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The Calculation of Enthalpy-Entropy Diagrams for
and the Specific Impulse of Rocket Fuel Systems

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INTRODUCTION AND SUMMARY

It is the purpose of this report to present the methods and fundamental data necessary for calculating the theoretical performance of rocket motors in such a way as to be immediately useful to the research engineer.

The ultimate aim of such calculations is to provide an enthalpy-entropy diagram for the products of combustion of a fuel-oxidant system. These diagrams facilitate the investigation of the effect of operating variables of combustion chamber pressure, fuel temperature, expansion ratio, etc., upon the performance of rocket engines. The calculations need not, however, be carried to completion to be useful. If, for instance, the adiabatic flame temperature and average molecular weight of a propellant system are desired, they may be obtained in what is believed to be a minimum of time through the data and methods presented here. The methods may be appropriately applied to any combustion process involving carbon, hydrogen, oxygen, and nitrogen, with particular reference to the many combinations commonly found in present-day rocket motors.

If, however, the calculations are carried to completion, they will yield enthalpy-entropy diagrams fundamentally similar to those of Hottel (Reference 2), which are based on the assumption of thermochemical equilibrium throughout the combustion cycle. Since this assumption is not certain, the specific impulse (pounds of thrust per pound of propellant burned per second) indicated by such diagrams is compared with that calculated by other assumptions and methods in Part II of this report. The comparison shows surprisingly little difference in theoretical specific impulse, some difference in predicted optimum mixture ratio, and a considerable difference in the theoretical exhaust temperature.

The preparation of an enthalpy-entropy diagram starts logically

with the calculation of the chemical composition of the reaction products
at appropriate temperatures and pressures. The calculated compositions allow
calculations of the enthalpy and entropy of the equilibrium mixture at cor-
responding temperatures and pressures. These calculated data may then be
expanded through cross-plotting and graphical interpolation to give the com-
plete enthalpy-entropy diagram. A detailed explanation of these steps
follows in Part I.

LIST OF SYMBOLS

Ⓒ, Ⓞ, Ⓗ, Ⓝ, gram atoms of carbon, oxygen, hydrogen, and nitrogen, respectively, per pound of propellant.

C_p	Specific heat at constant pressure, cal per gm mol $^\circ K$
F	Function
G	Weight rate of flow, lb per sec
H	Enthalpy, energy per lb
I	Specific impulse, sec
J	Conversion factor, 778 ft lb per Btu
K	Gas constant, psia ft cubed per $^\circ R$ or atmos ft cubed per $^\circ R$
K_1	Equilibrium constant based on partial pressure for reaction (1)
M	Average molecular weight
N	Total moles in system, gram moles per unit mass
P	Total pressure, atmos or psia, as noted
R	Universal gas constant
S	Entropy, energy per degree per unit mass
T	Temperature, $^\circ R$ or $^\circ K$ as noted
V	Volume, cu ft
X	Gram moles of component in system
f	Area
(g)	Gaseous state
g	Acceleration due to gravity, ft per sec per sec
h	Molal enthalpy
p	Partial pressure
q	Heat transferred to the system from the surroundings, per pound of fluid flowing
s	Molal entropy

u Axial component of velocity, ft per sec

v Velocity

w_s Work done by system on surrounding other than PV work

w_f Useful work converted into heat

Δ Increase, final condition minus initial condition

γ Ratio of specific heats, c_p/c_v

λ Ratio of oxidant to total of oxidant plus fuel

Σ Summation

Superscripts

o   Standard pressure state, one atmosphere

Subscripts

a   Surrounding atmosphere

i   i th component

m   Throat condition

n   n th component

c   Combustion chamber condition

e   Exhaust condition

1   Initial condition

2   Final condition

f   Friction

Logarithms to the base e are denoted by ln; logarithms to the base 10 are denoted by log.

PART I. - THE CALCULATION OF ENTHALPY-ENTROPY DIAGRAMS FOR PRODUCTS OF COMBUSTION

Generalized Equilibrium Calculation.

The euilibrium composition of a gaseous mixture is governed by the simultaneous equations of conservation of atomic species and of mass action. With complex systems such as are encountered in the combustion chambers of rocket motors, these equations present a baffling problem in their solution. One of the objects of this portion of the work has been the development of a straightforward series consisting of the minimum number of steps of calculation, which could be executed by one not versed in physical chemistry, homogeneous equilibrium, and the other aspects of thermochemistry involved. The procedure resulting from this work is presented herein. This method has been developed to permit an accurate evaluation of the equilibrium composition at a predetermined temperature and pressure. The procedure has been generalized to apply to any system composed entirely of atoms of carbon, oxygen, hydrogen, and nitrogen. For a complete derivation of these equations, the reader is referred to Appendix I.

It is convenient, although not necessary, to select 453.6 grams (one pound) of propellant mixture as the system for study. This is expedient because the design engineer prefers to work in English units and because composition calculations on this basis are made with easily written numbers (10 to 0.0001). This results in compositions which are, in fact, gram moles per pound, which, when used for summation of the enthalpy and entropy of the mixture, yield those energy functions per pound. Conversion from gram calories to BTU is the only conversion involved in starting with metric units, which are widely available, and ending with the desired English units for the enthalpy-entropy diagram. This rather unusual unit,

the gram molecule or energy quantity per 453.6 grams, is not necessary

to the method but will give much more easily handled figures leading to

the desired result with the minimum of arithmetic manipulation.

It should be noted that the system referred to includes both

fuel and oxidant. Thus a 3:1 ratio of oxidant to fuel means 0.75 pounds

(340.2 grams) of oxidant plus 0.25 pounds (113.4 grams) of fuel. The ratio

having been chosen, the atomic composition of the system is calculated in

gram atoms according to the principles of elementary stoichiometry. Let

these quantities be;

$\textcircled{C}$ - gram atoms carbon in the system, gram atoms per pound

$\textcircled{O}$ - gram atoms oxygen in the system, gram atoms per pound

$\textcircled{H}$ - gram atoms hydrogen in the system, gram atoms per pound

$\textcircled{N}$ - gram atoms nitrogen in the system, gram atoms per pound.

With the above quantities at hand, it remains only to choose

the temperature and pressure at which the equilibrium composition is

desired, in order to fix the composition (temperature, pressure, and

atomic concentration being determined) of the system,-that is, there

can be only one equilibrium composition of the system. This must be

calculated by trial and error according to the simultaneous equations

of mass action and of conservation of atomic species. These equations

have been reduced through algebraic manipulation to a systematic scheme.

The concentration values depend only upon the atomic concentrations and

certained constants determined by the temperature and pressure. As such,

the solution becomes a problem in algebra, requiring no knowledge of

chemistry outside of elementary stoichiometry. Nonetheless, some explan-

ation of the meaning of the symbols will be helpful in arriving at a

speedy solution.

The molecular symbols written in brackets, $[H_2O]$, $[H_2]$, etc.,

represent the concentration in gram formula weight per unit mass of the

various species. When the algebraic trial and error scheme has been

balanced, the obtained values of these symbols will be their respective

concentrations. $[H_2]$ and N must be assumed at the outset of the cal-

culation. $[H_2]$ obviously cannot exceed $\frac{1}{2}$(H) nor can it reach zero.

($[H_2]$ may become negligible but for the purposes of this scheme it can-

not be zero). N represents the total number of moles in the system at

equilibrium and as a first approximation may be taken as

$\left[\text{(C)} + \frac{1}{2}\text{(H)} + \frac{1}{2}\text{(N)} \right]$ for mixtures lean in fuel and $\left[\frac{1}{4}\text{(H)} + \frac{1}{2}\text{(O)} + \frac{1}{2}\text{(N)} \right]$ for

rich mixtures. Within these ranges, accuracy of the first assumption

will be improved only with considerable experience. The second assumption

of $[H_2]$ should be adjusted up or down from the first assumption as the

computed value is greater or less than the assumption. Plotting facil-

itates convergence. Occasionally, for very lean mixtures, extreme

accuracy of assumption is necessary for convergence. The necessity of

making the double assumption of N as well as $[H_2]$ does not introduce

any added difficulties since N is large, reasonably constant, and rela-

tively independent of $[H_2]$. N will normally be determined with final

accuracy on the second or third trial, whereas $[H_2]$ will usually not be

determined until the fourth or fifth trial. This requires about three

hours time, on the average.

With these facts in mind, it is now fitting to proceed to the

schematized equations used for composition calculations. The values

$2\sqrt{K_1 / P}$, $2\sqrt{P / K_9}$, K_8^2 / P, $\sqrt{K_2} / P$, K_{15}, and K_{10} are

parameters calculated from the equilibrium constants for appropriate

reactions, with subscripts following Lewis and Von Elbe's tabulation

of the values at different temperatures. (See Table 2). Their values

may be taken from Table 1, "Parameters for Equilibrium Calculations".

The scheme is as follows:

Assume: $[H_2]$ and N.

Calculate: $2[H] = 2\sqrt{K_1 / P} \sqrt{N [H_2]}$

$$[OH] + 2[H_2O] = Ⓗ - 2[H_2] - [H]$$

$$[OH] = \frac{[OH] + 2[H_2O]}{1 + (2\sqrt{P} / K_9) \sqrt{[H_2]/N}}$$

$$[H_2O] = \tfrac{1}{2}([OH] + 2[H_2O] - [OH])$$

$$[O_2] = (K_8^2/ P) \; N \; ([H_2O] / [H_2])^2$$

$$[O] = \sqrt{K_2 / P} \sqrt{N} \sqrt{[O_2]}$$

$$[NO] = K_{15} \sqrt{[O_2]} \sqrt{\tfrac{1}{2} Ⓝ - \tfrac{1}{2}[NO]}$$

$$\cong K_{15} \sqrt{[O_2]} \sqrt{\tfrac{1}{2} Ⓝ}$$

$$[CO_2] = Ⓞ - Ⓒ - [H_2O] - [OH] - 2[O_2] - [O] - NO$$

$$[CO] = Ⓒ - [CO_2]$$

Check:
$$[H_2] = \frac{[CO] [H_2O]}{[CO_2]} K_{10}$$

Check:
$$N = Ⓒ + \tfrac{1}{2}Ⓗ + \tfrac{1}{2}Ⓝ + \tfrac{1}{2}[H] + \tfrac{1}{2}[OH] + \tfrac{1}{2}[NO] + [O] + [O_2]$$

Revise assumptions and repeat if necessary.

When the above scheme has been balanced, the composition values
from the last trial constitute the desired composition of the system.

Table 1: Parameters for Equilibrium Calculations

Values for P = 1 atmosphere

(Based on Log K_p values reported by Lewis and Von Elbe, see Reference 11)

Temp. °K	$2\sqrt{K_1}/P$	$2\sqrt{P}/K_9$	K_8^2/P	$\sqrt{K_2}/P$	K_{15}	K_{10}
3200	.59640	10.139	.0085114	.22648	.15597	.13883
3000	.33656	19.953	.0023988	.11777	.12389	.14454
2800	.17521	43.752	5.4954×10^{-4}	.056562	.095726	.15170
2600	.08252	109.90	1×10^{-4}	.024324	.07080	.16069
2400	.03440	309.74	1.5136×10^{-5}	.0091312	.050122	.17298
2200	.01228	1099.0	1.5136×10^{-6}	.002848	.033192	.19187
2000	3.5732×10^{-3}	5023.4	9.1201×10^{-8}	7.0962×10^{-4}	.020186	.21979
1800	7.9352×10^{-4}	30,974	28.84×10^{-10}	5.2004×10^{-4}	.010991	.26303
1600	1.2206×10^{-4}	315,960	3.9811×10^{-11}	1.5669×10^{-5}	.0051884	.32734
1400	1.1119×10^{-5}	5,902,050	2.0893×10^{-13}	1.0352×10^{-6}	1.968×10^{-3}	.45604

Note: Three figures are significant; five are included to smooth calculation.

Table 1b:

Correction Factors for Pressures other than 1 Atmos.

Total Pressure P, Atm.	$\dfrac{1}{\sqrt{P}}$	$\sqrt{P}$	$\dfrac{1}{P}$
40	.15811	6.3246	.0250
30	.18258	5.4772	.0333
20	.22361	4.4721	.0500
10	.31623	3.1623	.1000
5	.44721	2.2361	.2000
2.5	.63247	1.5811	.4000
1	1.00000	1.0000	1.0000
0.5	1.4142	.70711	2.0000
0.25	2.0000	.50000	4.0000
0.10	3.1623	.31623	10.0000

Table 2: $Log_{10} K_f$ (Reference 11)

$$aA + bB = cC + dD$$

$$K_f = \frac{f_C^{\,c} f_D^{\,d}}{f_A^{\,a} f_B^{\,b}}$$

(1) $H_2 = 2H$ (9) $H_2O = OH + \frac{1}{2}H_2$

(2) $O_2 = 2O$ (10) $CO + H_2O = CO_2 + H_2$

(8) $H_2O = H_2 + \frac{1}{2}O_2$ (15) $\frac{1}{2}O_2 + \frac{1}{2}N_2 = NO$
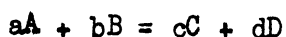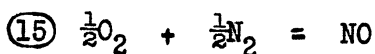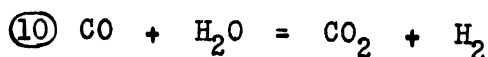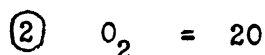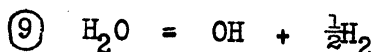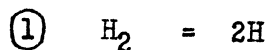
Note:
$f = P$ and
$K_f = K_p$, if perfect gases are assumed.

Temp	(1)	(2)	(8)	(9)	(10)	(15)
°K 300	-70.23	-80.2			+4.947	
400	-51.35	-58.6			+3.167	
600	-32.41	-36.9			+1.433	
800	-22.88	-26.1			+0.610	
1000	-17.13	-19.48	-10.05	-10.53	+0.147	-4.052
1200	-13.28	-15.10	-7.90	-8.17	-0.145	-3.267
1400	-10.51	-11.97	-6.34	-6.47	-0.341	-2.706
1600	-8.429	-9.61	-5.20	-5.20	-0.485	-2.285
1800	-6.803	-7.772	-4.27	-4.19	-0.580	-1.959
2000	-5.496	-6.298	-3.52	-3.40	-0.658	-1.695
2200	-4.424	-5.091	-2.91	-2.74	-0.717	-1.479
2400	-3.529	-4.078	-2.41	-2.19	-0.762	-1.300
2600	-2.769	-3.228	-2.00	-1.74	-0.794	-1.150
2800	-2.115	-2.495	-1.63	-1.34	-0.819	-1.019
3000	-1.548	-1.858	-1.31	-0.99	-0.840	-0.907
3200	-1.051	-1.290				-0.807
3500	-0.409	-0.577				-0.680
4000	+0.449	+0.379				-0.513

Calculation of Enthalpy and Entropy of Gaseous Mixtures

Assumptions: (1) No enthalpy change on mixing.

(2) Zero Joule-Thomson effect.

(3) $PV = NRT$ (equation of state)

Reference States: Processes involving changes in chemical composition as well as changes in temperature are best referred to chemical individuals in definite states of temperature and purity. These are arbitrary, but the chemicals must be such that balanced chemical equations may be written which will form any and all possible constituents of the mixture in prospect. Accordingly, a reference state has been chosen as the pure elements; C (graphite), H_2 (g), N_2 (g), and O_2 (g), at 298°K and one atmosphere. Thus the enthalpy of any constituent is equal to its heat of formation as a gas at 298°K plus its sensible heat above 298°K.

Enthalpy: In accordance with the above assumptions, the enthalpy of a gaseous mixture is given by:

$$H = \sum_{i=1}^{i=n} X_i\, h_i$$

where H = enthalpy of mixture, calories per unit mass,

X_i = moles of component i in mixture, gram moles per unit mass,

h_i = molal enthalpy of component i at temperature of mixture, calories per gram mole.

Values of h_i may be found in Table 3, Enthalpy and Entropy of Gases.

Entropy: The entropy of a gaseous mixture may be expressed* by:

$$S = \sum_{i=1}^{i=n} X_i S_i^{\,0} - \sum_{i=1}^{i=n} X_i\,(4.5753)\log X_i - N(4.5753)\log\frac{P}{N}$$

_____

* For derivation, see Appendix 2.

where S = entropy of mixture at temperature and pressure, calories per $^{\circ}$K unit mass

X_i = moles of component i in mixture, gram moles per unit mass

$S_i{}^{\circ}$ = molal entropy of component i at one atmosphere partial pressure, calories per $^{\circ}$K mole

P = total pressure, atmospheres

N = total moles in mixture, gram moles per init mass

$$N = \sum_{i=1}^{i=n} X_i \text{ , gram moles per unit mass.}$$

Values of $S_i{}^{\circ}$ may be found in Table 3, Enthalpy and Entropy of Gases.

Values of the function $F(X) = 4.5753 \, X \log X$ may be read from Figures 1 - 8.

For ease of computation, forms may be made up similar to Table 5.

(Values of H and S are taken from Table 3). For the sake of completeness, C_p values calculated by the original investigators are included in Table 4.

These values are the basis for the preparation of enthalpy and entropy tables.

Table 3: Enthalpy and Entropy of Gases

Reference States — Pure O_2, H_2, N_2, and C (graphite) at 298°K and 1 atm. pressure.

Units: — H° cal. per gm. mole; S° cal. per gm. mole per °K.

