific impulse, combustion-chamber temperature, nozzle-exit temperature, composition, mean molecular weight, characteristic velocity, coefficient of thrust, and ratio of nozzle-exit area to throat area as functions of mixture ratio. Values of specific impulse and temperature are also presented for two chamber pressures and several expansion ratios for the stoichiometric mixture.

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Because of the relatively low ionization potential of lithium (5.37 electron volts, reference 6), ionized lithium Li^+, electron gas e^-, and the negative ion of fluorine F^- may be formed as combustion products of lithium and fluorine. The effect of ionization is shown by a comparison of values of various parameters calculated both with and without ionized products of combustion.

SYMBOLS

The following symbols are used in this report:

$\frac{A_e}{w}$ nozzle-exit area per unit flow rate, (sq ft/lb/sec)

$\frac{A_e}{A_t}$ ratio of nozzle-exit area to throat area

$\frac{A_t}{w}$ throat area per unit flow rate, (sq ft/lb/sec)

a velocity of sound, (ft/sec)

C_F coefficient of thrust

c^* characteristic velocity, (ft/sec)

g acceleration due to gravity, 32.174 (ft/sec^2)

$(H_T^O)_i$ sum of sensible enthalpy and chemical energy of product i, (kcal/mole)

h	enthalpy per unit weight, (kcal/gram)
h_c	enthalpy per unit weight in combustion chamber, (kcal/gram)
h_e	enthalpy per unit weight at nozzle exit, (kcal/gram)
I	specific impulse, (lb-sec/lb)
M	mean molecular weight, (gram/mole)
M_c	mean molecular weight in combustion chamber, (gram/mole)
M_e	mean molecular weight at nozzle exit, (gram/mole)
M_t	mean molecular weight at nozzle throat, (gram/mole)
n	total number of moles
n_i	moles of product i
P_e	pressure at nozzle exit, (atm)
P_t	pressure at nozzle throat, (atm)
p_c	pressure in combustion chamber, (lb/sq ft)
R	universal gas constant, 1.98718 (cal/(mole)($^{\circ}$K))
T_c	temperature in combustion chamber, ($^{\circ}$K)
T_e	temperature at nozzle exit, ($^{\circ}$K)
T_t	temperature at nozzle throat, ($^{\circ}$K)
γ_t	ratio of average specific heat at constant pressure to average specific heat at constant volume (at throat)

METHOD OF CALCULATION

The equilibrium composition and the temperature in the combustion chamber and at the nozzle exit were computed by the method described in reference 7 using the thermodynamic tables of reference 8. The calculations were based on the following usual assumptions: perfect gas laws, adiabatic combustion at constant pressure, isentropic expansion, no friction, homogeneous mixing, and one-dimensional flow.

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The products of combustion were assumed to be gases and included the following substances: lithium fluoride LiF, fluorine F_2, ionized lithium Li^+, ionized fluorine F^-, lithium Li, monatomic fluorine F, and electron gas e^-. The liquid or solid phases of lithium and lithium fluoride were not included among the products of combustion inasmuch as they would not appear except in extremely fuel-rich mixtures or for very large expansion ratios.

The formulas used in computing the various parameters are as follows:

Specific impulse. - Specific impulse was calculated from the difference in enthalpy between the combustion chamber and the nozzle exit by the equation

$$I = 294.98 \sqrt{h_c - h_e} \tag{1}$$

where

$$h = \frac{\sum_i n_i \, (H_T^o)_i}{n\,M} \quad \text{(kcal/gram)}$$

Throat area per unit flow rate. - For equilibrium composition during expansion, the throat area per unit flow rate was obtained from the continuity equation and becomes

$$\left(\frac{A_t}{w}\right)_{equilibrium} = \frac{1.3144(T_t)}{P_t \, M_t \, a} \tag{2}$$

The velocity of sound and the conditions at the nozzle throat for equilibrium composition during expansion were determined by the method described in reference 7.

For frozen composition during expansion, the continuity and velocity-of-sound equations yield

$$\left(\frac{A_t}{w}\right)_{frozen} = \frac{0.0043937}{P_t} \sqrt{\frac{T_t}{M_t \, \gamma_t}} \tag{3}$$

Characteristic velocity. - The equation for characteristic velocity for a combustion pressure of 300 pounds per square inch absolute becomes

$$c^* = g \, p_c \, \frac{A_t}{w} = 1.3899 \times 10^6 \, \frac{A_t}{w} \tag{4}$$

Coefficient of thrust. - The coefficient of thrust was obtained from the defining equation

$$C_F = \frac{Ig}{c^*} = 32.174 \frac{I}{c^*} \qquad (5)$$

Area ratios. - In order to calculate ratio of nozzle-exit area to throat area A_e/A_t, values of the nozzle-exit area per unit flow rate were first obtained from the following equation:

$$\left(\frac{A_e}{w}\right) = \frac{0.040853\ T_e}{P_e\ M_e\ I} \qquad (6)$$

THERMOCHEMICAL AND THERMODYNAMIC DATA

Thermochemical and thermodynamic data for the products of combustion were taken from reference 8. The heats of formation contained in these data are listed in the following table:

		Heat of formation, ΔH_f (kcal/mole)	
Substance	Phase	0° K	298.16° K
F	Gas	17.8	---------
F_2	Gas	0	0
e^-	Gas	0	0
F^-	Gas	-78.5	--------
Li^+	Gas	-----	161.4664
Li	Gas	-----	36.150
LiF	Gas	-----	-83.760

The values of specific heat in reference 8 were taken as $\frac{5}{2}$ R for e^-, F^-, and Li^+ and were computed from spectroscopic data by the accurate summation method for F and Li, and by rigid rotator-harmonic-oscillator approximation for F_2 and LiF. Values of sensible enthalpy $H_T^O - H_O^O$ and entropy S_T^O were numerically integrated from the specific-heat function. Inasmuch as spectroscopic data for LiF were not found in the literature, the thermodynamic functions for LiF given in reference 8 were computed from an estimated value for the vibrational frequency. It is expected that the anharmonicities for LiF are sufficiently large to affect materially the computed values of the thermodynamic functions and could cause somewhat lower values of specific impulse. The data presented herein are computed to more figures than are entirely significant, but are considered sufficiently accurate until better thermodynamic data become available.

Physical and thermochemical properties of the propellants were taken from references 1 and 8 to 14 and are given in table I.