Temp °K	H_2 H°	H_2 S°	O_2 H°	O_2 S°	N_2 H°	N_2 S°	H_2O H°	H_2O S°	CO_2 H°	CO_2 S°
298	0	0	0	0	0	0	-57,796	-10.641	-94,031	+ 0.696
400	709	2.040	725	2.103	711	2.052	-57,102	- 8.270	-93,072	+ 3.452
600	+ 2,106	4.874	+ 2,212	5.099	+ 2,127	4.920	-55,288	- 4.878	-90,943	+ 7.751
1000	+ 4,943	8.494	+ 5,430	9.184	+ 5,132	8.746	-51,603	- 0.200	-86,036	+13.980
1200	+ 6,407	9.826	+ 7,116	10.715	+ 6,724	10.345	-49,582	+ 1.638	-83,382	+16.397
1400	+ 7,911	11.003	+ 8,837	12.040	+ 8,357	11.465	-47,465	+ 3.280	-80,644	+18.507
1600	+ 9,450	12.005	+10,587	13.208	+10,020	12.553	-45,248	+ 4.779	-77,845	+20.389
1800	+11,033	12.945	+12,361	14.258	+11,713	13.565	-42,935	+ 6.12	-74,995	+22.036
2000	+12,652	13.799	+14,154	15.204	+13,431	14.468	-40,543	+ 7.39	-72,109	+23.57
2200	+14,304	14.580	+15,971	16.063	+15,158	15.285	-38,095	+ 8.56	-69,195	+24.95
2400	+15,981	15.320	+17,811	16.867	+16,898	16.045	-35,598	+ 9.64	-66,253	+26.24
2600	+17,690	15.997	+19,669	17.602	+18,646	16.740	-33,055	+10.66	-63,284	+27.45
2800	+19,423	16.630	+21,545	18.293	+20,407	17.388	-30,478	+11.61	-60,300	+28.61
3000	+21,170	17.244	+23,437	18.961	+22,177	18.011	-27,876	+12.51	-57,297	+29.71
3200	+22,930	17.810	+25,352	19.57	+23,956	18.575				+30.79
3500	+25,583	18.614	+28,253	20.42	+26,627	19.382				+31.93

Temp °K	CO		O₁		NO		OH		H₁	
	H°	S°	H°	S°	H°	S°	H°	S°	H°	S°
298	-26,380	+21.435	+59,110	+13.965	+21,530	+ 2.944	- 5,929	+ 3.776	+51,911	+11.786
400	-25,668	+23.491	+59,617	+15.429	+22,259	+ 5.043	- 5,205	+ 5.866	+52,418	+13.250
600	-24,243	+26.379	+60,611	+17.443	+23,720	+ 8.002	- 3,794	+ 8.725	+53,412	+15.264
1000	-21,195	+30.258	+62,599	+19.982	+26,853	+11.986	- 929	+12.378	+55,400	+17.803
1200	-19,582	+31.655	+63,593	+20.889	+28,500	+13.484	+ 551	+13.728	+56,394	+18.710
1400	-17,929	+33.020	+64,587	+21.654	+30,188	+14.784	+ 2,088	+14.914	+57,388	+19.475
1600	-16,248	+34.115	+65,581	+22.318	+31,900	+15.921	+ 3,670	+15.961	+58,382	+20.139
1800	-14,541	+35.130	+66,575	+22.904	+33,633	+16.951	+ 5,283	+16.916	+59,376	+20.725
2000	-12,813	+36.040	+67,569	+23.426	+35,381	+17.869	+ 6,925	+17.786	+60,370	+21.247
2200	-11,069	+36.861	+68,563	+23.901	+37,142	+18.698	+ 8,593	+18.577	+61,364	+21.722
2400	- 9,318	+37.627	+69,557	+24.333	+38,915	+19.476	+10,300	+19.322	+62,358	+22.154
2600	- 7,560	+38.327	+70,551	+24.732	+40,696	+20.184	+12,023	+20.007	+63,352	+22.553
2800	- 5,792	+38.977	+71,545	+25.099	+42,484	+20.837	+13,765	+20.649	+64,346	+22.920
3000	- 4,015	+39.605	+72,539	+25.442	+44,278	+21.471	+15,534	+21.267	+65,340	+23.263
3200	- 2,233	+40.163	+73,533	+25.763	+46,078	+22.034	+17,325	+21.826	+66,334	+23.584
3500	+ 450	+40.981	+75,024	+26.209	+48,787	+22.834	+20,026	+22.616	+67,825	+24.030

Original data are from reference cited by Lewis and Von Elbe (Reference 11), graphically interpolated where necessary. Slight corrections for temperature base were made by using the C_p equations of K. K. Kelley, (Reference 9). ΔH of formation was taken from Perry (Reference 12), ΔS of formation from original works.

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Table 4: Molal Specific Heats, C_p, of Gaseous Molecules

Temp °K	(4) CO	(7) O_2	(4) N_2	(6) OH	(3) NO	(5) H_2	(8) CO_2	(1) H_2O
1					5.120			
10					6.945			
20		6.950			6.973			
30					7.115			
40					7.363			
50	6.954	6.962	6.955		7.590			
100	6.954	6.962	6.955		7.733			
150					7.468			
200	6.955	6.961	6.956		7.292			
250				7.195	7.129	6.772		
298.1		7.018		7.139	7.144			8.000
300	6.964		6.960			6.896	8.908	8.002
350				7.098	7.140	6.950		7.066
400	7.013	7.197	6.991	7.072	7.168	6.974	9.885	8.155
450								8,260
500	7.122	7.434	7.071	7.047	7.294	6.992	10.676	8.379
550								8.504
600	7.279	7.675	7.200	7.053	7.476	7.008	11.324	8.635
650								8.771
700	7.455	7.890	7.355	7.087	7.663	7.035	11.862	8.910
750								9.053
800	7.629	8.069	7.516	7.150	7.840	7.079	12.312	9.199
850								9.347
900	7.792	8.216	7.676	7.236	7.996	7.141	12.689	9.497

Table 4: Cont.

Temp °K	(4) CO	(7) O_2	(4) N_2	(6) OH	(3) NO	(5) H_2	(8) CO_2	(1) H_2O
1000	7.936	8.339	7.821	7.336	8.132	7.220	13.005	9.799
1050								9.948
1100							13.27	10.095
1125				7.476	8.273			
1150								10.240
1200		8.558				7.488	13.50	10.382
1250				7.613	8.389		13.60	10.522
1300	8.269		8.169				13.69	10.656
1500	8.422	8.702	8.334	7.881	8.561	7.718	14.00	11.153
1750	8.564		8.489	8.114	8.686	7.963	14.3	11.67
2000	8.667		8.604	8.311	8.774	8.181	14.5	12.09
2250								12.4
2400								12.7
2500	8.807		8.761	8.611	8.896	8.531	14.8	
3000	8.900		8.863	8.844	8.982	8.796	15.0	13.1
3500	8.964		8.935			8.997	15.2	
4000	9.016		8.990	9.165	9.108	9.155		
4500	9.060		9.037			9.286		
5000	9.099		9.077	9.509	9.209	9.392		

Note: Numbers in parentheses at heads of columns indicate References from which quoted values were obtained.

$F(X) = 4.5753 \times \text{Log } X$

Fig. 1

$$F(X) = 4.5753 \times \text{Log } X$$

fig. 2

$$F(X) = 4.5753 \times Log \, X$$

Fig. 3

F(X)=4.5753 X Log X

Fig. 4

F(X)=4.5753 X Log X

Fig. 5

$F(X) = 4.5753 \times \text{Log } X$

Fig. 6

Fig.7

$F(X) = 4.5753 \times Log X$

Fig. 8

F(X)
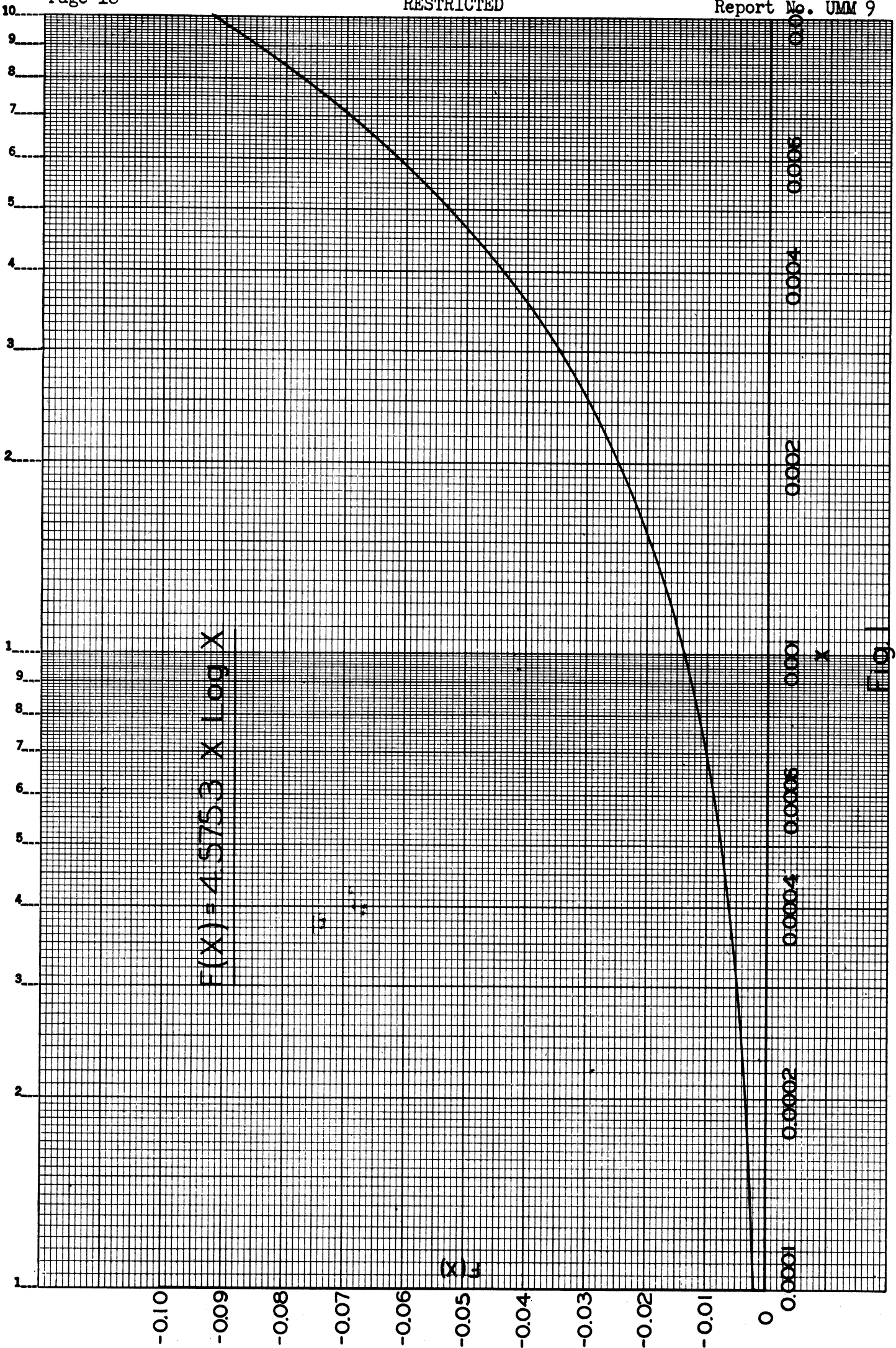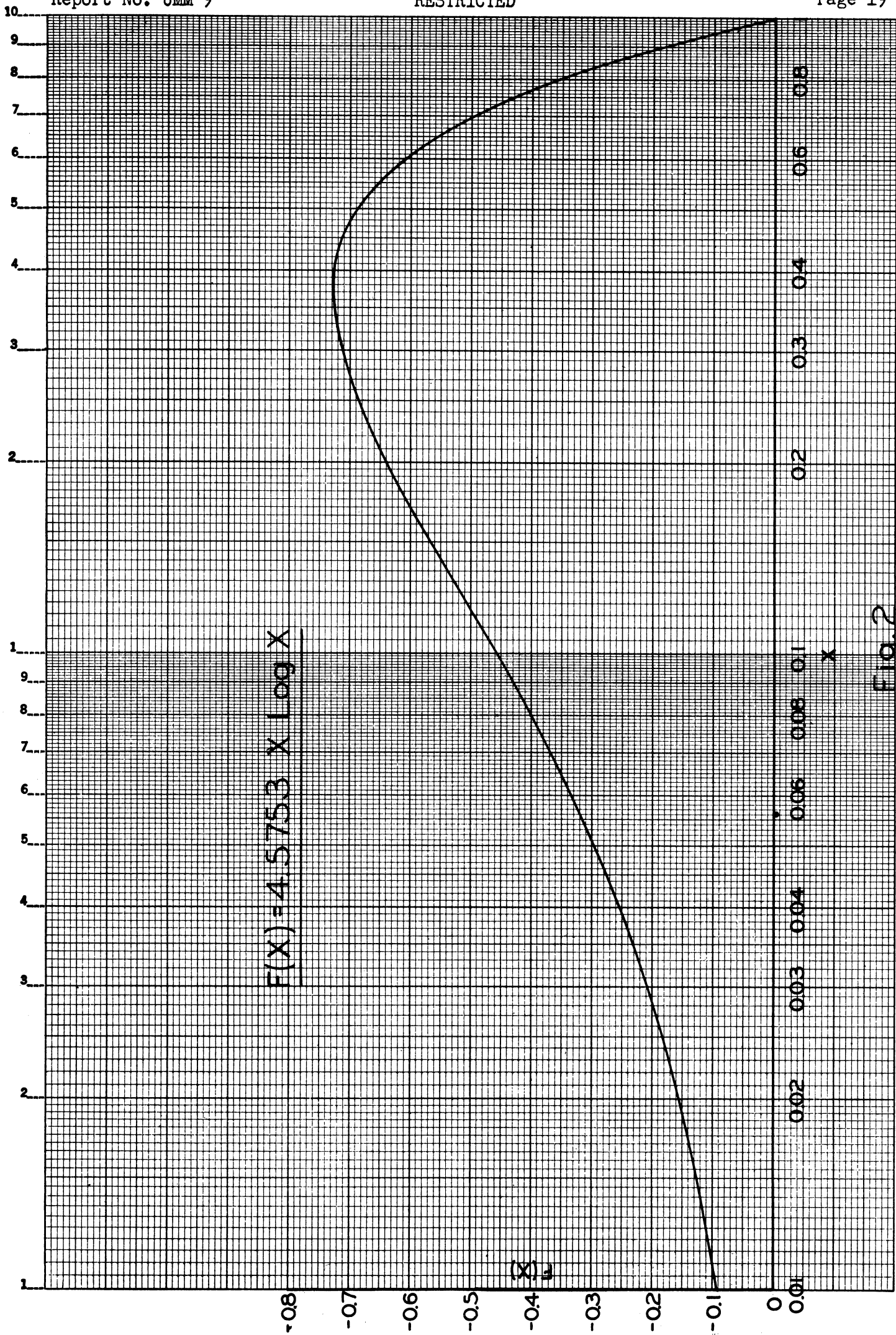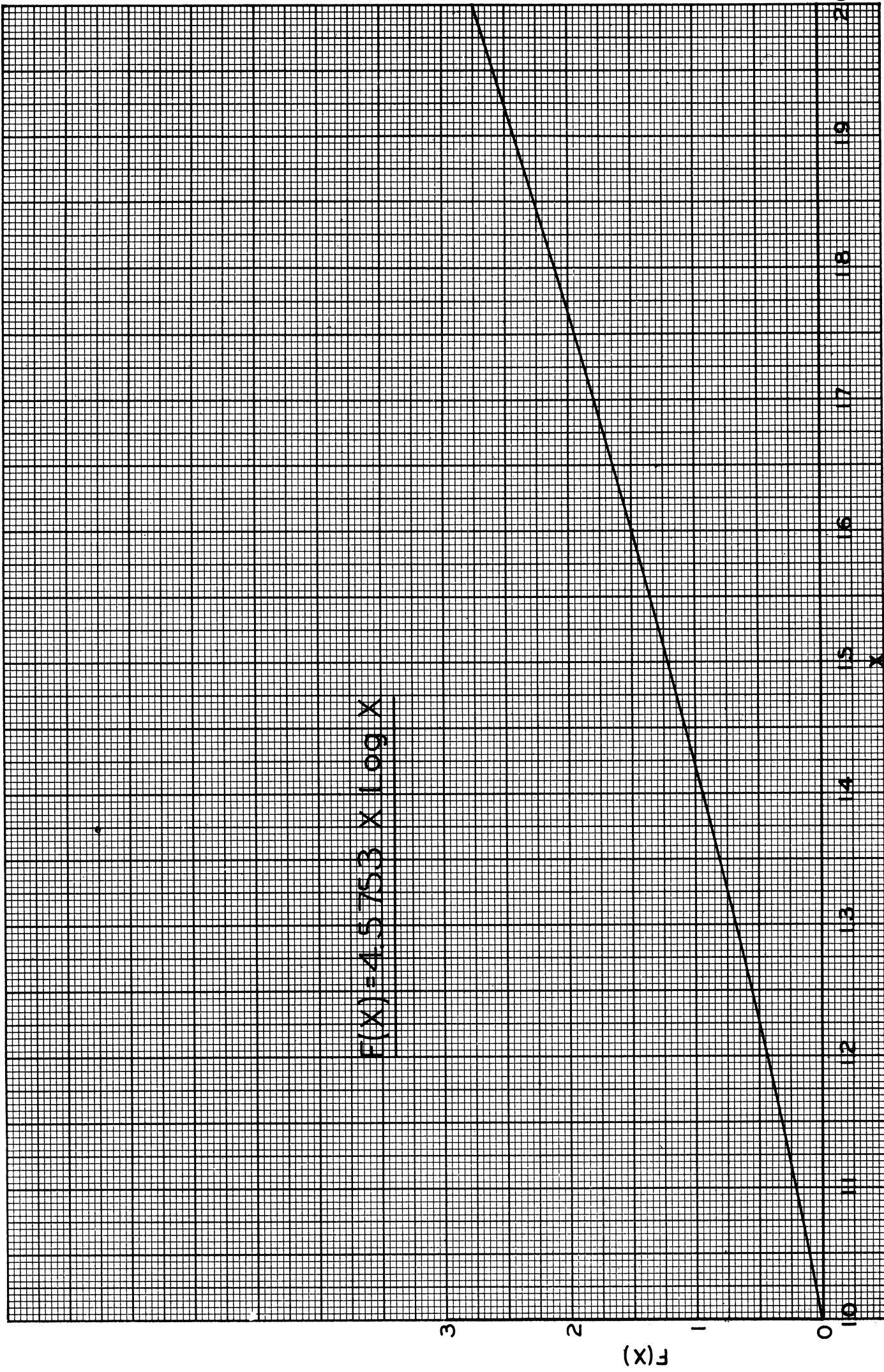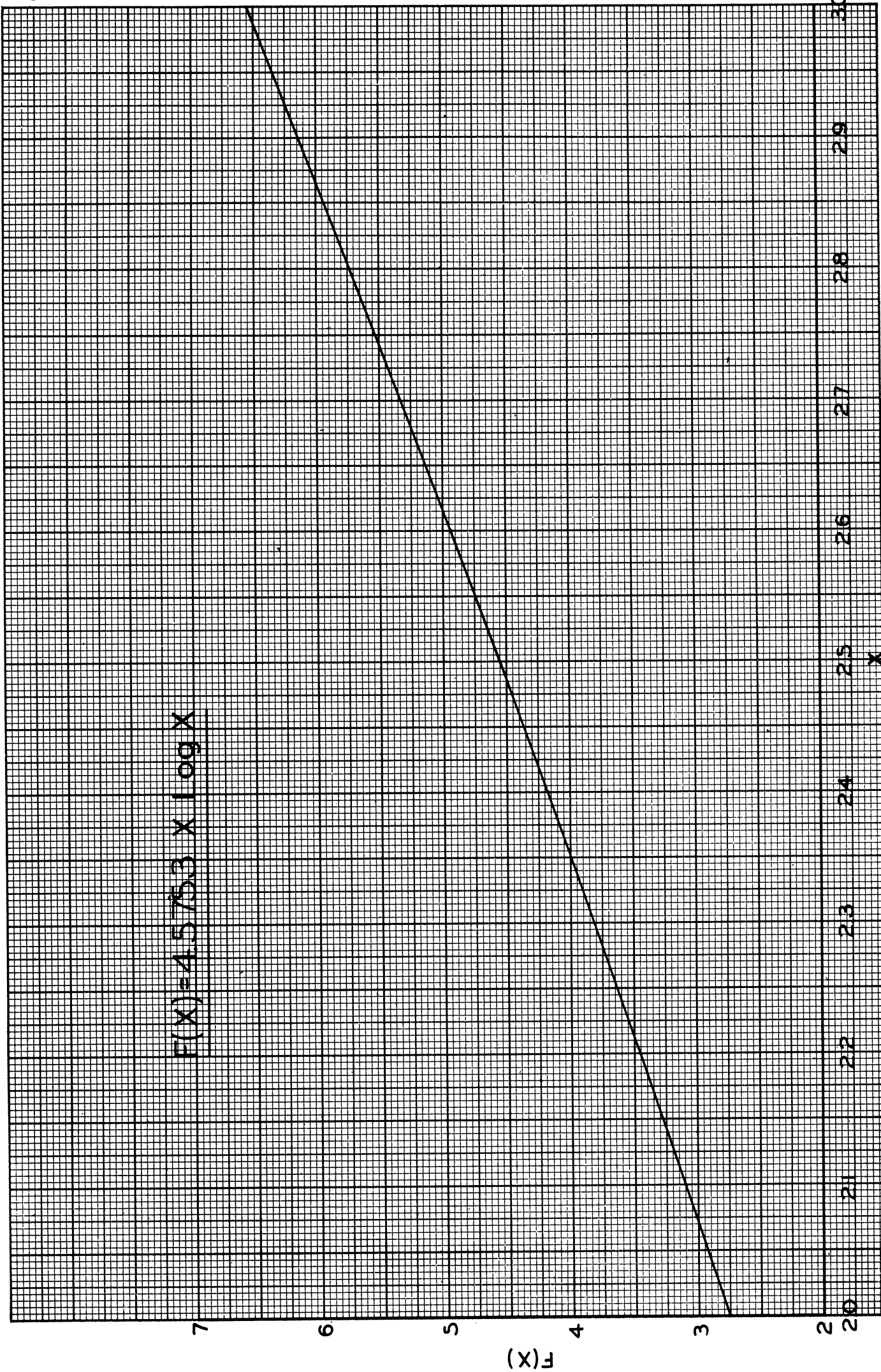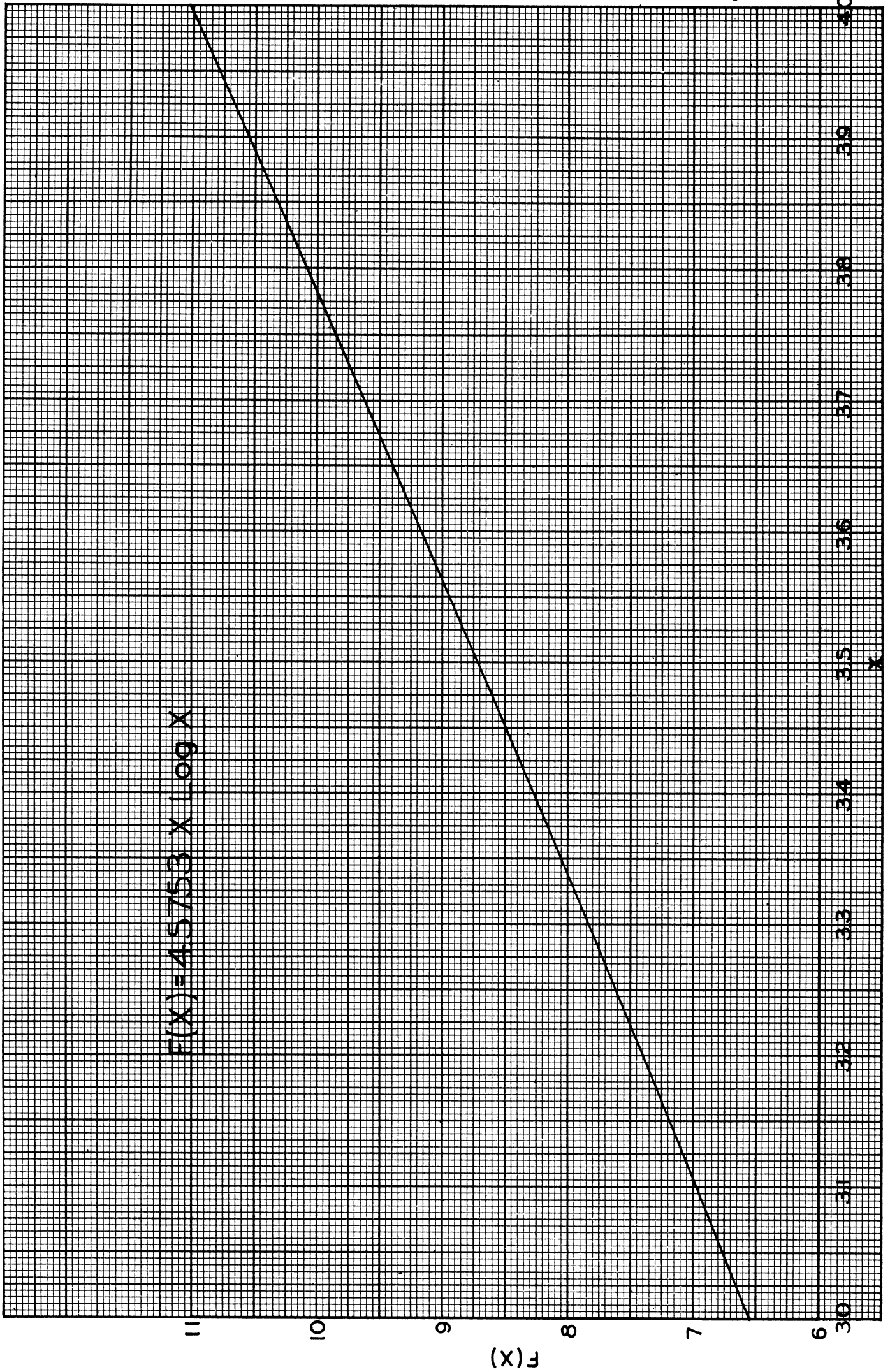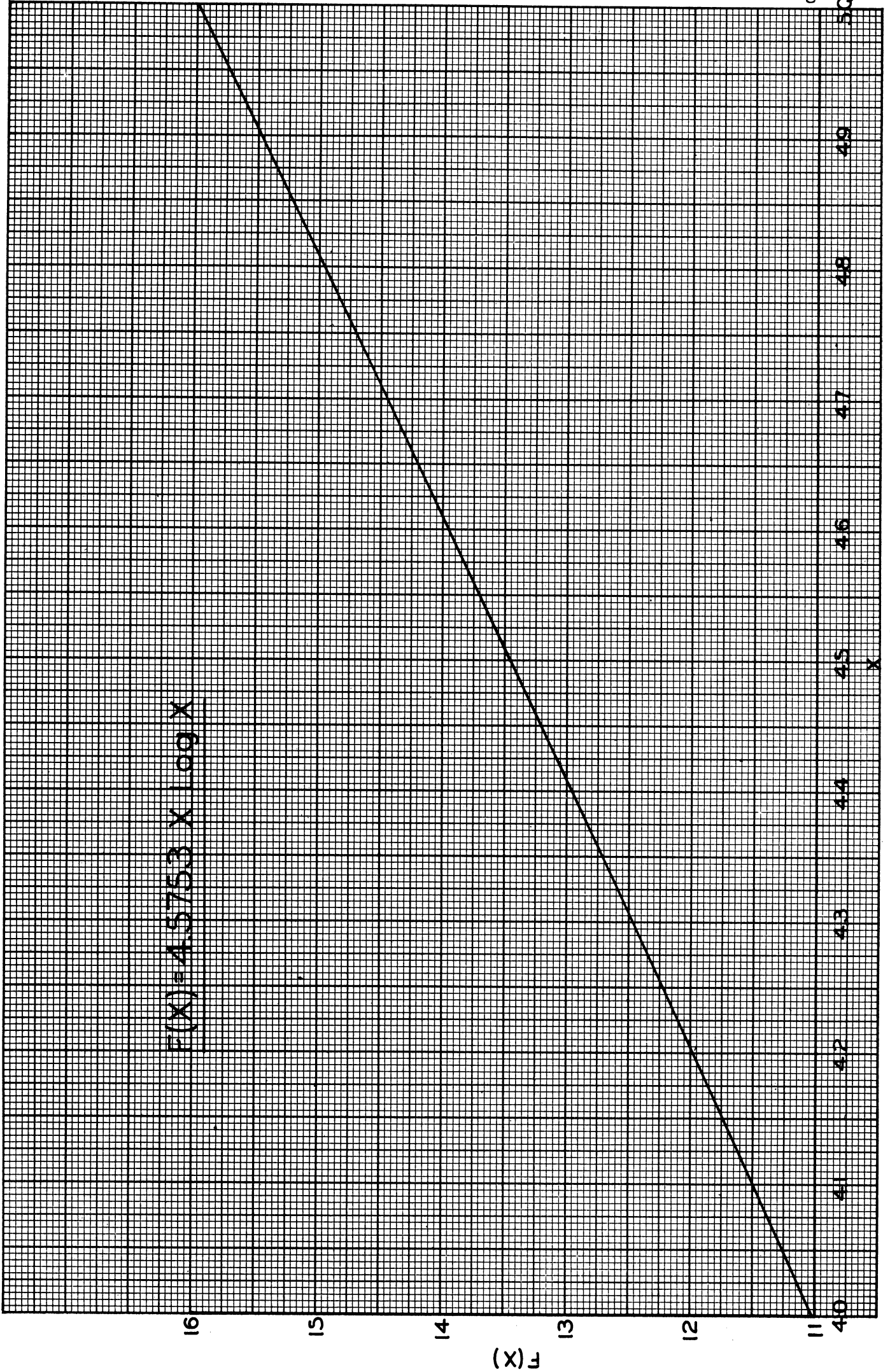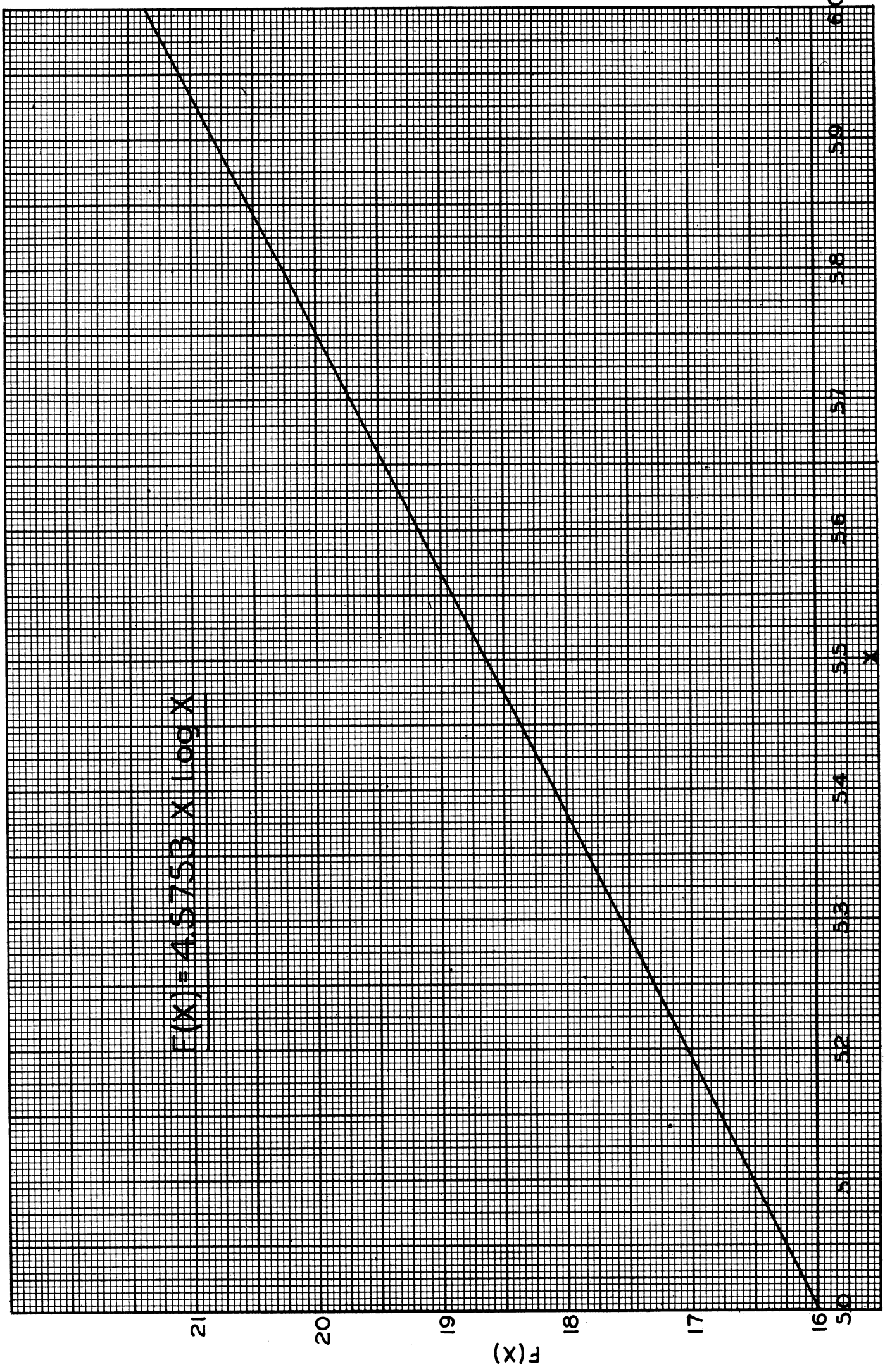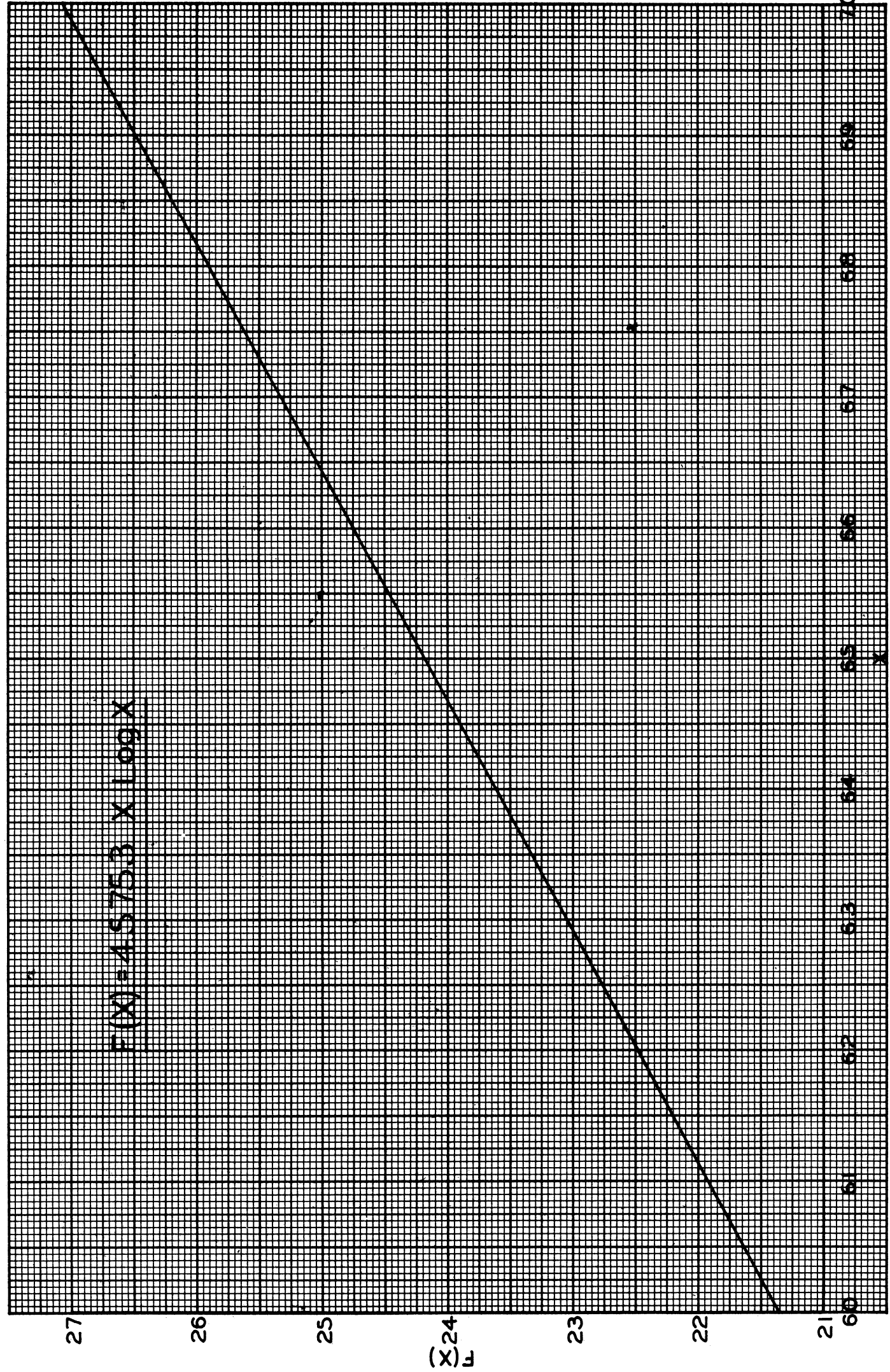
Table 5: Form for H-S Calculation