The value of 0.512 for the density of liquid lithium at 179° C was calculated from the value of 0.534 for the density of the solid at 20° C (reference 9), the thermal coefficient of cubical expansion (reference 10, p. 463), and the value of 1.5 percent for expansion on melting (reference 10, p. 474).

THEORETICAL PERFORMANCE

The calculated values of the various performance parameters of the lithium-fluorine combination for a combustion-chamber pressure of 300 pounds per square inch absolute and an exit pressure of 1 atmosphere are given in table II. The maximum values of frozen and equilibrium specific impulse occurred at 35.40 and 31.35 weight percent of fuel, respectively. Values of the various parameters corresponding to maximum specific impulse are shown as follows:

	Frozen composition	Equilibrium composition
Weight percent fuel	35.40	31.35
Propellant density, (gram/cc)	0.785	0.812
Combustion-chamber temperature, (°K)	4877	5055
Combustion-chamber mean molecular weight	18.32	19.21
Specific impulse, (lb-sec/lb)	308.8	335.5
Characteristic velocity, (ft/sec)	7211	7572
Coefficient of thrust	1.3779	1.4257
Ratio of nozzle-exit area to throat area	2.998	3.919
Nozzle-exit temperature, (°K)	2154	3756
Nozzle-exit mean molecular weight	18.32	21.42

The parameters are plotted in figures 1 and 2 against weight percent of fuel in the mixture. The quantities plotted in figure 1 are combustion-chamber temperature, nozzle-exit temperature, specific impulse, and mean molecular weight. The combustion-chamber temperature is high, reaching a maximum of 5139° K. The maximum difference between the curves of frozen and equilibrium specific impulse is approximately 9 percent of the equilibrium value at about 25 percent by weight of fuel in mixture.

The quantities plotted in figure 2 are characteristic velocity, coefficient of thrust, and ratio of nozzle-exit area to throat area. The maximum difference between the curves for frozen and equilibrium composition was approximately 6.1 percent for characteristic velocity, 3.5 percent for coefficient of thrust, and 25 percent for area ratio. The variation of coefficient of thrust and area ratio with fuel-oxidant ratio is many times greater for equilibrium composition than for frozen composition.

The compositions of the products of combustion in the combustion chamber and at the nozzle-exit are shown in figures 3(a) and 3(b), respectively. The ionized products of combustion comprise about 3.2 percent of the total in the combustion chamber for the region near the stoichiometric mixture and about 1.2 percent of the total at the nozzle exit.

The calculated values of various performance parameters for the stoichiometric mixture at combustion pressures of 300 and 900 pounds per square inch absolute for several expansion ratios are listed in table III. For constant combustion-chamber pressure, the effect of expansion ratio on specific impulse is shown in figure 4, where the data for a combustion-chamber pressure of 300 pounds per square inch absolute are plotted against expansion ratio. Increases of 36.2 and 22.7 percent in specific impulse for equilibrium and frozen composition, respectively, resulted from increasing the expansion ratio from 20.41 to 1021. On the basis of data in reference 15, it is expected that the effect of expansion ratio on specific impulse would be somewhat less for other fuel-oxidant ratios. For constant expansion ratio, the effect of combustion-chamber pressure on specific impulse can be found from table III. For an expansion ratio of 20.41, increases of 1.9 and 2.7 percent on specific impulse for equilibrium and frozen composition, respectively, resulted from increasing the combustion-chamber pressure from 300 to 900 pounds per square inch absolute.

EFFECT OF IONIZATION ON PERFORMANCE

In order to determine the effect of ionization on the performance parameters, a second set of calculations was made that omitted the ionized products and included only LiF, F_2, Li, and F as products of combustion. The results of these calculations for a combustion-chamber pressure of 300 pounds per square inch absolute and an exit pressure of 1 atmosphere are given in table II. The results for the stoichiometric mixture at combustion-chamber pressures of 300 and 900 pounds per square inch absolute for several expansion ratios are given in table III.

The effect of ionization on specific impulse is shown in figures 5 and 6. Curves of specific impulse calculated both with and without ionized products of combustion for both equilibrium and frozen composition during expansion are shown plotted against weight percent of fuel in figure 5 and against expansion ratio in figure 6. Curves of the difference in specific impulse between the values with and without ionized products of combustion are also shown.

The difference between the two sets of values of specific impulse in figure 5 was less than 1.2 pound-seconds per pound assuming equilibrium composition, and less than 2.0 pound-seconds per pound assuming frozen composition during expansion over the entire range of weight percent of fuel.

The difference between the two sets of values of specific impulse in figure 6 was less than 1.2 pound-seconds per pound assuming equilibrium composition and less than 2.2 pound-seconds per pound assuming frozen composition during expansion over the range of expansion ratios from 1 to 1021.

A comparison of the two sets of specific impulse values in table III for a combustion-chamber pressure of 900 pounds per square inch absolute shows a maximum reduction of 2.1 pound-seconds per pound due to ionization. Because this value is of the same magnitude as the reduction in performance due to ionization at a combustion-chamber pressure of 300 pounds per square inch absolute, it is therefore concluded that the effect of ionization on performance is negligible for practical operating conditions.

SUMMARY OF RESULTS

A theoretical investigation of the performance parameters of lithium and fluorine as a rocket propellant yielded the following results:

1. For a combustion-chamber pressure of 300 pounds per square inch absolute and an exit pressure of 1 atmosphere, specific impulse based on equilibrium composition reached a maximum value of 335.5 pound-seconds per pound at a weight percent of fuel in mixture of 31.35 percent, whereas the maximum value of specific impulse based on frozen composition was 308.8 pound-seconds per second at a weight percent of fuel in mixture of 35.40 percent.

2. The maximum combustion temperature for a chamber pressure of 300 pounds per square inch absolute was 5139° K.

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3. An increase in expansion ratio from 20.41 to 1021 with a chamber pressure of 300 pounds per square inch absolute resulted in a 22.7 percent increase in equilibrium specific impulse for the stoichiometric mixture.

4. At an expansion ratio of 20.41, an increase in chamber pressure from 300 to 900 pounds per square inch absolute resulted in a 1.9 percent increase in equilibrium specific impulse for the stoichiometric mixture.

5. Although ionized products of combustion constituted up to 3.2 percent of the total combustion products, the maximum reduction in specific impulse due to ionization was less than 2.2 pound-seconds per pound over a wide range of fuel-oxidant ratios, chamber pressures, and expansion ratios. It is therefore concluded that the effect of ionization on the performance of the lithium-fluorine propellant combination is negligible.