Temp ___3200___ °K   P _____ λ _____

	H^O	S^O	X	XH^O	XS^O	f_x 4.5753X log X
H_2O	-25,224	13.37				
H_2	22,930	17.810				
O_2	25,352	19.57				
O	73,533	25.763				
H	66,334	23.584				
OH	17,325	21.826				
CO_2	-54,289	30.79				
CO	- 2,233	39.174				
NO	46,078	22.034				
N_2	23,956	18.575				
Σ						

P / N = _____ $-\Sigma f_x$ = _____

log P / N = _____   -4.5753 N log P/N = _____

H = _____ Btu / lb   S = _____ cal/453.6 gm°K

S = _____ Btu / lb °R

Note: Values in the X column are composition coefficients from an equilibrium calculation, with units of gram moles per 453.6 grams; their summation is equal to N. The summation of the XH^O product column is the enthalpy in calories per 453.6 gm; it is converted into Btu per pound by the factor 0.0039683 Btu / lb per cal / 453.6 gm. Values in the f_x column are read from Figures 1. through 8. The summation of f_x is then written (with a minus sign) directly below the summation of the product XS^O. The sum of the values (XS^O) plus ($-\Sigma f_x$) plus (-4.5753 N log P/N) is the entropy in cal/453.6 gm °K; it is converted to entropy in Btu per lb °R by dividing by 453.6.

See the sample calculation on Page 27.

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Sample Calculation

Form for H-S Calculation

Temp __2800__ °K   P __40__ λ____.80____

	H^O	S^O	X	XH^O	XS^O	f_x $4.5753X \log X$
H_2O	-30,478	11.61	6.0113	-183,212.4	69.791	21.420
H_2	19,423	16.630	.2337	4,539.2	3,886	- 0.697
O_2	21,545	18.293	.1454	3,132.6	2.660	- 0.559
O	71,545	25.099	.0136	973.0	.341	- 0.118
H	64,346	22.920	.0268	1,724.5	.614	- 0.192
OH	13,765	20.649	.3595	4,948.5	7.423	- 0.727
CO_2	-60,300	28.61	4.6531	-280,581.9	133.125	14.420
CO	- 5,792	38.977	1.1924	- 6,906.4	46.476	0.420
NO	42,484	20.837	.0671	2,850.7	1.398	- 0.360
N_2	20,407	17.388	3.3444	68,249.2	58.152	8.020
Σ			16.0473	-384,283.0	323.866	41.627

P/N = __2.4926__ $-\Sigma f_x$ = | -41.627 |

log P/N = __.39665__   -4.5753 N log P/N = | -29.123 |

H = __-1,525.0__ Btu / lb   S = | 253.116 | cal/453.6 gm°K

S = __.55802__ Btu / lb °R

Preliminary Cross Plots for Diagram

An enthalpy-entropy diagram for the products of combustion of a given fuel system is begun by calculation of equilibrium compositions for several points of temperature and pressure. These compositions are used to calculate enthalpy and entropy points. If a complete diagram is desired, about twenty such points must be calculated. These are cross plotted; enthalpy versus temperature with lines of constant pressure, enthalpy versus pressure with lines of constant temperature, and so on, until the final H-S plot is completed. Less complete diagrams, which are sufficient for some purposes, may be made without cross plotting from about six compositions at carefully chosen temperatures and pressures.

Table 6 illustrates the results of equilibrium calculations and Table 7 shows the enthalpy and entropy for these compositions. Figures 9 through 12 illustrate the cross plots and Figures 13 through 17 are final results. Volume constants are determined from the total moles per unit mass and the perfect gas equation $(pv = nRT)$.

Materials

Red Fuming Nitric Acid (RFNA) specifications were obtained from E. I. du Pont de Nemours and Co., Inc. as follows:

HNO_3 - 98 %

H_2O - 2 %

NO_2 - 6.5%

The above is herein referred to as 6.5 % RFNA, meaning 6.5% NO_2, or simply as RFNA.

Aniline, unless otherwise noted, is pure aniline.

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Enthalpy of Unburned Propellant

The enthalpy of the unburned propellant must be referred to the same datum as the products of combustion. The datum chosen for the diagrams presented herein is the pure gaseous elements at 298°K and one atmosphere pressure. This makes the enthalpy of the fuel (or oxidant) equal to its heat of formation at 298°K, plus its sensible heat above 298°K, plus its pressure-volume energy above one atmosphere. The heats of formation for aniline, nitric acid, nitrogen dioxide, and water were calculated from the heats of combustion given by Lange (Reference 17). These are 143 Btu per pound for aniline and -1200 Btu per pound for 6.5 % RFNA (taking no account of the heat of solution of NO_2 and H_2O) at 25°C. Specific heats were obtained from Hougan and Watson (Reference 18). From these data the enthalpy of the unburned propellant for any given fuel-oxidant ratio may be calculated as a function of temperature. This has been done for each of the mixture ratios presented and the function appears on the upper, left-hand, corner of the enthalpy-entropy diagrams. No consideration of P-V energy is included, since it is very small, but it may be added by the user if desired.

Table 6: Composition Summary

Units: gram moles per one pound total

.80 lb 6.5% RFNA
.20 lb pure aniline

	P atm	3200°K	3000°K	2800°K	2600°K	2200°K	1800°K	1400°K	1000°K	600°K
H_2O	40	5.4033	5.7578	6.0113	6.1197					
	30	5.3038	5.6936	5.9731	6.0553					
	20		5.5909	5.9126	5.9716					
	10	4.8300	5.3801	5.7869						
	5			5.6278	5.6699	6.2354				
	1					6.1911	6.2217	6.1301	5.9042	5.9042
	.5					6.1582	6.2210			
	.25					6.1121	6.2196			
H_2	40	.4550	.3255	.2337	.1989					
	30	.4927	.3498	.2482	.2231					
	20		.3891	.2713	.2555					
	10	.6698	.4700	.3201						
	5			.3816	.3744	.1765				
	1					.1904	.2143	.3080	.5339	.5339
	.5					.2020	.2142			
	.25					.2199	.2143			
O_2	40	.5088	.3083	.1454	.0753					
	30	.5623	.3495	.1707	.1177					
	20		.4129	.2113	.1748					
	10	.7864	.5344	.2947						
	5			.3968	.3784	.0060				
	1					.0253	.0002			
	.5					.0445				
	.25					.0741				
O	40	.1052	.0420	.0136	.0060					
	30	.1282	.0516	.0172	.0106					
	20		.0691	.0234	.0182					
	10	.2677	.1122	.0394						
	5			.0649		.0004				

Species	P	1	2	3	4	5	6	7	8
O cont	1				.0608	.0018			
	.5					.0034			
	.25					.0062	.0001		
H	40	.1310	.0616	.0268	.0164	.0046	.0007		
	30	.1580	.0738	.0320	.0246	.0106	.0010		
	20	.3253	.0958	.0410	.0374	.0156	.0015		
	10		.1504	.0634	.1026	.0230			
	5			.0986					
OH	40	1.0286	.6480	.3595	.2227	.0478	.0034		
	30	1.1254	.7156	.4016	.2948	.1026	.0048		
	20	1.5514	.8203	.4674	.3846	.1402	.0069		
	10		1.0203	.5988	.6850	.1892			
	5			.7588					
CO$_2$	40	3.6393	4.2047	4.6531	4.8610	5.0952	5.1685	5.2634	5.4913
	30	3.5020	4.1025	4.5894	4.7549	5.0398	5.1693		5.4913
	20	2.9241	3.9447	4.4887	4.6171	4.9919	5.1684		
	10		3.6444	4.2854	4.1429	4.9231			
	5			4.0403					
CO	40	2.2062	1.6408	1.1924	.9845	.7502	.6770	.5801	.3542
	30	2.3435	1.7430	1.2556	1.0906	.8057	.6762		.3542
	20	2.9214	1.9008	1.3568	1.2284	.8536	.6771		
	10		2.2011	1.5601	1.7026	.9224			
	5			1.8052					

Table 6, continued

	P atm	3200°K	3000°K	2800°K	2600°K	2200°K	1800°K	1400°K	1000°K	600°K
NO	40	.2014	.1264	.0671						
	30	.2116	.1331	.0728						
	20		.1447	.0808	.0357					
	10	.2495	.1645	.0956	.0446					
	5			.1100	.0544	.0046				
	1				.0800	.0096	.0002			
	.5					.0128	.0002			
	.25					.0166	.0002			
N₂	40	3.2772	3.3147	3.3444						
	30	3.2721	3.3114	3.3415						
	20		3.3055	3.3375	3.3600					
	10	3.2531	3.2957	3.3301	3.3556					
	5			3.3229	3.3507	3.3756				
	1				3.3379	3.3731	3.3777	3.3779	3.3779	3.3779
	.5					3.3715	3.3778			
	.25					3.3696	3.3778			
N	40	16.9560	16.4298	16.0473						
	30	17.0995	16.5239	16.1026						
	20		16.6738	16.1908	15.8801					
	10	17.7787	16.9783	16.3745	15.9718					
	5			16.6070	16.0927	15.6963				
	1				16.5345	15.7500	15.6635	15.6615	15.6615	15.6615
	.5					15.7937	15.6646			
	.25					15.8562	15.6661			

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Table 7: Enthalpy-Entropy Summary

.80 lb 6.5% RFNA   P - atmospheres pressure   N - gram moles per lb
.20 lb pure aniline   H - Btu per lb   K - psia cu ft per °R
                      S - Btu per lb per °R

Temp °K		P = 40	P = 30	P = 20	P = 10	P = 5	P = 1	P = .5	P = .25
3200	H	-767.6	-698.6		-374.0				
	S	.7005	.7340		.8764				
	N	16.9560	17.0995		17.7786				
	K	.40116	.40456		.42062				
3000	H	-1181.8	-1135.6	-1063.0	-916.2				
	S	.6275	.6575	.7010	.7815				
	N	16.4298	16.5239	16.6739	16.9783				
	K	.38871	.39094	.39449	.40169				
2800	H	-1525.0	-1497.9	-1454.9	-1365.5	-1252.9			
	S	.5580	.5840	.6224	.6901	.7604			
	N	16.0473	16.1026	16.1908	16.3745	16.6070			
	K	.37966	.38097	.38306	.38740	.39291			
2600	H			-1762.4	-1717.6	-1658.6	-1444.3		
	S			.5559	.6147	.6769	.8396		
	N			15.8801	15.9717	16.0927	16.5345		
	K			.37571	.37787	.38074	.39119		
2200	H					-2157.7	-2131.9	-2110.7	-2080.4
	S					.5588	.8765	.7301	.7865
	N					15.6963	15.7500	15.7937	15.8562
	K					.37136	.37263	.37366	.37515
1800	H						-2470.6	-2470.5	-2469.9
	S						.5812	.6288	.6763
	N						15.6645	15.6646	15.6661
	K						.37061	.37061	.37064
1400	H						-2759.3	-2759.3	-2759.3
	S						.4809	.5285	.5760
	N						15.6615	15.6615	15.6615
	K						.37054	.37054	.37054
1000	H						-3034.3	-3034.3	-3034.3
	S						.3500	.3976	.4452
	N						15.6615	15.6615	15.6615
	K						.37054	.37054	.37054
600	H						-3290.5	-3290.5	-3290.5
	S						.2920	.3396	.3872
	N						15.6615	15.6615	15.6615
	K						.37054	.37054	.37054

CROSSPLOT FOR 0.80 LB
RFNA AND 0.20 LB ANILINE

Fig. 9

CROSSPLOT FOR 0.80 BRFNA AND 0.20 LB ANILINE

5760°R

5400°R

5040°R

4680°R

3960°R

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PRESSURE - PSIA

ENTHALPY - BTU PER LB

Fig. 10

CROSSPLOT FOR 0.80
LB RFNA AND 0.20 LB
ANILINE

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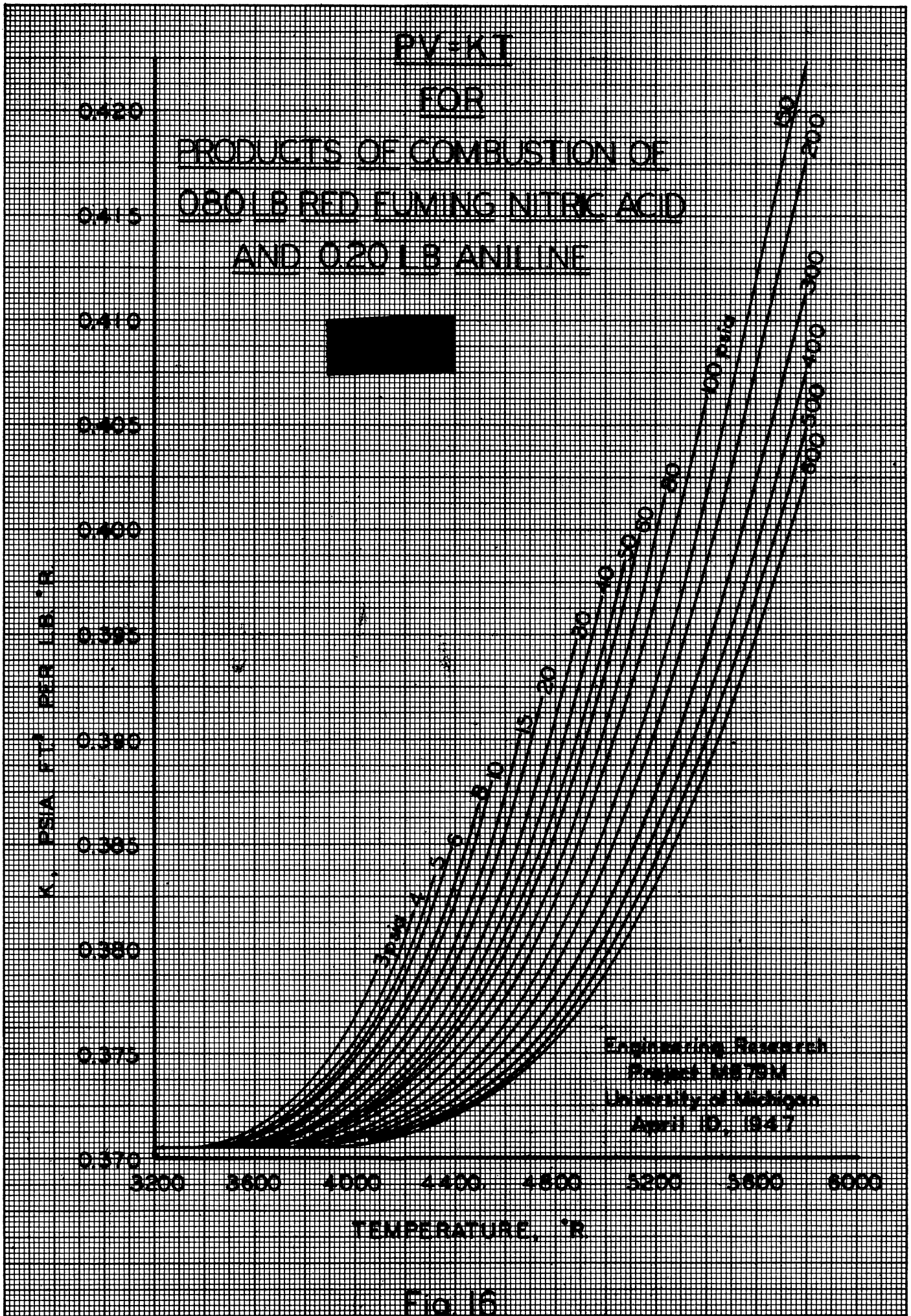University of Michigan, April 28, 1947