Lewis Flight Propulsion Laboratory,
National Advisory Committee for Aeronautics,
Cleveland, Ohio.

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TABLE I - PHYSICAL-CHEMICAL PROPERTIES OF PROPELLANTS

[Temperatures in superscripts, °C.]

Propellants	Molecular weight M	Density (gram/cc)	Freezing point (°C)	Boiling point (°C)	Viscosity (centipoises)	Enthalpy of formation ΔH_f (kcal/mole)	Enthalpy of vaporization ΔH (kcal/mole)	Enthalpy of fusion ΔH (kcal/mole)
Lithium	6.940	(liquid) [a]0.512^{179}	[b]179	[c]1326	[d]0.6 ± 0.1^{180}	(liquid) [e]2.305	[f]32.365^{1326}	[b]1.1^{179}
Fluorine	38.000	(liquid) [g]1.14^{-200}	[h]-217.96	[h]-187.92	------------	(liquid) [e]-3.030	[h]$1.51^{-187.92}$	[h]$0.372^{-217.96}$

[a]Calculated from data of references 9 and 10.
[b]Reference 11.
[c]Reference 12.
[d]Reference 1.
[e]Reference 8.
[f]Reference 13.
[g]Reference 10.
[h]Reference 14.

TABLE II - CALCULATED PERFORMANCE OF LITHIUM AND FLUORINE

[Combustion-chamber pressure, 300 lb/sq in. absolute; exit pressure, 1 atmosphere.]

Fuel (percent by weight)	Propellant density (gram/cc)	Combustion chamber		Frozen composition					Equilibrium composition					
		Temperature T_c (°K)	Mean molecular weight M_c	Specific impulse I (lb-sec/lb)	Characteristic velocity c* (ft/sec)	Coefficient of thrust C_F	Ratio of nozzle-exit area to throat area A_e/A_t	Temperature at nozzle exit T_e (°K)	Specific impulse I (lb-sec/lb)	Characteristic velocity c* (ft/sec)	Coefficient of thrust C_F	Ratio of nozzle-exit area to throat area A_e/A_t	Temperature at nozzle exit T_e (°K)	Mean molecular weight at nozzle exit M_e
Including ionized products of combustion														
15.44	0.939	4599	22.05	269.1	----	----	----	1910	278.2	----	----	----	2140	22.48
20.36	.896	5056	21.40	288.5	6742	1.3771	2.957	2168	315.9	7179	1.4156	3.774	3564	23.65
24.74	.860	5139	20.56	298.1	----	----	----	2240	327.5	----	----	----	3904	23.14
[a]26.75	.845	5136	20.16	301.4	7036	1.3782	2.991	2252	330.9	7454	1.4283	3.974	3917	22.70
28.66	.831	5115	19.77	304.1	----	----	----	2252	333.4	----	----	----	3888	22.21
31.35	.812	5055	19.21	307.0	7166	1.3784	3.002	2234	335.5	7572	1.4257	3.919	3756	21.42
35.40	.785	4877	18.32	308.8	7211	1.3779	2.998	2154	331.9	7590	1.4068	3.503	3044	19.60
39.00	.762	4548	17.42	305.1	7131	1.3765	2.973	1985	315.4	7358	1.3792	3.081	2241	17.80
42.21	.743	3935	16.40	290.5	----	----	----	1669	292.1	----	----	----	1698	16.44
47.73	.712	2423	14.54	238.2	----	----	----	957	238.2	----	----	----	957	14.54
Excluding ionized products of combustion														
15.44	0.939	4664	22.10	270.9	----	----	----	1941	278.5	----	----	----	2133	22.48
20.36	.896	5117	21.42	290.3	6780	1.3776	2.959	2198	317.0	7185	1.4195	3.762	3574	23.69
24.74	.860	5197	20.57	299.8	----	----	----	2269	328.6	----	----	----	3923	23.18
[a]26.75	.845	5194	20.17	303.2	7079	1.3779	2.992	2280	332.0	7495	1.4254	3.952	3936	22.73
28.66	.831	5174	19.78	305.9	----	----	----	2280	334.6	----	----	----	3906	22.25
31.35	.812	5114	19.23	308.8	7210	1.3779	3.002	2263	336.7	7605	1.4244	3.900	3774	21.46
35.40	.785	4939	18.35	310.7	7254	1.3780	3.001	2186	332.9	7631	1.4037	3.455	3030	19.60
39.00	.762	4612	17.47	307.0	7173	1.3772	2.981	2020	315.9	7385	1.3762	3.054	2233	17.80
42.21	.743	3963	16.42	291.5	----	----	----	1683	292.2	----	----	----	1695	16.44
47.73	.712	2423	14.54	238.2	----	----	----	957	238.2	----	----	----	957	14.54

[a]Stoichiometric.

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TABLE III - CALCULATED PERFORMANCE PARAMETERS OF LITHIUM AND FLUORINE AT VARIOUS PRESSURES FOR STOICHIOMETRIC RATIO

Nozzle-exit pressure P_e (atm)	Expansion ratio	Frozen composition		Equilibrium composition		
		Specific impulse I (lb-sec/lb)	Temperature at nozzle exit T_e (°K)	Specific impulse I (lb-sec/lb)	Temperature at nozzle exit (°K)	Mean molecular weight at nozzle exit M_e
Including ionized products of combustion P_c = 300 lb/sq in. absolute; T_c = 5136° K; M_c = 20.16						
5	4.083	227.3	3515	237.5	4504	21.37
1	20.41	301.4	2252	330.9	3917	22.70
.2	102.1	340.4	1434	391.5	3422	23.93
.02	1021	369.7	740	450.8	2762	25.40
Including ionized products of combustion P_c = 900 lb/sq in. absolute; T_c = 5484° K; M_c = 20.52						
3	20.41	309.6	2440	337.2	4093	23.09
1	61.24	339.7	1803	381.0	3701	23.95
Excluding ionized products of combustion P_c = 300 lb/sq in. absolute; T_c = 5194° K; M_c = 20.17						
5	4.083	228.5	3559	238.5	4539	21.39
1	20.41	303.2	2280	332.0	3936	22.73
.2	102.1	342.4	1452	392.6	3430	23.97
.02	1021	371.8	750	451.7	2756	25.42
Excluding ionized products of combustion P_c = 900 lb/sq in. absolute; T_c = 5550° K; M_c = 20.54						
3	20.41	311.6	2475	338.4	4112	23.13
1	61.24	341.8	1829	382.1	3710	23.99

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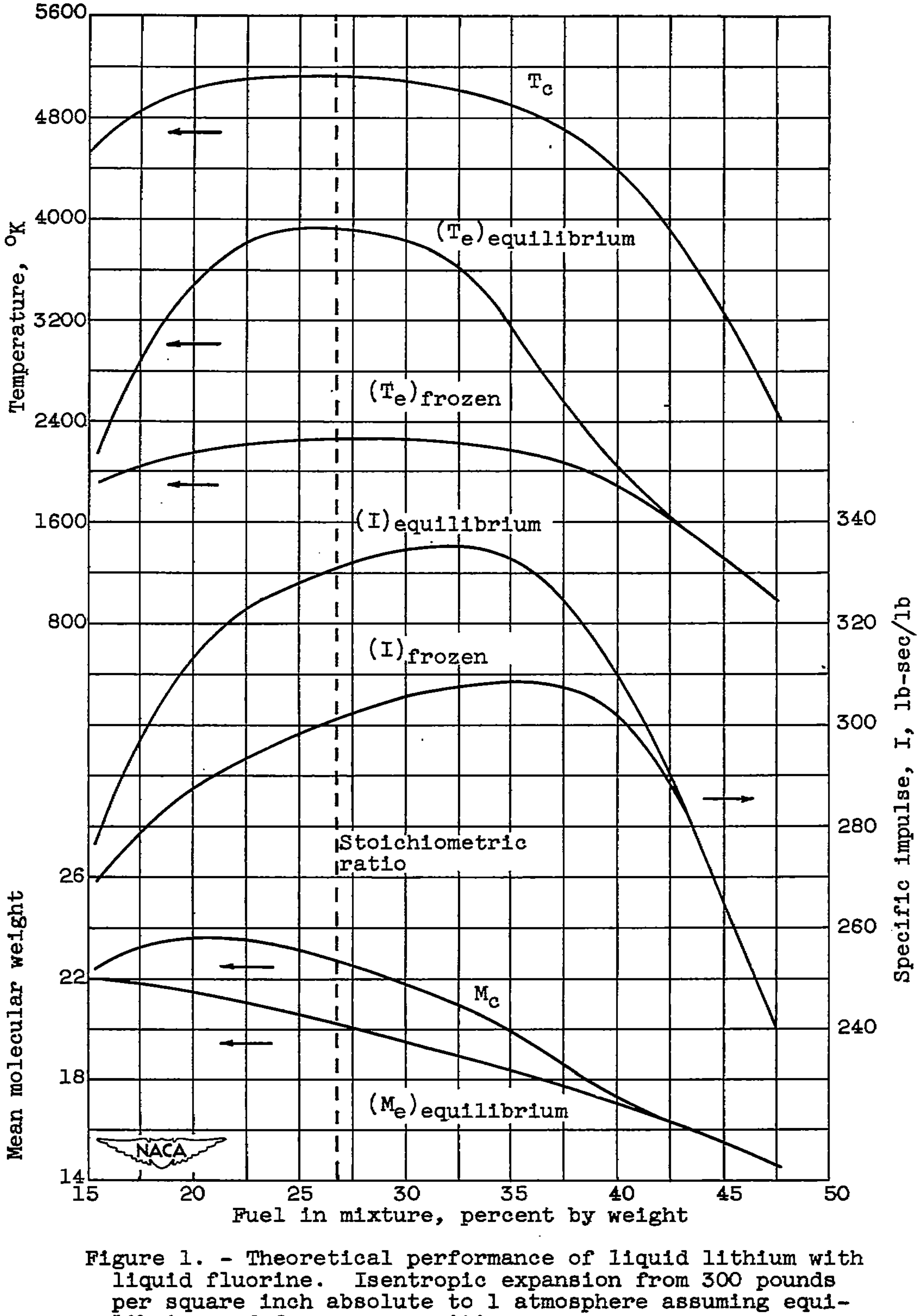

Figure 1. - Theoretical performance of liquid lithium with liquid fluorine. Isentropic expansion from 300 pounds per square inch absolute to 1 atmosphere assuming equilibrium and frozen composition.