Fig. 11

CROSSPLOT FOR 0.80 LB RFNA AND 0.20 LB ANILINE

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Fig. 12

ENTHALPY-ENTROPY DIAGRAM FOR
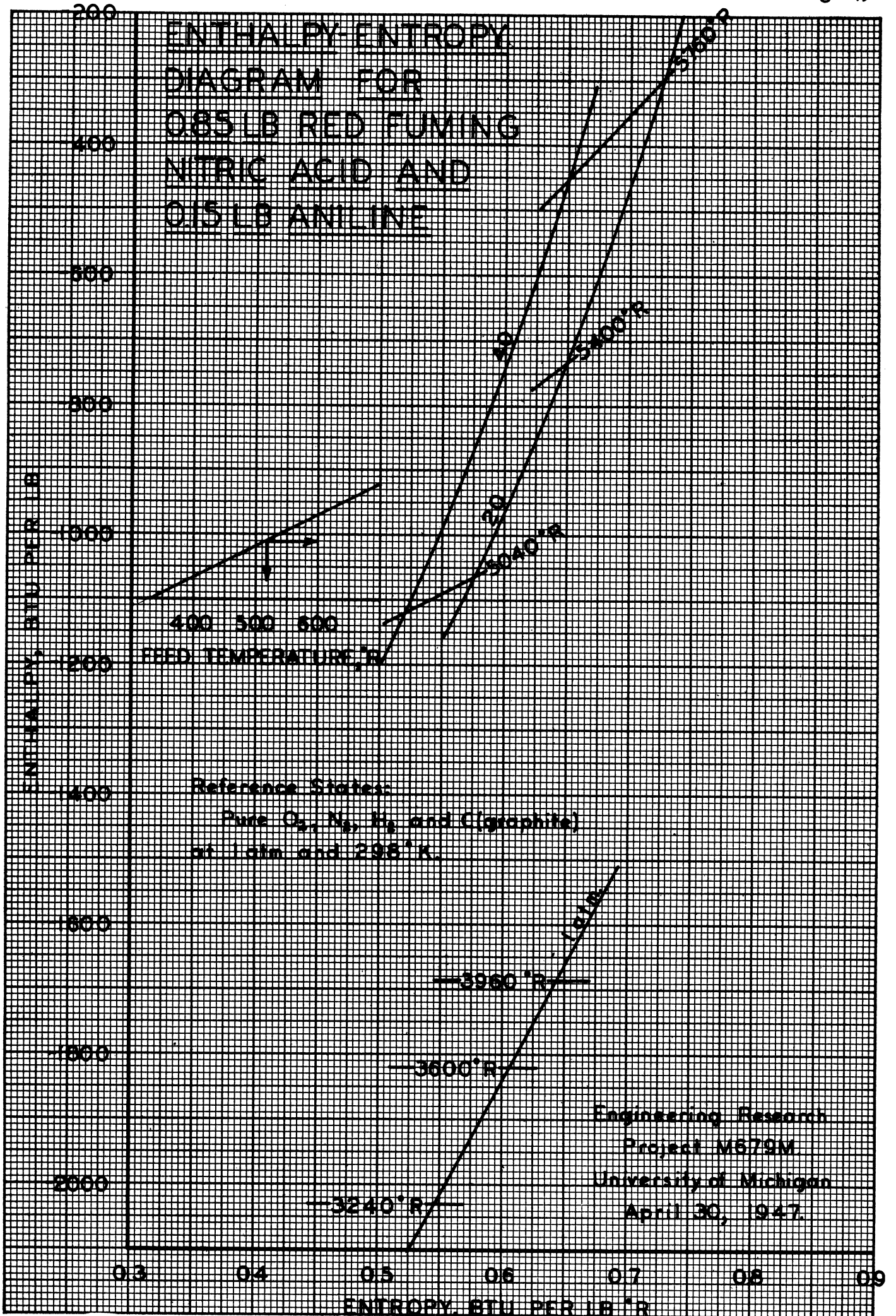
0.70 LB RED FUMING NITRIC ACID

AND 0.30 LB ANILINE
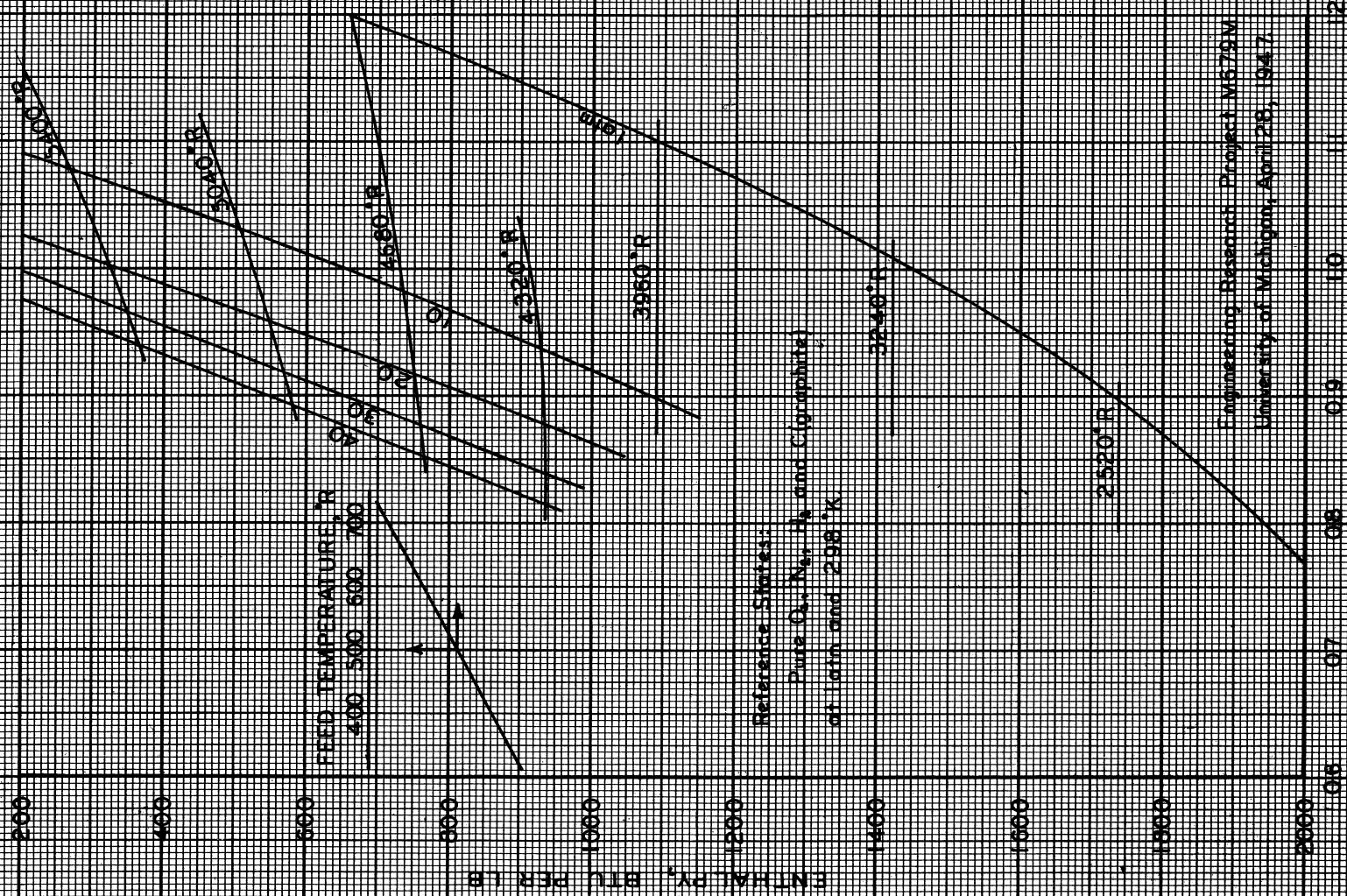
Fig. 13

PV=KT
FOR
PRODUCTS OF COMBUSTION OF
0.80 LB RED FUMING NITRIC ACID
AND 0.20 LB ANILINE

Fig. 16

ENTHALPY-ENTROPY DIAGRAM FOR 0.85 LB RED FUMING NITRIC ACID AND 0.15 LB ANILINE

Reference States:
Pure O_2, N_2, H_2 and C(graphite) at 1 atm and 298°K.

Engineering Research
Project M679M
University of Michigan
April 30, 1947.

ENTHALPY, BTU PER LB

ENTROPY, BTU PER LB °R

Fig. 17

Theory and Use of Enthalpy-Entropy Diagrams

Basic Theory - For any flow process, the laws of thermodynamics give:

$$\Delta H + \Delta \frac{v^2}{2gJ} + \frac{\Delta Z}{J} = q - w_s \tag{1}$$

where $\quad \Delta H$ = increase in enthalpy, per lb fluid flowing

$\Delta \dfrac{v^2}{2gJ}$ = increase in directed kinetic energy per lb fluid flowing

$\dfrac{\Delta Z}{J}$ = increase in position energy, per lb fluid flowing

q = heat added to system by surrounding, per lb fluid flowing

w_s = work done by system on surroundings other than Δpv,

per lb fluid flowing

In the case of an adiabatic rocket motor, this reduces to

$$\Delta H + \Delta \frac{v^2}{2gJ} = 0 \tag{2}$$

moreover, for the combustion process itself,

$$\Delta H = 0 \tag{3}$$

Since the combustion process and possibly also the expansion process entails a change in chemical composition, it is necessary that enthalpy be referred to definite chemical compounds at an arbitrary but definite temperature. The reference state used in the above diagram is such that the enthalpy of any constituent is its heat of formation at 298° K plus its sensible heat above 298° K.

For the expansion process, Equation 2 may be rearranged and solved letting $v_c = 0$ to give (since $\Delta \dfrac{v^2}{2gJ} = \dfrac{v_e^2 - v_c^2}{2gJ}$):

$$\frac{v_e}{g} \quad 6.95 \sqrt{-\Delta H} = I$$

where v_e = exhaust velocity, ft per sec

g = acceleration due to gravity, 32.2 ft per sec^2

$\triangle H$ = increase in enthalpy, BTU per lb

I = specific impulse, sec

(Note: See Part II for discussion of specific impulse)

Utilization - Figure 18 illustrates the use of the H-S diagrams in calculating theoretical specific impulse.

Flow with friction and heat transfer may be approximated if these are known as follows (See Figure 19).

By definition:

$$\int TdS = q + w_f \cong T_{av}\triangle S \qquad (5)$$

Rearranging Equation 5, we obtain

$$\triangle S_{12} \cong \frac{q_{12} + w_{f_{12}}}{T_{12_{av}}} \qquad (6)$$

where w_f = (1 - energy efficiency) $\triangle H$ isentropic.

Thus if efficiency and heat transfer are known over a pressure interval, the expansion path may be plotted.

The velocity path may be calculated by rearranging Equation 1:

$$v_2^2 - v_1^2 = 2g \left(q_{12} - \triangle H_{12}\right) \qquad (7)$$

The following theoretical specific impulse curves have been obtained using isentropic expansion to one atmosphere with fuel temperature of 520° R (Figures 20-24).
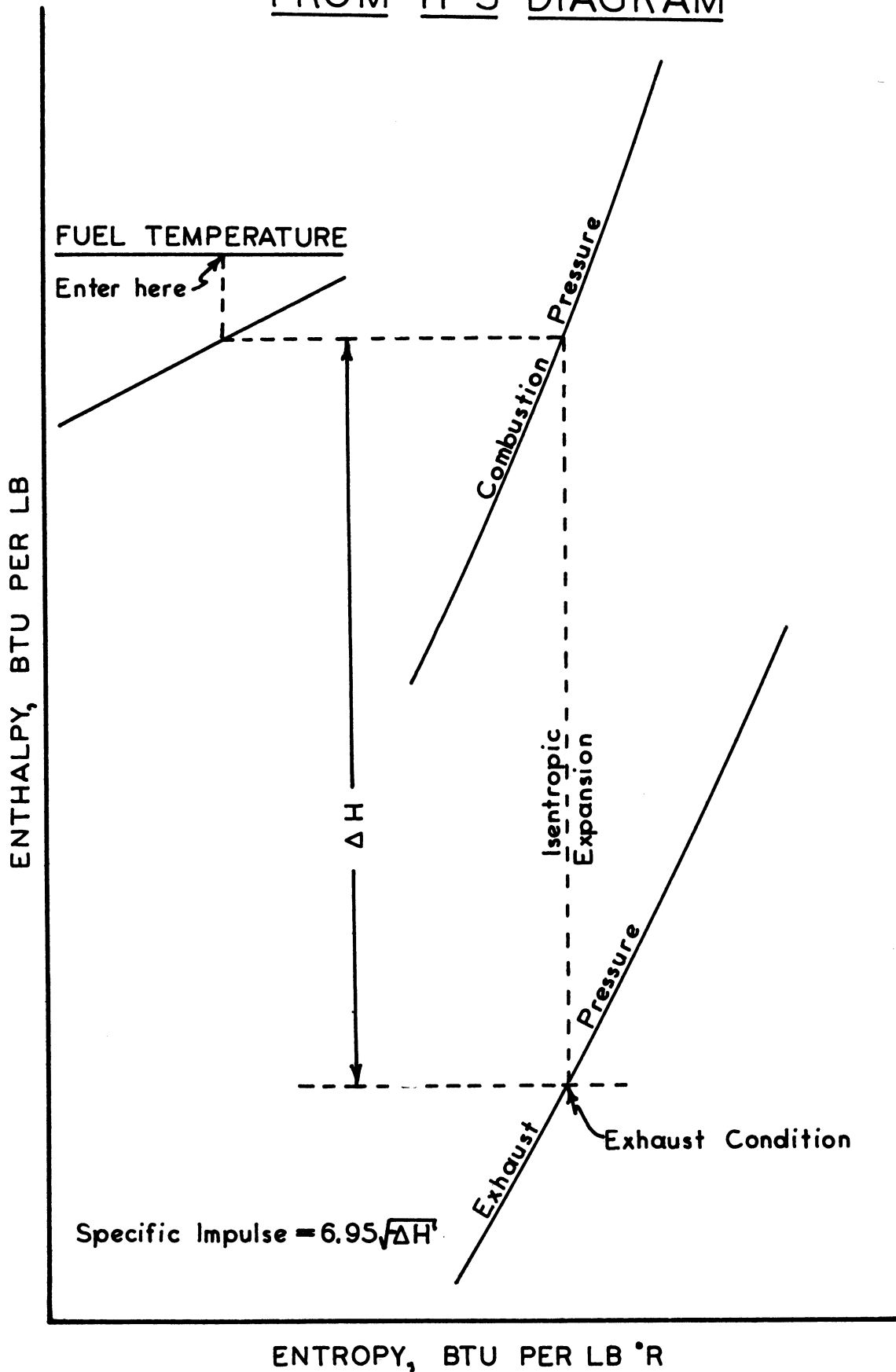
THEORETICAL SPECIFIC IMPULSE
FROM H-S DIAGRAM

Fig. 18

FLOW WITH FRICTION AND
HEAT TRANSFER

$$\Delta S_{12} \cong \frac{q_{12} + w_{f_{12}}}{T_{12av}}$$

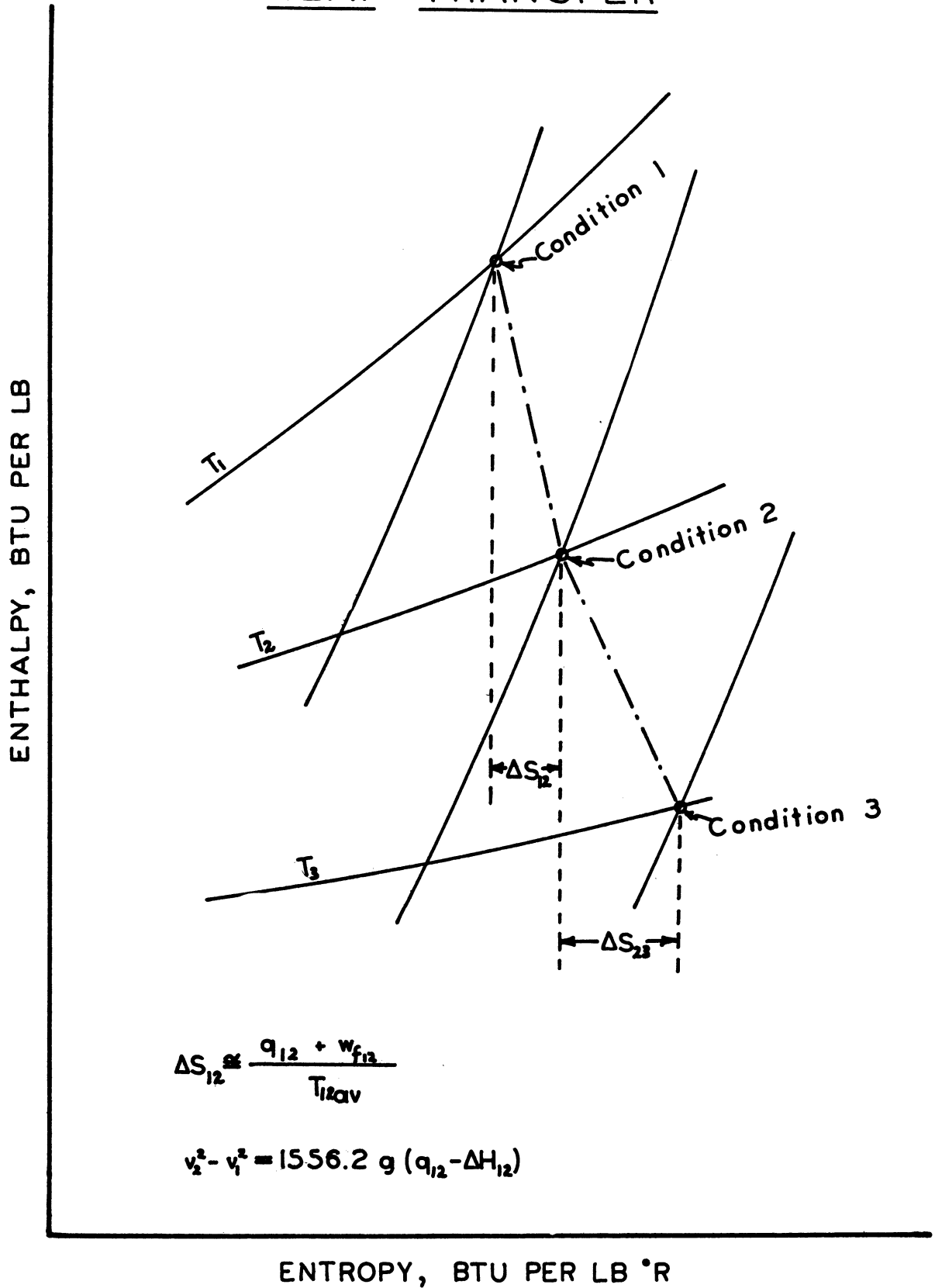$$v_2^2 - v_1^2 = 1556.2 \; g \; (q_{12} - \Delta H_{12})$$