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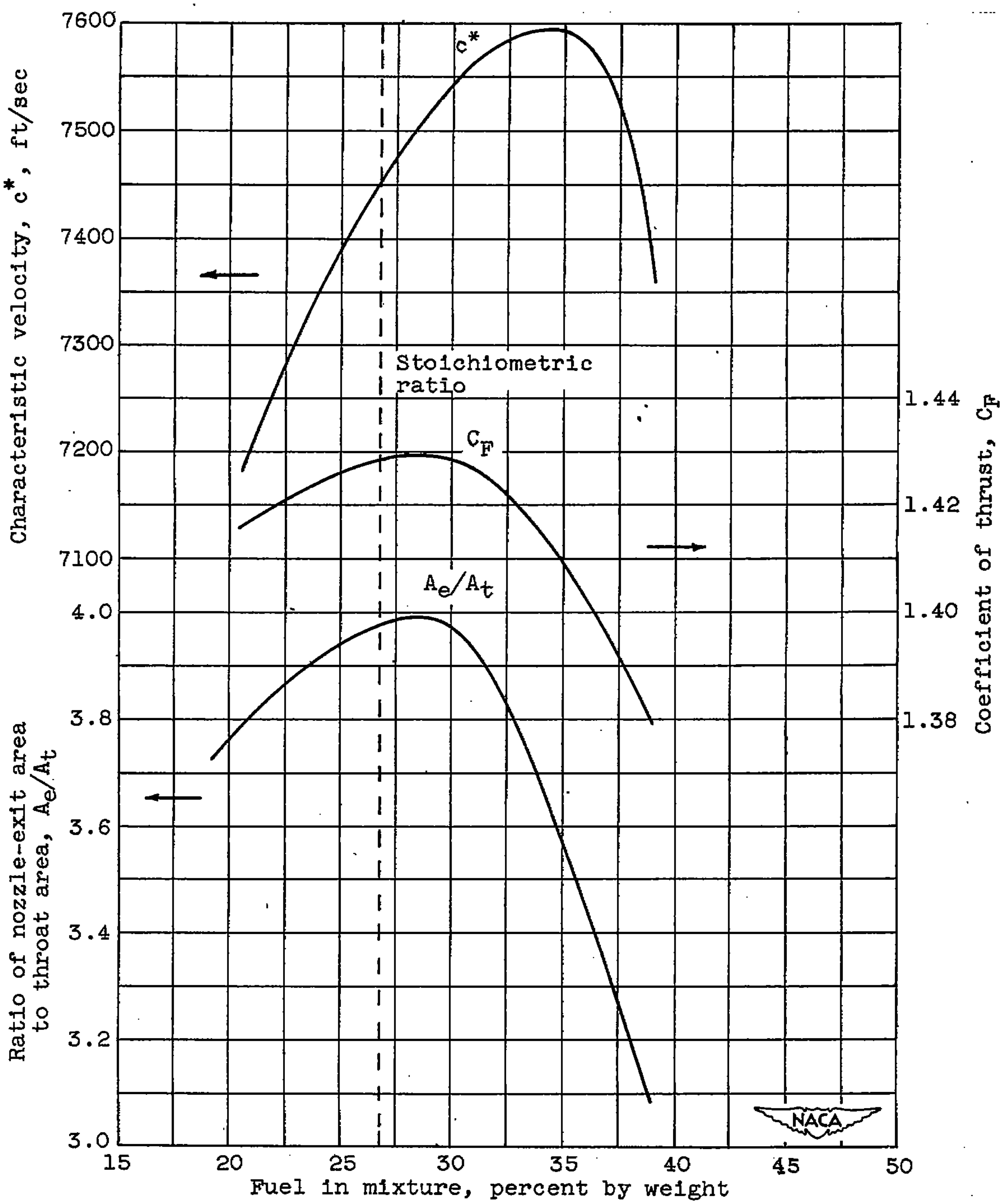
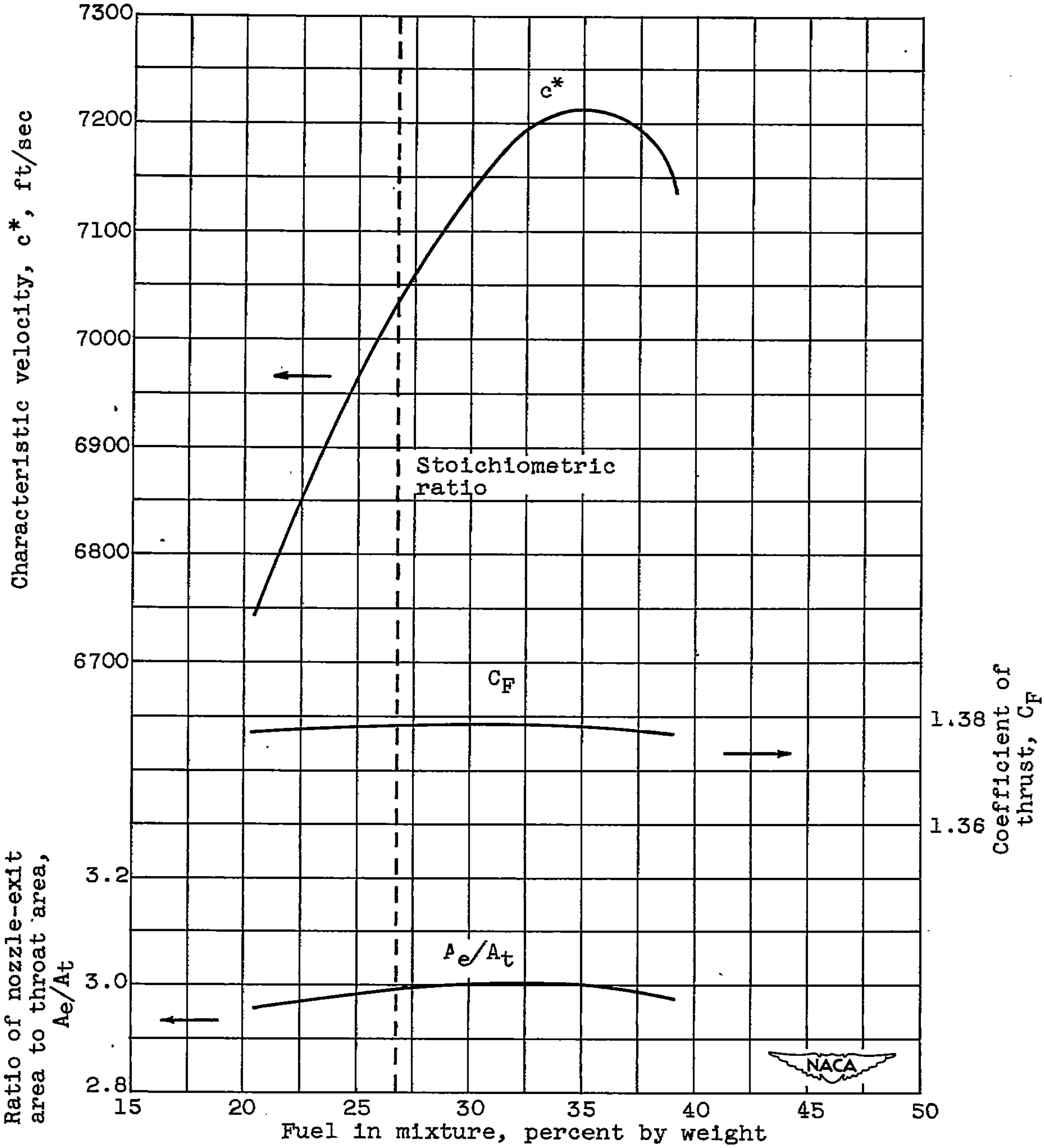


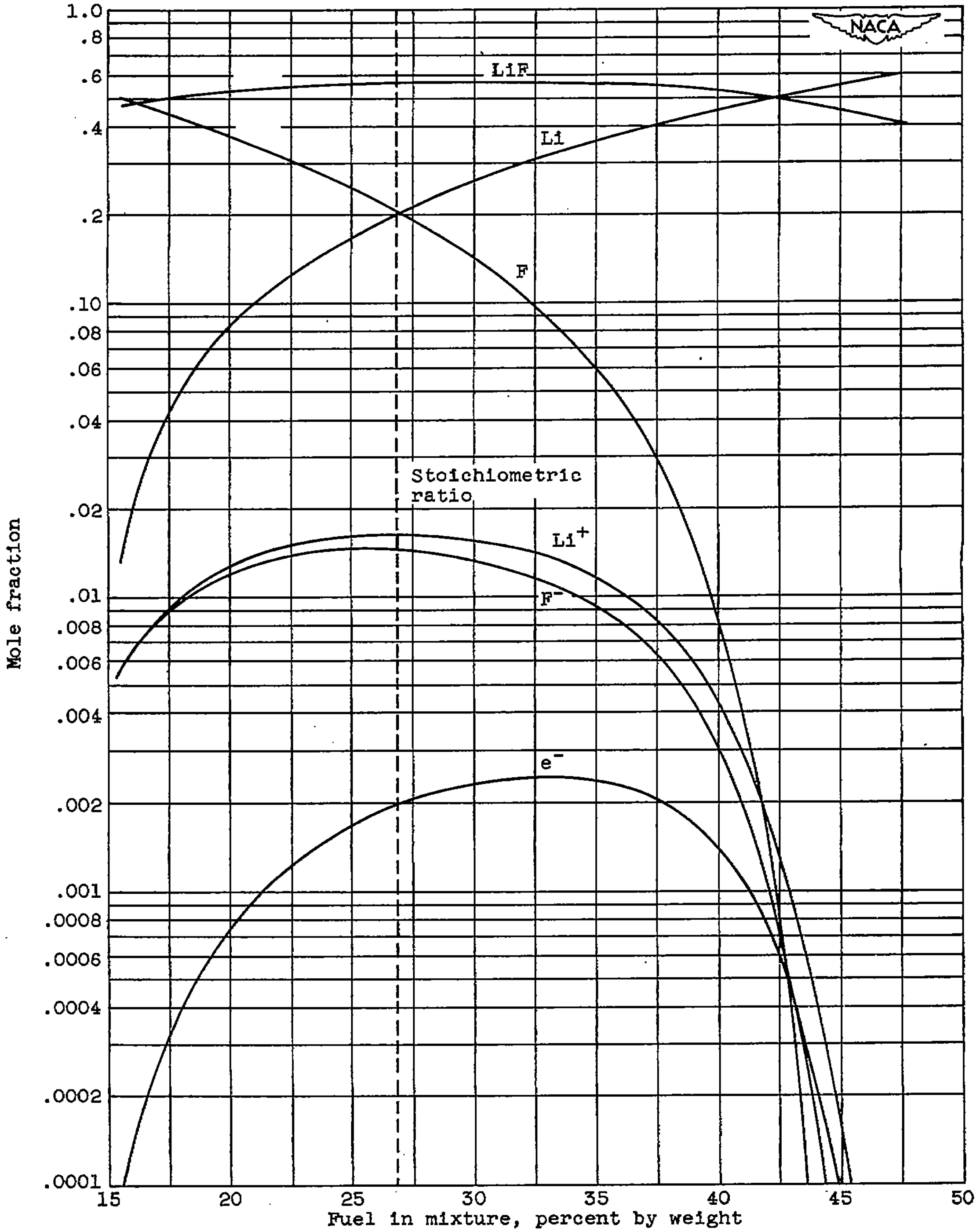
(a) Equilibrium composition.

Figure 2. - Theoretical characteristic velocity, coefficient of thrust, and area ratio of liquid lithium with liquid fluorine. Isentropic expansion from 300 pounds per square inch absolute to 1 atmosphere.



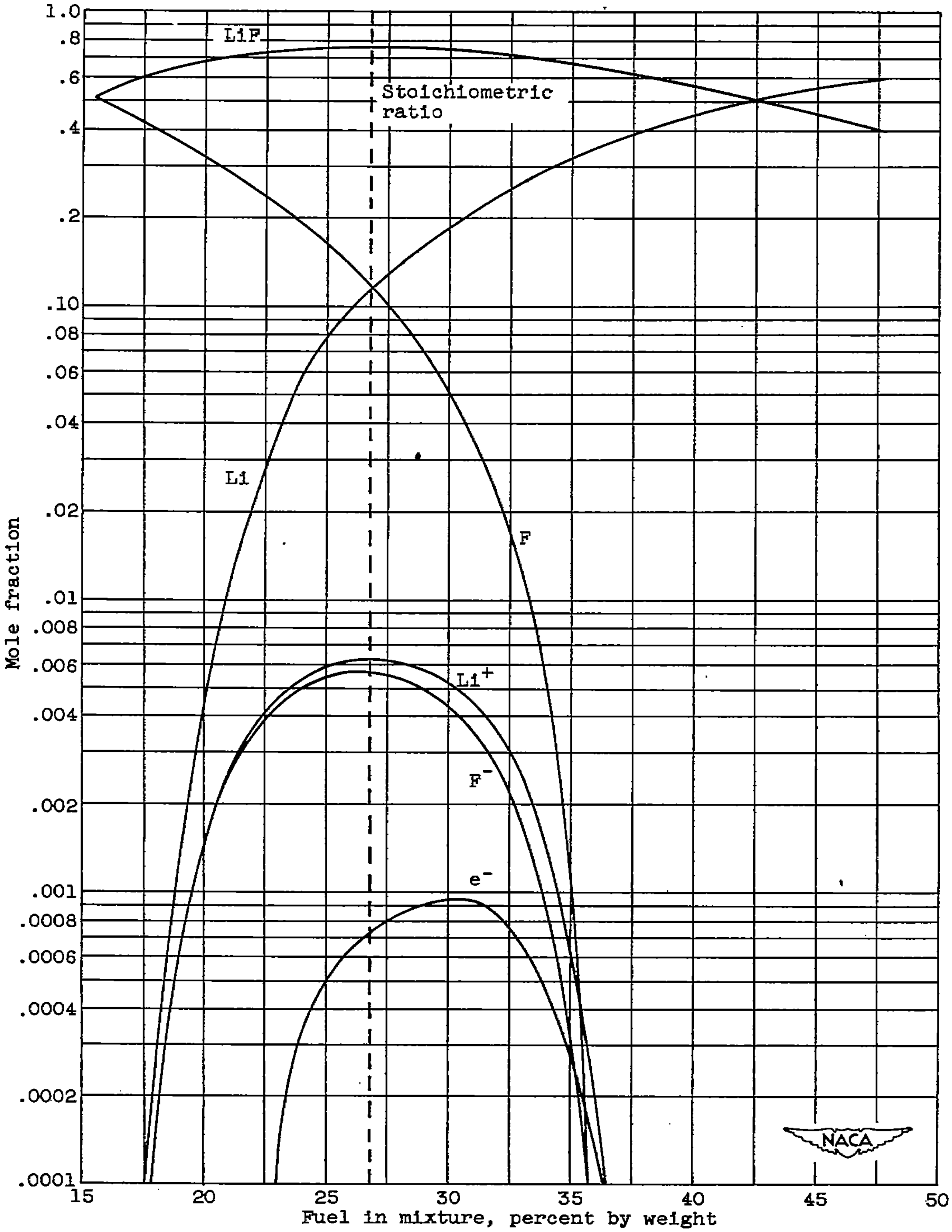
(b) Frozen composition.