ENTROPY, BTU PER LB °R

Fig. 19

VARIATION IN THEORETICAL SPECIFIC IMPULSE
WITH MIXTURE RATIO

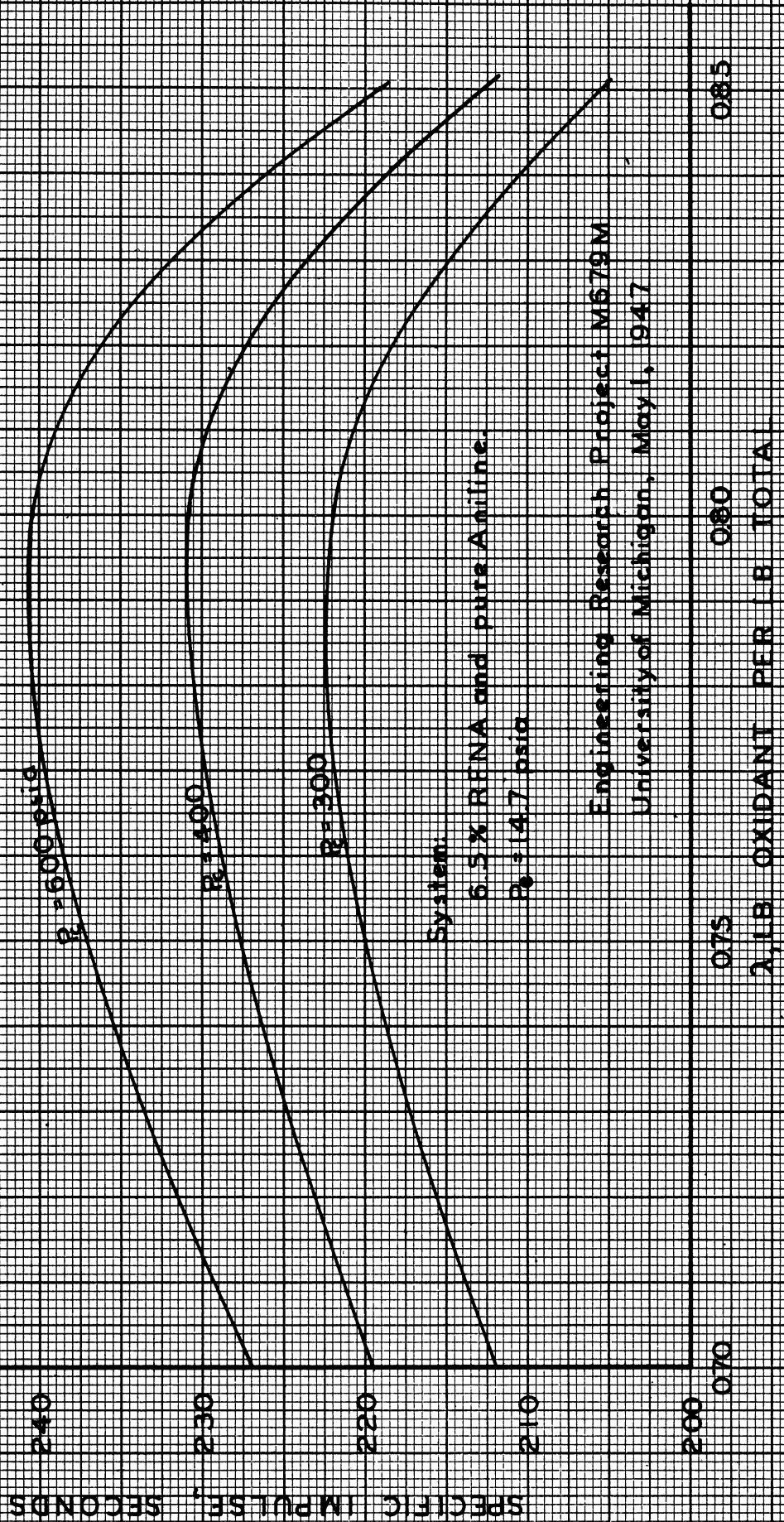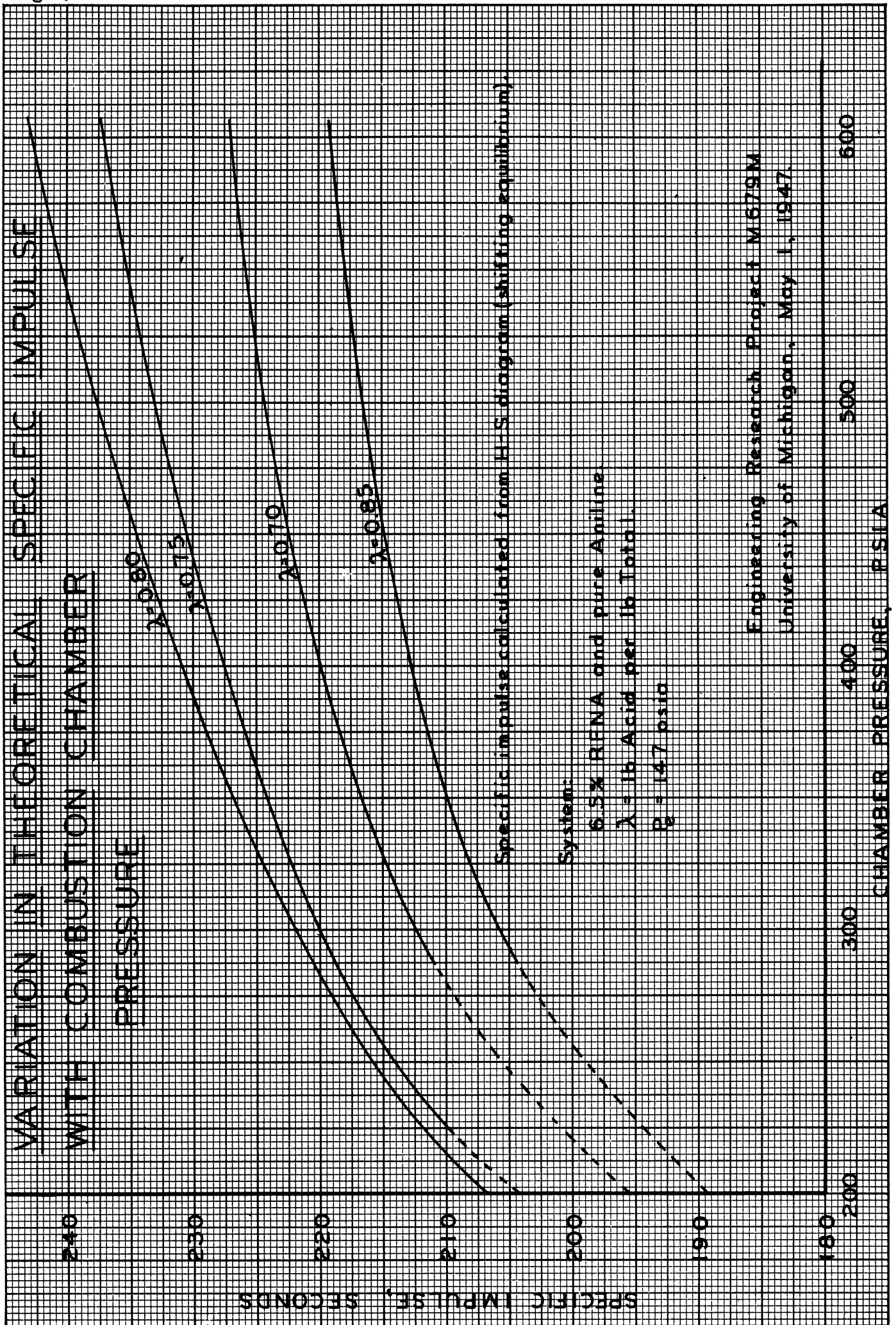Specific impulse calculated from H-S diagrams (shifting equilibrium)

$P_c = 600$ psia
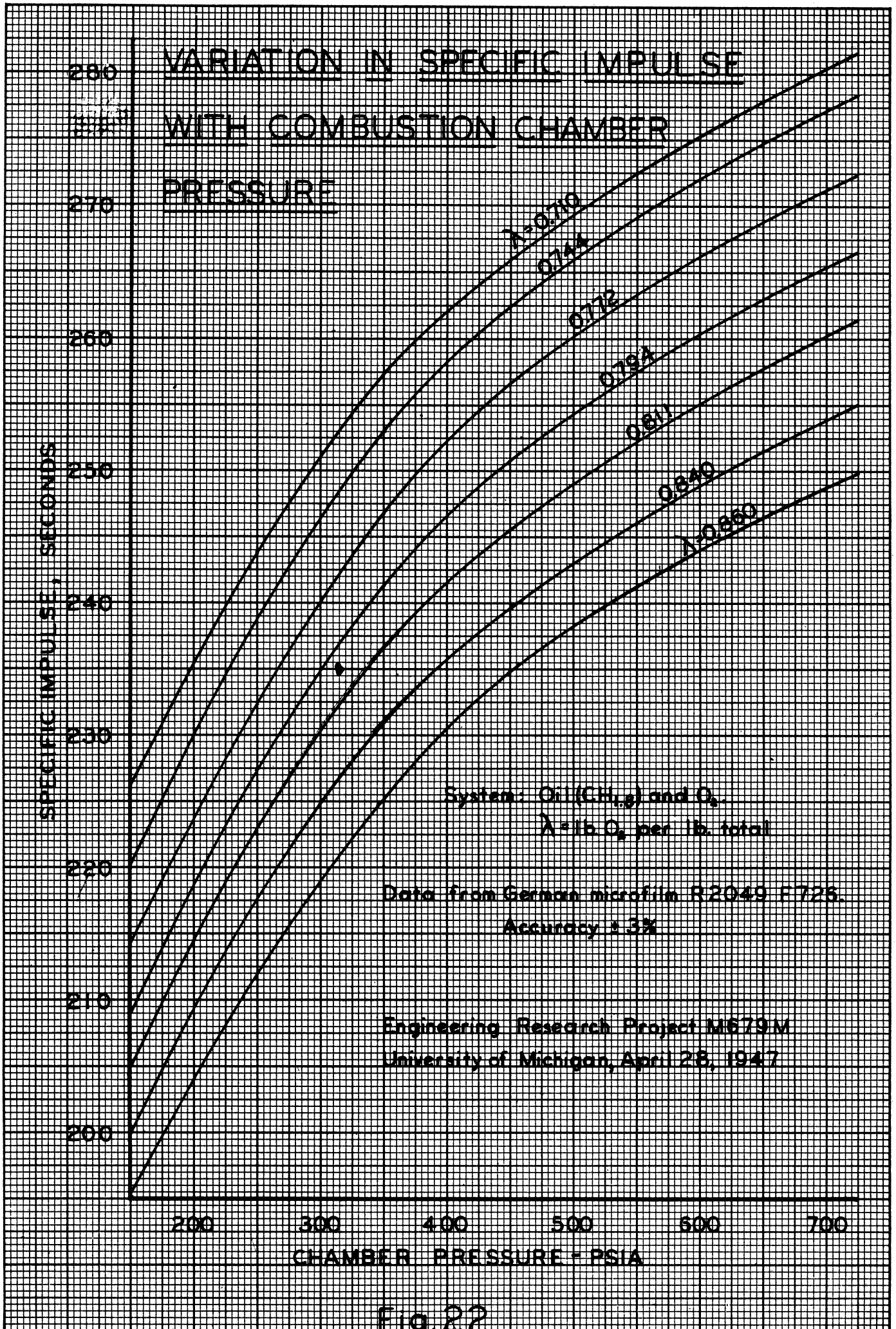
$P_c = 400$ psia

$P_c = 300$

System:
6.5% RFNA and pure Aniline.
$P_e = 14.7$ psia

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Fig. 20

λ, LB OXIDANT PER LB TOTAL

SPECIFIC IMPULSE, SECONDS

VARIATION IN THEORETICAL SPECIFIC IMPULSE
WITH COMBUSTION CHAMBER PRESSURE

λ=0.80
λ=0.75
λ=0.70
λ=0.85

Specific impulse calculated from H-S diagram (shifting equilibrium).

System:
6.5% RFNA and pure Aniline
λ = lb Acid per lb Total.
P_e = 14.7 psia

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CHAMBER PRESSURE, PSIA

SPECIFIC IMPULSE, SECONDS

Fig. 21

VARIATION IN SPECIFIC IMPULSE
WITH COMBUSTION CHAMBER
PRESSURE

$\lambda = 0.710$
0.744
0.772
0.794
0.811
0.840
$\lambda = 0.860$

System: Oil ($CH_{1.9}$) and O_2
λ = lb. O_2 per lb. total

Data from German microfilm R2049 F725.
Accuracy ± 3%

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SPECIFIC IMPULSE, SECONDS

280
270
260
250
240
230
220
210
200

200　　300　　400　　500　　600　　700
CHAMBER PRESSURE - PSIA

Fig. 22

VARIATION IN THEORETICAL
SPECIFIC IMPULSE WITH
COMBUSTION CHAMBER PRESSURE

System:
Hexane – Liquid O_2
λ = lb O_2 per lb. total

$\lambda = 0.690$

Data from German H-S diagram
microfilm PGM9 - Arch 20/10.

University of Michigan, August 11, 1947

SPECIFIC IMPULSE, SECONDS

250

240

230

220

100   200   300

CHAMBER PRESSURE, PSIA

Fig. 23

THEORETICAL SPECIFIC IMPULSE VS.
COMBUSTION CHAMBER PRESSURE

System: 76% Ethanol – Liquid O_2.
$\lambda = $ lb O_2 per lb total.

Data from German H–S diagram, Film PGMD Arch 20/3

Engineering Research Project M679M
University of Michigan, April 29, 1947

$\lambda = 0.59$

CHAMBER PRESSURE, PSIA

Fig. 24

SPECIFIC IMPULSE, SECONDS

PART II CALCULATION OF THEORETICAL SPECIFIC IMPULSE

Thermodynamic Approach

In general, specific impulse is given by:

$$I = \frac{u_e}{g} + \frac{f_e}{G} (P_e - P_a) \quad \text{(see reference 10)}$$

where I = specific impulse, sec

u_e = axial component of exit velocity

g = units conversion factor, 32.2 ft per sec^2

f_e = exit area, ft^2

G = weight rate of flow, lbs per sec

P_e = exhaust pressure, lbs per ft^2

P_a = surrounding atmospheric pressure, lbs per ft^2

For the present analysis, however, it will be assumed that the nozzle

is so designed that $P_e = P_a$ making specific impulse equal to:

$$I = \frac{u_e}{g}$$

Furthermore, the difference between u_e and v_e will be neglected since

this is a function of the particular nozzle used, not of the fuel system.

Thus, for the purposes of fuel system analysis, specific impulse will be

taken as:

$$I = \frac{v_e}{g}$$

The prediction of rocket motor thrust from theoretical considerations

requires some assumptions in regard to the state of chemical reactions and

physical conditions through the motor, and this situation will obtain until

considerably more is known of reaction mechanisms and rates for the complex

products of reaction. It is universal practice to assume that equilibrium

is reached in the combustion chamber, and to build the combustion chamber

large enough to accomplish this for the fuel system contemplated. This

assumption permits the evaluation of composition and enthalpy content of materials entering the nozzle. The rate and extent of conversion of this enthalpy to velocity energy depends in part on the kinetics of chemical reactions for which a shift in equilibrium composition may occur during expansion.

The most optimistic assumption is that equilibrium is maintained through the nozzle, with the resultant release of a considerable amount of dissociation energy to velocity energy. If this is true, the general thermodynamic energy balance is the basis for calculating theoretical specific impulse;

$$\Delta H + \Delta \frac{v^2}{2g} = q - w_s$$

and in an adiabatic and frictionless nozzle, this becomes

$$\Delta v^2 = -2g \Delta H = v_e^2 - v_c^2 = v_e^2 \quad \text{(essentially)}$$

and

$$I = \frac{v_e}{g} = \sqrt{\frac{2}{g}} \sqrt{-\Delta H}$$

where units are consistent.

The assumption of thermochemical equilibrium of the gases entering the nozzle is not subject to too serious criticism. After the expansion process, however, the state of the system is not so easily assumed, since the gases are at a very high temperature and have undergone a very rapid decrease in temperature and pressure. Knowledge of the degree of attainment of equilibrium will be necessary for accurate evaluation of ΔH.