Figure 2. - Concluded. Theoretical characteristic velocity, coefficient of thrust, and area ratio of liquid lithium with liquid fluorine. Isentropic expansion from 300 pounds per square inch absolute to 1 atmosphere.



(a) Combustion-chamber conditions. Combustion pressure, 300 pounds per square inch absolute.

Figure 3. - Composition of products of reaction of liquid lithium with liquid fluorine.



(b) Nozzle-exit conditions. Combustion pressure, 300 pounds per square inch absolute; isentropic expansion to 1 atmosphere assuming equilibrium composition.

Figure 3. - Concluded. Composition of products of reaction of liquid lithium with liquid fluorine.

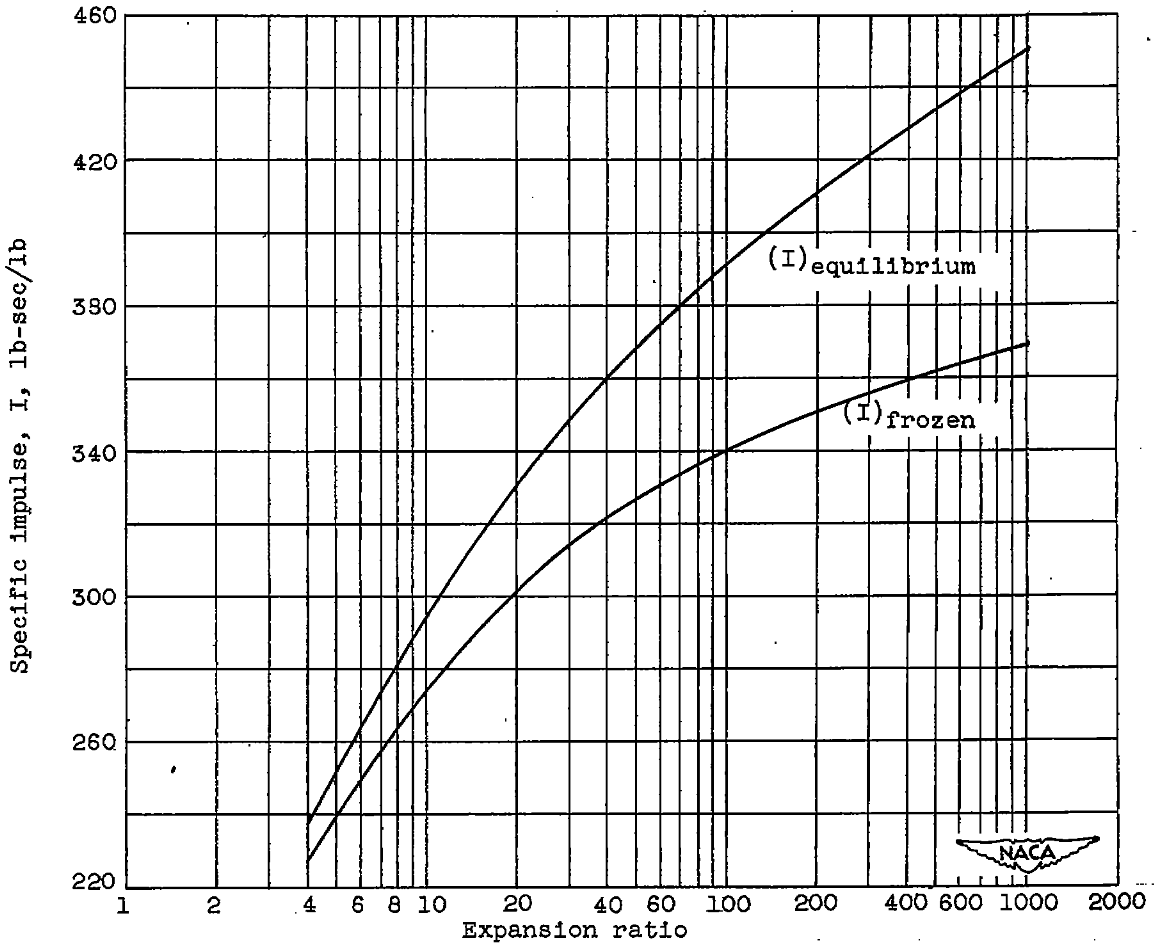


Figure 4. - Theoretical performance of liquid lithium with liquid fluorine for stoichiometric mixture at various expansion ratios assuming equilibrium and frozen composition. Combustion pressure, 300 pounds per square inch absolute.