Inspection of the meager kinetics data available indicates that the water-gas reaction, for instance, will not maintain equilibrium concentrations under such rapidly changing conditions of temperature and pressure. Association of atoms of hydrogen and oxygen will probably

approach equilibrium more closely, and these represent a considerably greater energy release than the sluggish water-gas reaction. Considerably more confidence can be placed in computations based on analysis of individual reaction rates rather than the assumption that equilibrium will be maintained down to exit temperature, or some arbitrarily chosen intermediate temperature, or that composition of the combustion chamber gases will be "frozen." Attainment of this will require a comprehensive study of kinetics of reactions, and the half-lives of various atomic, molecular, and radical species involved in the complex combustion process.

A Mollier-type diagram may be constructed for the products of combustion, assuming complete equilibrium or frozen composition at combustion conditions or at any intermediate extent of reaction believed to obtain. This diagram gives immediately the ΔH between any two conditions included therein.

The complete thermodynamic enthalpy function may be applied:

$$\Delta H = \int T dS + \int V dP + \int \mu \, dM + etc$$

where T = Temperature

S = Entropy

V = Volume

P = Pressure

μ = Chemical Potential

M = Mass

etc = all other energy effects such as electrical, surface, nuclear, etc.

If isentropic expansion at "frozen" composition is assumed, with the miscellaneous energy effects zero, this reduces to

$$\Delta H = \int V dP$$

This integral can be readily evaluated between limits if a relation

between P and V is known. For the case of perfect gases with constant

specific heats and zero Joule-Thomson effect

$$PV^{\gamma} = P_c V_c^{\gamma}$$

where γ = ratio specific heat at constant pressure to that at

constant volume, i.e., c_p/c_v.

Appropriate substitution and integration permits evaluation of $\triangle H$, hence

specific impulse according to the procedure designated as Method (1). It

should be noted that this integration is possible only if γ is assumed

constant. Since both specific heat at constant pressure and specific heat

at constant volume change with temperature, an average value of their

changing ratio is necessary. Various methods of averaging are explored

in the variations of Method (1).

Another procedure is possible if frozen composition is assumed, which

obviates the uncertain assumption of constant γ.

$$dH = (\frac{\partial H}{\partial T})_P \, dT + (\frac{\partial H}{\partial T})_T \, dP$$

For zero Joule-Thomson effect, this becomes:

$$dH = (\frac{\partial H}{\partial T})_P \, dT = c_p \, dT$$

or $\triangle H = \int c_p \, dT$

Since accurate specific heats (c_p) for gases formed in combustion

processes are available, it is possible to prepare tables or graphs of

the enthalpy (and entropy) as a function of temperature for these gases.

(e.g. Table 3) These tables may be used in evaluating $\triangle H$ through calcu-

lation of two isobars of an H-S diagram $(P = P_c$ and $P = P_e)$ in the proper

entropy region so that $\triangle S = 0$. This procedure is used in Method (3).

The most favorable assumption of maintenance of thermochemical and

thermophysical equilibrium is used in Method (2), using $\triangle H$ values read

from an equilibrium enthalpy-entropy diagram.

Much work is being done to clarify the points of uncertainty mentioned. In the meantime, the researcher must evaluate new fuel combinations, and the designer must plan new motors without accurate knowledge of the theoretical maximum energy which can be extracted in the expansion process. Moreover, unless each knows the theoretical maximum, there remains the danger of overlooking an important possibility such as a new fuel, or of wasted effort on the part of the designer to improve a motor already performing at a maximum.

Accurate comparison of experimental results with theoretical prediction is impossible without accurate knowledge of friction losses and proper evaluation of the lateral components of velocity of the jet gases.

There follow more detailed elucidations of these various methods, with comparative results tabulated and graphed. It will be seen by inspection of these results that:

1. Specific impulses predicted by the various methods show surprisingly little spread.

2. Predicted fuel-oxidant ratio for optimum thrust may be affected considerably by method of calculation.

3. Exit gas temperature as predicted by various methods differ considerably.

The thermal, chemical, and physical processes involved in rocket motors require further study for determination of:

1. Theoretical maximum specific impulse with a greater degree of certainty.

2. Optimum mixture ratio

3. Temperature of gases for analysis of the required cooling system.

Methods for Calculating Theoretical Specific Impulse

Calculations of theoretical specific impulse differ primarily in assuming either frozen or shifting equilibrium. Three methods will be outlined here covering both assumptions.

Method (1) - Adiabatic Expansion Formula (Reference 10)

Assumptions - 1. Frozen equilibrium at the combustion chamber composition.

2. Perfect gases.

3. Constant ratio of specific heats.

Procedure - The combustion chamber composition and temperature is calculated. Average molecular weight is calculated and average ratio of specific heats is estimated. Exhaust temperature is calculated and this assumption verified by:

$$\frac{T_c}{T_e} = \left[\frac{P_c}{P_e}\right]^{\frac{\gamma-1}{\gamma}}$$

Specific impulse is given by:

$$I = 6.95 \sqrt{\frac{T_e}{M}\left\{\frac{2\gamma}{\gamma-1}\left[1 - \left(\frac{P_e}{P_c}\right)^{\frac{\gamma-1}{\gamma}}\right]\right\}^{\frac{1}{2}}}$$

Where T_c = combustion chamber temperature, $^\circ R$

T_e = exhaust temperature, $^\circ R$

P_c = combustion chamber pressure

P_e = exhaust pressure

γ = ratio of specific heats

I = specific impulse, sec

M = average molecular weight

The average γ required may be obtained by several different methods:

a. Arithmetic average γ between T_c and T_e

b. Obtain γ from arithmetic average c_p

c. Obtain γ from arithmetic average temperature between T_c and T_e

d. Obtain γ from integrated average c_p

Method (2) Enthalpy Entropy Diagram

Assumptions - 1. Shifting equilibrium throughout nozzle i.e.,

thermochemical equilibrium is maintained.

2. PV = NRT equation of state

Procedure - Compositions, enthalpies, and entropies are calculated for two or more temperatures at the combustion chamber pressure. When properly chosen, these points "straddle" the flame temperatures. The same is done for the exhaust pressure except that the points are chosen to straddle the combustion chamber entropy. A partial H-S diagram is constructed (see Figures 12, 17, 18) and the proper interpolation gives the enthalpy change for the expansion process. Theoretical specific impulse is given by

$$I = 6.95 \sqrt{-\Delta H}$$

where I = specific impulse, sec

ΔH = enthalpy change on expansion, Btu per lb

The enthalpy-entropy diagram may be as complete as desired by calculation of more points and by cross plotting (see Figures 14-16). This has the advantage of allowing ready investigation of temperature and volume conditions with changing pressure and fuel conditions. Efficiency and heat transfer may also be taken into account (see Figure 19).

This method has been used in Germany (References 13 and 16) but apparently very little in this country.

Method (3) H-S diagram - "frozen" equilibrium

This method has not, to the best of the writer's knowledge, been used at all, but is proposed as an improvement on Method (1).

Assumptions: 1.   "Frozen" equilibrium

2. $PV = NRT$

Procedure - The flame temperature and composition are calculated as in

Method (1). The enthalpy and entropy of this state are calculated as

in Method (2). Using this composition, two or three points (H,S) are

calculated at the exhaust pressure so as to straddle the combustion

chamber entropy. In other words the assumptions of Method (1) are used

with the procedure of Method (2) with the exception of the averaging of

specific heats. By use of properly constructed enthalpy-entropy tables

the uncertainty introduced by averaging the ratio of specific heats is

eliminated. A partial H-S diagram is constructed, and I is calculated as

in Method (2).

Tabular and graphical comparisons of these methods follow.

Table 8: Theoretical Performance of the RFNA-Aniline
System by Three Methods of Calculation for
Four Conditions of Chamber Pressure and
Mixture Ratio.

Method	1a (av γ)	1b (av C_p)	1c (av temp)	1d (integral of av C_p)	2 (shifting H-S)	3 (frozen H-S)
λ	.75	.75	.75	.75	.75	.75
P_c (atm)	40	40	40	40	40	40
T_c	5364°R	5364°R	5364°R	5364°R	5364°R	5364°R
T_e	2671°R	2678°R	2713°R	2693°R	2981°R	2700°R
M	25.176	25.176	25.176	25.176	--	25.176
γ_{av}	1.2331	1.2320	1.2269	1.2294	--	--
I	233.9	233.9	234.6	234.2	237	233.7

Method		1b	1c		2	3
λ	--	.80	.80	--	.80	.80
P_c (atm)	--	40	40	--	40	40
T_c	--	5616°R	5616°R	--	5616°R	5616°R
T_e	--	2923°R	2952°R	--	3917°R	2943°R
M	--	27.129	27.129	--	--	27.129
γ_{av}	--	1.2151	1.2112	--	--	--
I	--	232.7	233.3	--	243	232.2

Method	1a	1b	1c	1d	2	3
λ	--	.75	.75	--	.75	.75
P_c (atm)	--	20	20	--	20	20
T_c	--	5292°R	5292°R	--	5292°R	5292°R
T_e	--	3028°R	3047°R	--	3360°R	3044°R
M	--	25.133	25.133	--	--	25.133
γ_{av}	--	1.2291	1.2259	--	--	--
I	--	216.1	216.4	--	220	215.5

Method	1a	1b	1c	1d	2	3
λ	--	.80	.80	--	.80	.80
P_c (atm)	--	20	20	--	20	20
T_c	--	5494°R	5494°R	--	5494°R	5494°R
T_e	--	3236°R	3247°R	--	4200°R	3241°R
M	--	26.964	26.964	--	--	26.964
γ_{av}	--	1.2144	1.2129	--	--	--
I	--	214.0	214.2	--	222	213.0

Note: $P_e = 1$ atm. in all cases
Values from Table 8 are plotted on Figures 25 and 26 for easy comparison.

VARIATION IN THEORETICAL SPECIFIC IMPULSE WITH
COMBUSTION CHAMBER PRESSURE AND
METHOD OF CALCULATION

Method 2

Method 1

Method 3

System:
6.5% RFNA and pure Aniline
0.80 lb Acid per lb Total
$P_e = 14.7$ psia

Engineering Research Project M679M
University of Michigan, May 26, 1947

CHAMBER PRESSURE, PSIA

Fig 25

SPECIFIC IMPULSE, SECONDS

VARIATION IN THEORETICAL SPECIFIC IMPULSE
WITH MIXTURE RATIO

Fig. 26

System:
6.5% RFNA and pure Aniline
$P_c = 14.7$ psia

Engineering Research Project M679M
University of Michigan, May 26, 1947
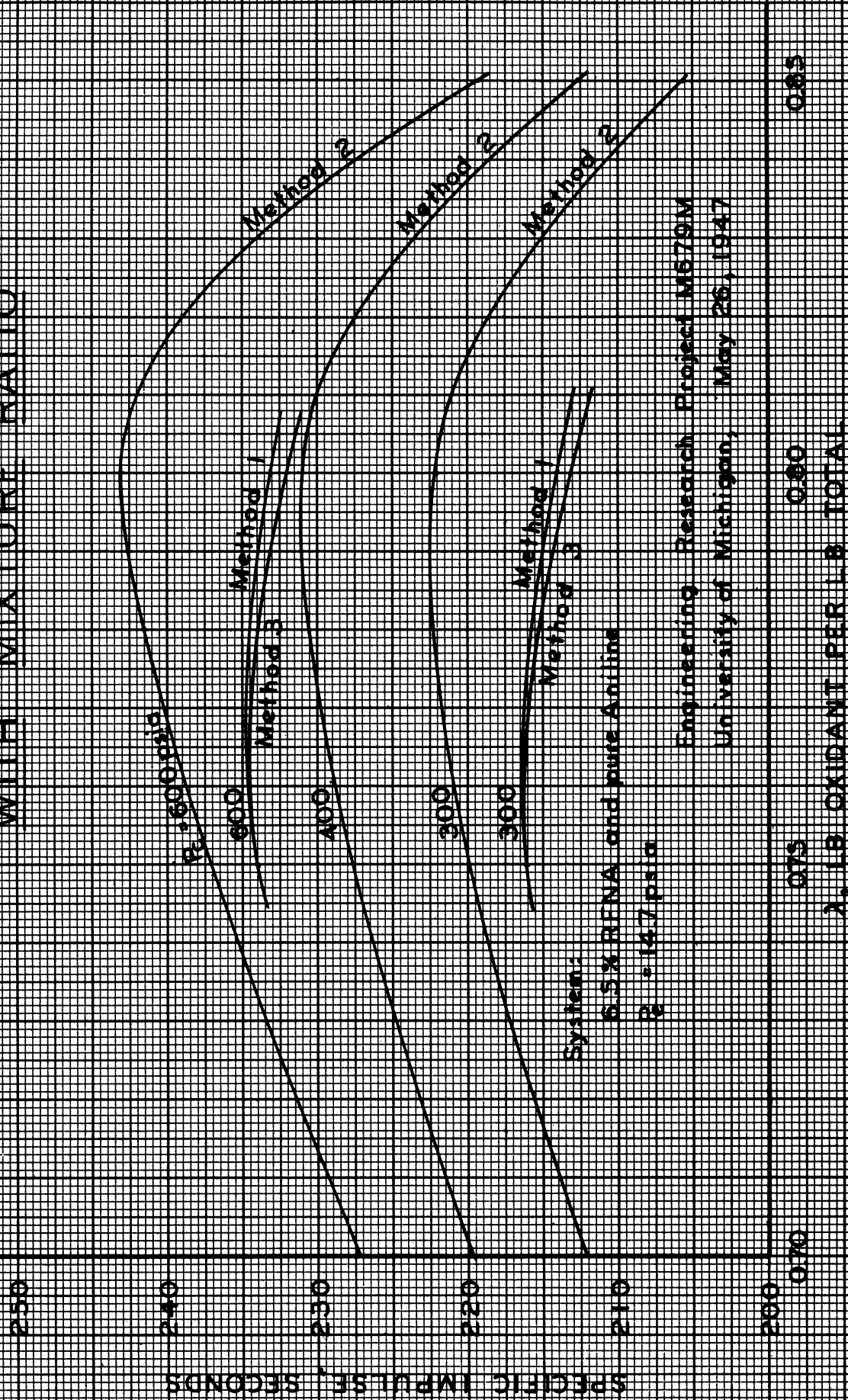
Discussion

Every method of calculation presented in this report involves at least one questionable assumption.

The assumption that chemical equilibrium is attained in the combustion chamber is basic to any method of computation now in use. The maintenance of an equilibrium mixture during the expansion is one of the uncertain points in explanation of which much study of combustion kinetics is required. The H-S diagram (Method 2) assumes maintenance of equilibrium, while computation from isentropic perfect gas formulae assumes "frozen" composition. The latter, however, required the further assumption of constant ratio of specific heats over a temperature and pressure range. This last assumption is obviously dangerous, whether composition changes or not. A true average ratio for any interval is extremely elusive.

Inspection of Table 8 shows that Methods (1a), (1b), (1c), (1d), and (3) do not differ considerably in results. These methods are based on the same assumption (namely frozen equilibrium) the difference being only in the use of constant ratio of specific heats. Method (3) obviates this assumption and is therefore theoretically sounder.

The difference in results obtained using frozen or shifting equilibrium assumptions is illustrated in Table 8 and Figure 26. Exhaust temperature is the largest point of variance, being considerably higher with shifting equilibrium (Method 2). Figure 26 indicates some difference in optimum mixture ratio as predicted from the two assumptions but specific impulses that are substantially the same.

For the fuel systems herein reported, there are certain ratios of fuel to oxidant at which theoretical specific impulses from the two methods described check well. At leaner mixtures, the H-S diagram evaluation indicates

a higher maximum specific impulse at a leaner fuel ratio than perfect-gas equations. There is considerable difference in the temperatures and some difference in volumes at exit as predicted by the two methods.

The labor of evaluating one set of conditions is considerably greater for the H-S diagram, but for a comprehensive study of a system, the labor involved is not greatly different.

The difference in theoretical results introduces some question into theoretical analysis of performance, with separation of friction losses, chemical inefficiencies, and nozzle disturbances as the objective. It appears that much study is required on each of these factors before complete understanding is attained.

REFERENCES

1. Gordon, J. G., J Chem. Phys. 2, 65, 549 (1934)

2. Hottel, H. C., Hershey, R. L., and Eberhardt, J. E., Soc. Auto. Engr's. J. 39, 409-424 (Oct. 1936)

3. Johnston and Chapman, A.T., J.A.C.S., 55 153 (1935)

4. Johnston and Davis, J.A.C.S., 56, 271 (1934)

5. Johnston and Davis, J.A.C.S., 56, 1045 (1934)

6. Johnston and Dawson, J.A.C.S., 55, 2744 (1933)

7. Johnston and Walker, J.A.C.S., 57, 682 (1935)

8. Kassel, J.A.C.S., 56, 1838 (1934)

9. Kelley, K.K., U.S. Bur. Mines Bul. 371 (1934)

10. Lemmon, A.W. Jr., "Fuel Systems for Jet Propulsion," JPMP of OSRD No. 267 (May 1945)

11. Lewis and Von Elbe, "Combustion Flames and Explosion of Gases," London (1938)

12. Perry, J.H., "Chemical Engineers' Handbook," 2nd Ed., New York (1941)

13. Sänger and Brebt, "A Rocket Drive for Long Range Bombers," Ainring (Obererbaren) (Aug 1944)

14. Wenner, R.R., "Thermochemical Calculations," New York (1941)

15. Wilson, B.E. Jr., "The Present State of the Statistical Method of Calculating Thermodynamic Functions," Chem. Rev., 27, 17-37 (1940) (179 References on specific compounds).

16. German Microfilm, PGI8, Arch 20/1

17. Lange, "Handbook of Chemistry", 6th Ed. Handbook Publishers Inc., Sandusky, Ohio (1946)

18. Hougen and Watson, "Industrial Chemical Calculations", Boston (1936)

APPENDIX I

Derivation of Generalized Equilibrium Calculation Scheme

The system to be considered is one of unit mass composed entirely of atoms of carbon, oxygen, hydrogen, and nitrogen. By preliminary inspection of equilibrium constant data, it was estimated that ten molecular species should be included. Subsequent check showed this estimate to be substantially correct up to $3200^{\circ}K$. These species are: H_2O, H_2, O_2, O, H, OH, CO_2, CO, NO, and N_2. The equilibrium composition of such a system is governed by the laws of conservation of atomic species, conservation of mass, and mass action. Since there are four atomic species there are four equations of their conservation:*

(30) $\quad \text{C} = [CO_2] + [CO]$

(31) $\quad \text{O} = [H_2O] + 2[O_2] + [O] + [OH] + 2[CO_2] + [CO] + [NO]$

(32) $\quad \text{H} = 2[H_2O] + 2[H_2] + [H] + [OH]$

(33) $\quad \text{N} = [NO] + 2[N_2]$

The equation of conservation of mass is:

(34) $\quad N = [H_2O] + [H_2] + [O_2] + [O] + [H] + [OH] + [CO_2] + [CO]$
$\qquad\qquad + [NO] + [N_2]$

where $\quad \text{C} =$ gm atoms of carbon in the system

$\qquad \text{O} =$ gm atoms of oxygen in the system

$\qquad \text{H} =$ gm atoms of hydrogen in the system

$\qquad \text{N} =$ gm atoms of nitrogen in the system

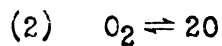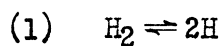$\qquad N =$ total number of gm moles in the system

$\qquad [H_2O] =$ gm moles of water in the system at equilibrium

$\qquad [H_2] =$ gm moles of hydrogen in the system at equilibrium, etc.

---

*Equations are arbitrarily numbered here to avoid confusion with mass action equations, which are numbered to correspond to those of Lewis and Von Elbe. (Reference 11)

The introduction of N, total number of moles in the system at equilibrium, introduces an eleventh unknown. Thus an algebraic scheme of eleven simultaneous equations and eleven unknowns is being built up. The remaining six equations must be six independent mass action equations. The following six hypothetical reversible chemical reactions will yield mass action equations satisfying this requirement: The numbering is from Lewis and Von Elbe (Reference 11).

(1) $H_2 \rightleftharpoons 2H$

(2) $O_2 \rightleftharpoons 2O$

(8) $H_2O \rightleftharpoons H_2 + \frac{1}{2} O_2$

(9) $H_2O \rightleftharpoons OH + \frac{1}{2} H_2$

(10) $CO + H_2O \rightleftharpoons CO_2 + H_2$

(15) $\frac{1}{2} O_2 + \frac{1}{2} N_2 \rightleftharpoons NO$
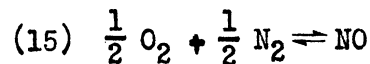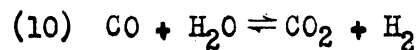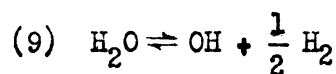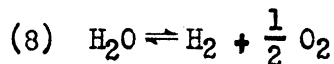
The mass action equations are:

(1) $K_1 = \dfrac{\left(\dfrac{[H]}{N} P\right)^2}{\left(\dfrac{[H_2]}{N} P\right)}$

(2) $K_2 = \dfrac{\left(\dfrac{[O]}{N} P\right)^2}{\left(\dfrac{[O_2]}{N} P\right)}$

(8) $K_8 = \dfrac{\left(\dfrac{[H_2]}{N} P\right)\left(\dfrac{[O_2]}{N} P\right)^{\frac{1}{2}}}{\left(\dfrac{[H_2O]}{N} P\right)}$

(9) $K_9 = \dfrac{\left(\dfrac{[OH]}{N} P\right)\left(\dfrac{[H_2]}{N} P\right)^{\frac{1}{2}}}{\left(\dfrac{[H_2O]}{N} P\right)}$

(10) $K_{10} = \dfrac{\left(\dfrac{[CO_2]}{N} P\right)\left(\dfrac{[H_2]}{N} P\right)}{\left(\dfrac{[CO]}{N} P\right)\left(\dfrac{[H_2O]}{N} P\right)}$

$$(15) \quad K_{15} = \frac{\left(\frac{[NO]}{N}P\right)}{\left(\frac{[O_2]}{N}P\right)^{\frac{1}{2}}\left(\frac{[N_2]}{N}P\right)^{\frac{1}{2}}}$$

where K_1, K_2, etc. are the appropriate equilibrium constants

P = pressure in atmospheres

In formulating the above equations, ideal gas behavior has been assumed allowing total pressure times mole fraction to be used in place of the more exact fugacity. This is not an unreasonable assumption in the range of interest since the temperature is high where the pressure is high, and the pressure is low where the temperature is low.

An algebraic system of eleven equations and eleven unknowns has now been formulated. It remains to manipulate them into solvable form:

Solving (1) for $[H]$:

$$(1.1) \quad [H] = \sqrt{K_1/P}\ \sqrt{N}\ \sqrt{[H_2]}$$

Rearranging equation (32):

$$(32.1) \quad [H_2O] + \frac{1}{2}[OH] = \frac{1}{2}(H) - [H_2] - \frac{1}{2}[H]$$

Rearranging (9):

$$(9.1) \quad [H_2O] = [OH]\sqrt{[H_2]}\ \frac{\sqrt{P/N}}{K_9}$$

Writing an identity:

$$(34) \quad [H_2O] + \frac{1}{2}[OH] = [H_2O] + \frac{1}{2}[OH]$$

And substituting the value of $[H_2O]$ from (9.1) into the left-hand side of (34):

$$(35) \quad \frac{1}{2}[OH] + [OH]\frac{\sqrt{P}}{K_9}\sqrt{\frac{[H_2]}{N}} = [H_2O] + \frac{1}{2}[OH]$$

Solving (35) for $[OH]$:

$$(35.1) \quad \tfrac{1}{2}[OH] = \frac{[H_2O] + \tfrac{1}{2}[OH]}{1 + \left(\frac{2\sqrt{P}}{K_9}\right)\sqrt{\frac{[H_2]}{N}}}$$

Solving (8) for $[O_2]$:

$$(8.1) \quad [O_2] = (K_8^2/P)\ N\ ([H_2O]/[H_2])^2$$

Solving (2) for $[O]$:

$$(2.1) \quad [O] = \sqrt{K_2/P}\ \sqrt{N}\ \sqrt{[O_2]}$$

Solving (15) for $[NO]$:

$$(15.1) \quad [NO] = K_{15}\sqrt{[O_2]}\ \sqrt{[N_2]}$$

Substituting from (33) into (15.1)

$$(15.2) \quad [NO] = K_{15}\sqrt{[O_2]}\ \sqrt{\tfrac{1}{2}\,\textcircled{N} - \tfrac{1}{2}[NO]}$$

Substituting (30) into (31)

$$(31.1) \quad \textcircled{O} - \textcircled{C} = [H_2O] + 2[O_2] + [O] + [OH] + [CO_2] + [NO]$$

Solving (31.1) for $[CO_2]$:

$$(31.2) \quad [CO_2] = \textcircled{O} - \textcircled{C} - [H_2O] - [OH] - 2[O_2] - [O] - [NO]$$

Rearranging (30):

$$(30.1) \quad [CO] = \textcircled{C} - [CO_2]$$

Solving (10) for $[H_2]$:

$$(10.1) \quad [H_2] = \frac{[CO]\,[H_2O]}{[CO_2]}\,K_{10}$$

Substituting (30), (31), and (33) into (34):

$$(34.1) \quad N = \textcircled{C} + \tfrac{1}{2}\,\textcircled{H} + \tfrac{1}{2}\,\textcircled{N} + \tfrac{1}{2}[H] + \tfrac{1}{2}[OH] + \tfrac{1}{2}[NO] + \textcircled{O} + [O_2]$$

The equations are now ready for stepwise trial and error calculation:

Assume: $[H_2]$ and N

Calculate $2[H]$: $(1.1) \quad 2[H] = 2\sqrt{K_1/P}\ \sqrt{N\,[H_2]}$

Calculate $[OH] + 2[H_2O]$: $(32.1) \quad [OH] + 2[H_2O] = \textcircled{H} - 2[H_2] - [H]$

Calculate $[OH]$: (35.1) $\quad [OH] = \dfrac{[OH] + 2[H_2O]}{1 + (2\sqrt{P/K_9})\ \sqrt{[H_2]/N}}$

Calculate $[H_2O]$: $\quad [H_2O] = \dfrac{1}{2}\left([OH] + 2[H_2O] - [OH]\right)$

Calculate $[O_2]$: (8.1) $\quad [O_2] = (K_8^2/P)\ N\ ([H_2O]/[H_2])^2$

Calculate $[O]$: (2.1) $\quad [O] = \sqrt{K_2/P}\ \sqrt{N}\ \sqrt{[O_2]}$

Calculate $[NO]$: (5.2) $\quad [NO] = K_{15}\sqrt{[O_2]}\ \sqrt{\tfrac{1}{2}\textcircled{N} - \tfrac{1}{2}[NO]}$

$$\cong K_{15}\sqrt{\tfrac{1}{2}\ \textcircled{N}}\ \sqrt{[O_2]}$$

Calculate $[CO_2]$: (31.1) $\quad [CO_2] = \textcircled{O} - \textcircled{C} - [H_2O] - [OH] - 2[O_2] - [O] - [NO]$

Calculate $[CO]$: (30.1) $\quad [CO] = \textcircled{C} - [CO_2]$

Check $[H_2]$: (10.1) $\quad [H_2] = \dfrac{[CO]\ [H_2O]}{[CO_2]}\ K_{10}$

Check N: (34.1) $\quad N = \textcircled{C} + \tfrac{1}{2}\textcircled{H} + \tfrac{1}{2}\textcircled{N} + \tfrac{1}{2}[H] + \tfrac{1}{2}[OH] + \tfrac{1}{2}[NO] + \textcircled{\textcircled{O}} + [O_2]$

Revise assumptions and repeat if necessary.

Thus a systematic method is established for solving the simultaneous equations governing the equilibrium composition of a gaseous mixture.

APPENDIX II

Derivation of Entropy Calculation Equation

The entropy of a gaseous mixture is usually given (Reference 14) by:

$$S = \sum_{i=1}^{i=n} X_i S_i \tag{1}$$

where S = entropy of mixture at temperature and total pressure

X_i = number of moles of component i present in mixture

S_i = molal entropy of component i at temperature and partial pressure of component i.

For a pure constituent or a mixture of constant composition, the change in entropy with pressure at constant temperature is given by:

$$\Delta S_T = -NR \ln P_2/P_1 \tag{2}$$

where: ΔS_T = increase in entropy at constant temperature

N = number of moles in system

R = universal gas constant

P_2 = final pressure

P_1 = initial pressure

If N represents the total number of moles in the system, the partial pressure of component i is:

$$P_i = \frac{X_i}{N} P \tag{3}$$

where P_i = partial pressure of component i

X_i = number of moles of component i in system

N = total moles in system

P = total pressure

The molal entropy of component i at the temperature of the mixture and

partial pressure of component i is given by:

$$S_i = S_i^{\,0} - R \ln \frac{X_i}{N} \frac{P}{P^0} \tag{4}$$

where $S_i^{\,0}$ = molal entropy of component i at temperature and reference

pressure P^0

P^0 = reference pressure, taken here as 1 atm

Therefore;

$$S_i = S_i^{\,0} - R \ln \frac{X_i}{N} P \tag{4.1}$$

S_i from Equation 4.1 may now be substituted into Equation 1:

$$S = \sum_{i=1}^{i=n} X_i \left(S_i^{\,0} - R \ln \frac{X_i}{N} P \right) \tag{5}$$

Suppose, for the moment, that the total pressure is numerically equal to N.

(Composition to remain constant) Equation 5 becomes:

$$S = \sum_{i=1}^{i=n} \left(S_i^{\,0} X_i - X_i R \ln X_i \right) \tag{5.1}$$

Now correcting the total pressure of the mixture as given by (5.1) to the

actual pressure P by Equation 2 gives:

$$S = \sum_{i=1}^{i=n} X_i S_i^{\,0} - \sum_{i=1}^{i=n} X_i R \ln X_i - N R \ln P/N \tag{6}$$

Substituting numerical value for R and changing logarithm base gives the

equation used in computation:

$$S = \sum_{i=1}^{i=n} X_i S_i^{\,0} - \sum_{i=1}^{i=n} 4.5753 \, X_i \log X_i - N \, 4.5753 \log P/N \tag{7}$$

APPENDIX III

Enthalpy-Entropy Diagrams from German Data

Captured German documents have provided us with several enthalpy-entropy diagrams very similar in principle and construction to those described in Part I of this report. The differences are as follows:

Thermochemical equilibrium is assumed above $2000^{\circ}K$; below this temperature, the composition is assumed invarient at the $2000^{\circ}K$ value. This assumption should cause only slight differences between what they have calculated and what we would calculate since the only reaction occuring to any extent below $2000^{\circ}K$ is the water-gas reaction, and this introduces only small changes in enthalpy and entropy. The German diagrams are based on the arbitrary reference state of H_2O (g), CO_2 (g), and O_2 (g) at $298^{\circ}K$ for enthalpy and H_2O (g), CO_2 (g), and O_2 (g) at $2000^{\circ}K$ for entropy. Thus the enthalpy of the unburned propellant is equal to its heat of combustion at $298^{\circ}K$ plus its sensible heat above $298^{\circ}K$. The tables of enthalpy and entropy used in constructing the diagrams have not yet been located, but presumably they have been prepared from the same original works as the enthalpy-entropy tables presented in Part I of this report. Thus the following German diagrams, when entered at the unburned propellant enthalpy consistant with the reference state for the diagram, should give theoretical performance characteristics almost exactly as do our own.
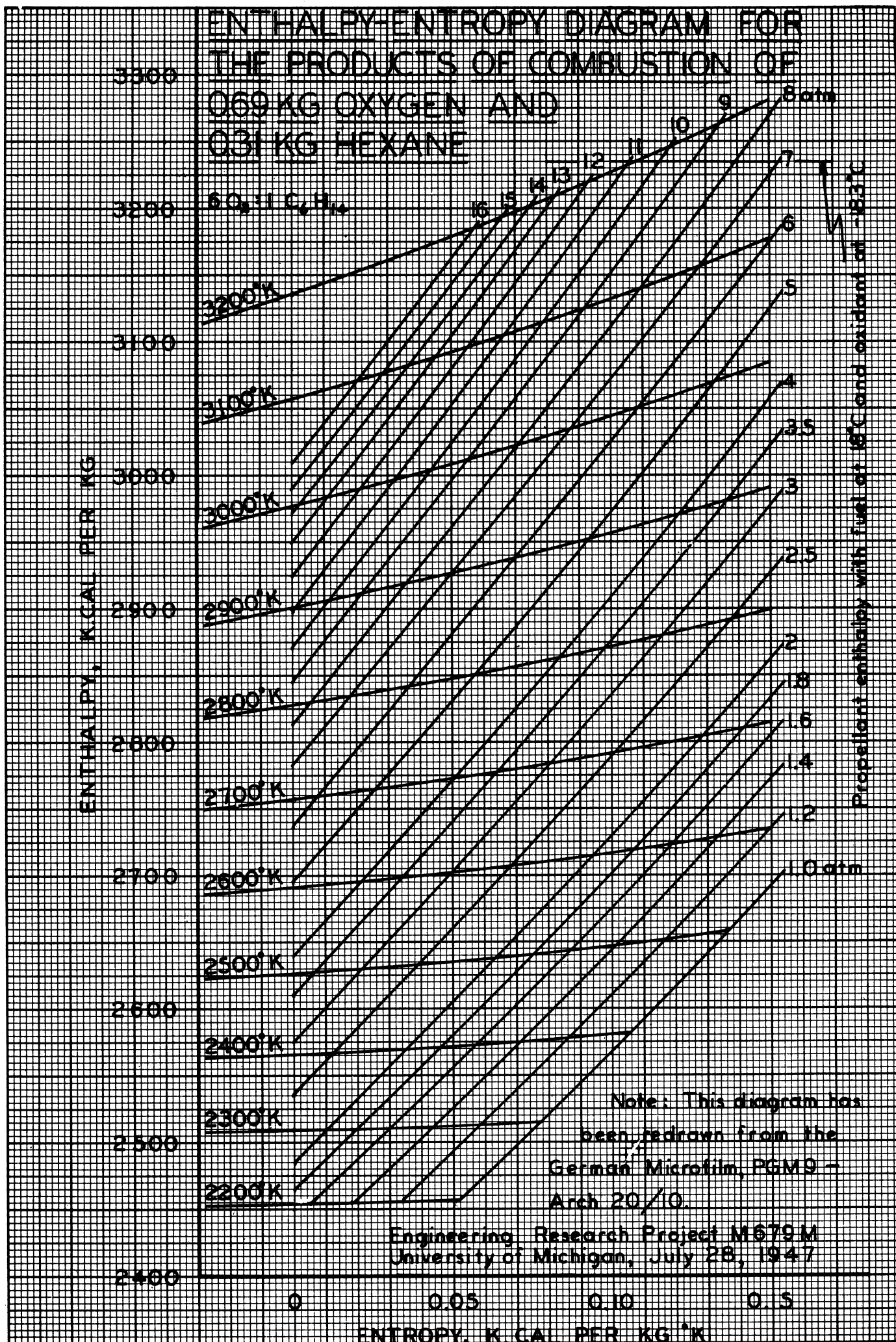
ENTHALPY-ENTROPY DIAGRAM FOR THE PRODUCTS OF COMBUSTION OF 0.69 KG OXYGEN AND 0.31 KG HEXANE

FIG. 27

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