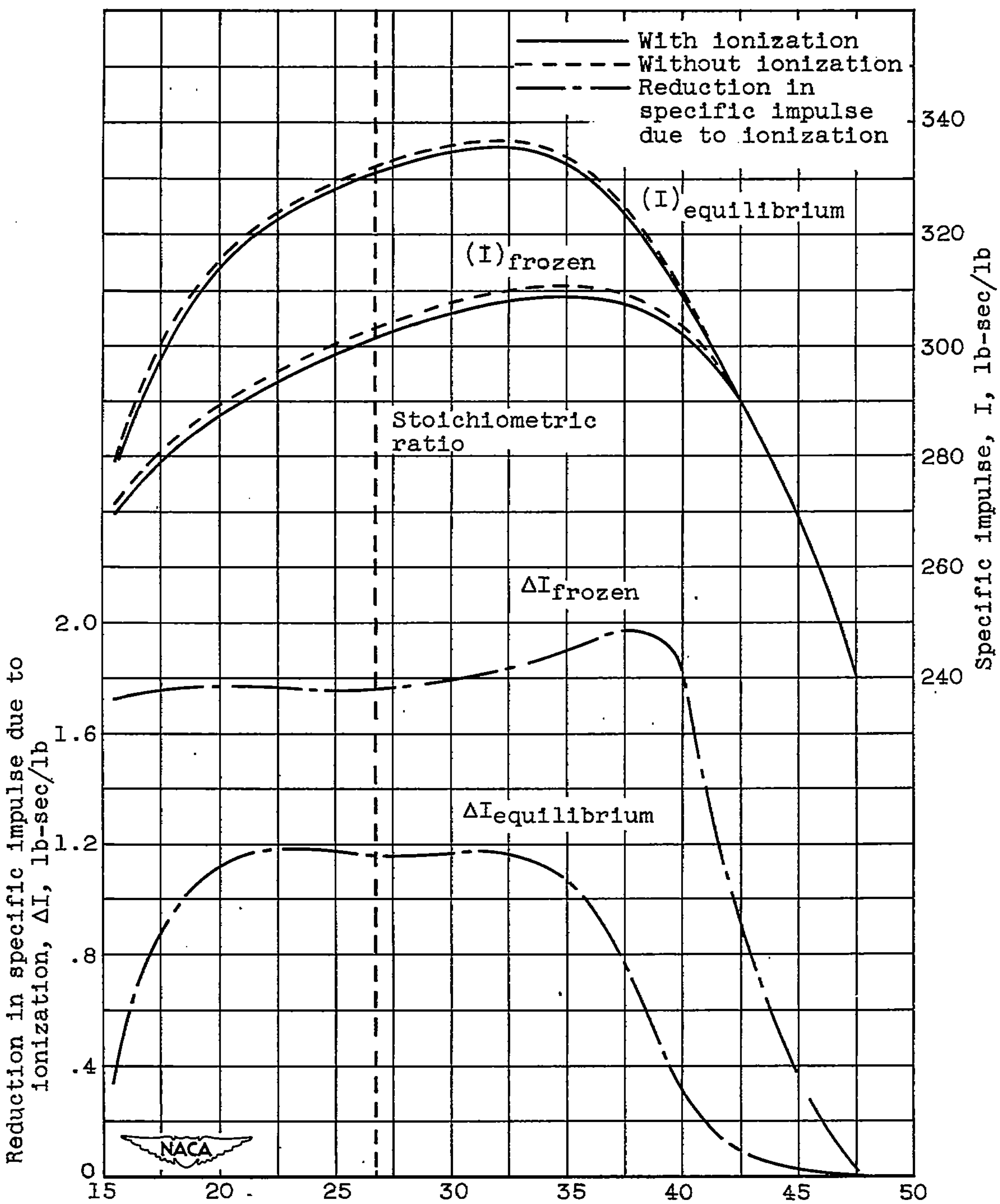


Figure 5. - Comparison of theoretical specific impulse calculated with and without ionized products of combustion. Combustion pressure, 300 pounds per square inch absolute. Isentropic expansion to 1 atmosphere assuming equilibrium and frozen composition.

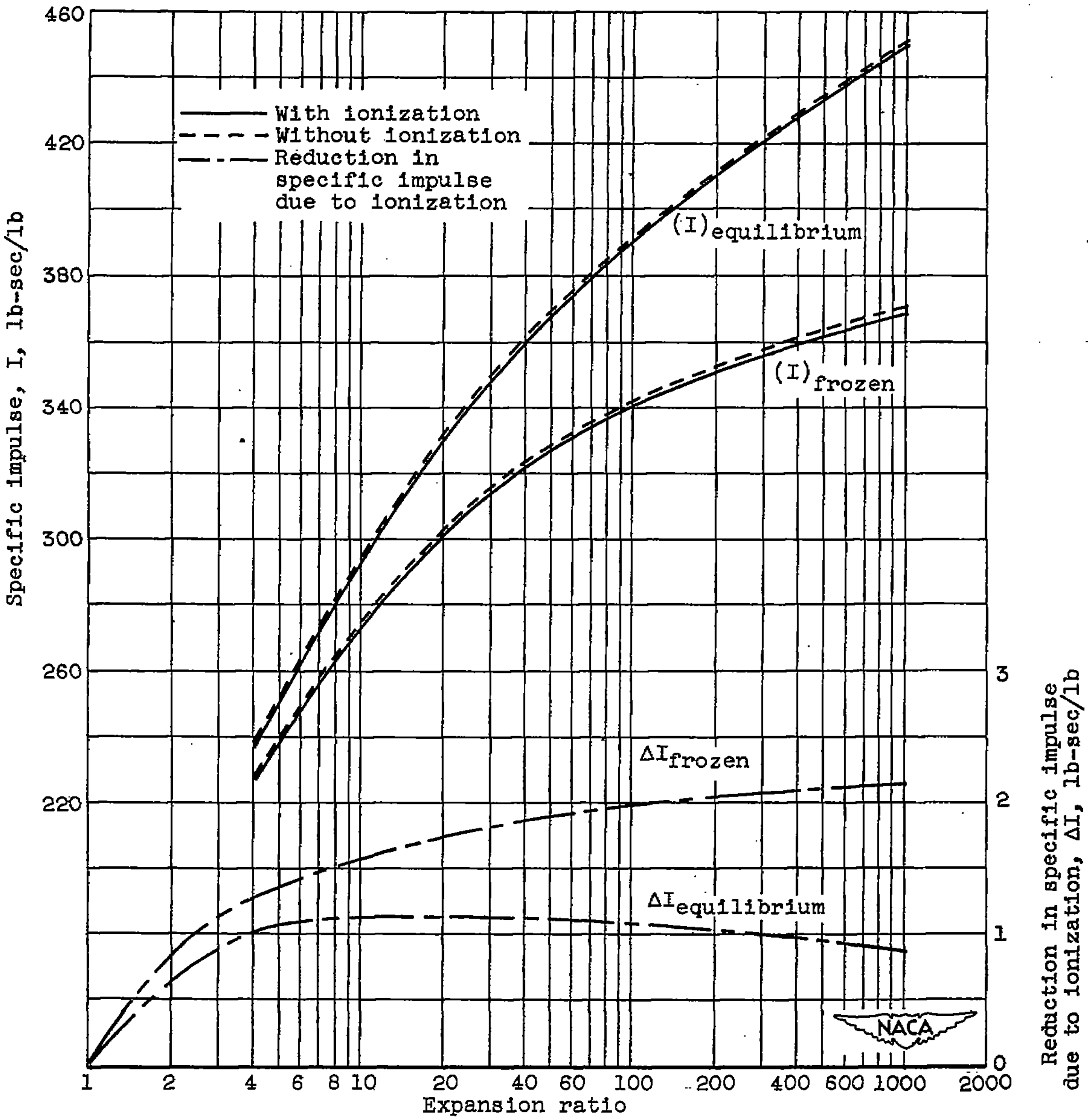


Figure 6. - Comparison of theoretical specific impulse for stoichiometric mixture at various expansion ratios calculated with and without ionized products of combustion. Isentropic expansion assuming equilibrium and frozen composition. Combustion pressure, 300 pounds per square inch absolute.