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Cool Propellants: Flame Temperatures and Force Constants:
New Calculations Taking into Account the Formation of
Methane and Ammonia

D. L. Hodge and (Miss) S. D. Huggins

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SUMMARY OR SID REPORT: Explosives Research & Development Establishment Report 34/R/50 is by D.L.Hodge and S.D.Huggins. New calculations of "true" flame temperature of experimental propellants taking into account the formation of C_2H_2 & NH_3 gives an increase of approximately 100°K with the picrite series and 200°K with the non picrite series. Force constants have been calculated on the new basis.

COMMENT: These propellants are to be given an extended test in the high rate fire gun "rate fixer" to determine wear values, a discussion of the program was held at the Explosives and Propellants A-B-C Conferences in U.K. 1949 and Canada 1950. Copy No. 21 is for the R&D Bd. Copy No. 34 for Mr. Anderson - ORDTA. Copy will be of interest to Picatinny Arsenal. The U.S. Naval and Air Attaches, London, have received copies of the inclosure.

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Cool Propellants: Flame Temperatures and Force Constants:
New Calculations Taking into Account the Formation of
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by

D.L. Hodge and (Miss) S.D. Huggins

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Reference: XR.411/4.

1. ABSTRACT.

Calculations of the flame temperatures and force constants of certain "cool" gun propellants have been carried out, taking into account the formation of methane and ammonia. It has been shown that for propellants F.527/155 and F.428/180 the 'true' flame temperatures are 2045°K. and 2050°K. compared with the 'nominal' values of 1942°K. and 1950°K. obtained by neglecting the formation of these gases. The 'true' force constants are respectively 1493 and 1453 inch-tons/lb. compared with 1474 and 1436 inch-tons/lb.

In the case of the propellants F.527/156 and F.428/181 having a 'nominal' flame temperature of 1700°K. the true flame temperatures are 1905 and 1915°K. respectively and the corresponding force constants nearly 5 per cent. above those obtained by neglecting the formation of methane and ammonia.

Conditions for the deposition of carbon do not exist for any of these propellants under conditions of maximum pressure but in the case of F.428/180 and F.428/181 conditions are such that carbon deposition could occur if equilibrium were attained at the moment of shot ejection.

2. OBJECT OF INVESTIGATION.

To calculate the effect of the formation of methane and ammonia and of the possible deposition of carbon on the adiabatic flame temperatures and force constants of cool gun propellants and to ascertain the extent to which the values so obtained differ from those derived from the 'nominal' values obtained by neglecting these reactions.

3. INTRODUCTION.

Reduction of gun erosion is of great importance for modern artillery, particularly that participating in defence against attack by aircraft, as the operational requirement is for maximal rate of fire of high-velocity projectiles.

On the assumption that both chemical and physical (thermal) factors are operative in barrel wear, trials have been arranged of a series of (a) picrite and (b) non-picrite propellants, at flame-temperature levels down to 1700°K. For certain practical reasons, propellants in the two series of flame temperature 1950°K. were chosen for the first comparison. It was found that the picrite propellant produced much less erosion than the non-picrite counterpart, at the same ballistics and under the slow-rate-of-fire conditions of the trial. It is therefore concluded that at the flame temperature concerned, and under the slow-rate-of-fire conditions of the trial, erosion is markedly reduced by lowering the concentration of carbonaceous (and therefore iron-reactive) constituents of the muzzle gases, achieved in the case of picrite propellants by their high contents of nitrogen.

In formulating these compositions to give the desired flame-temperature, certain simplifying assumptions were made, particularly that of the non-

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formation of appreciable proportions of ammonia and methane during the combustion of the propellant in the gun.

This report presents a re-calculation of the flame temperatures of certain propellants in the trial series, with allowance for the effect thereon of the formation of ammonia and methane, which are proved likely to be present in significant proportions in the muzzle gases.

It is shown that the compositions formulated to give flame-temperatures of 1950°K. give in fact about 2050°K.; that the nominally 1700°K. propellants give about 1900°K.; and that the corresponding values for the force-constants are respectively 1.3 per cent. and 3 to 5 per cent. higher than hitherto assumed; only the latter difference is likely to produce a ballistically-detectable effect.

It is also shown that with the non-picrite propellants of both 1700° and 1950°K. nominal flame-temperature, conditions may occur under which deposition of carbon is theoretically possible. No report of carbon deposition during the firings so far carried out has been received; the effect will be watched for during any further firings in the trials concerned.

4. CALCULATION OF THE GAS COMPOSITION AND ADIABATIC FLAME TEMPERATURE.

4.1. The usual method of calculating the adiabatic flame temperature (T_0) produced by the explosion of a propellant is by estimating an approximate value for this quantity, calculating the composition of the explosion products at this temperature and comparing the heat content of the gases so formed with that derived from the heat of explosion calculated from the heats of formation. Successive values of T_0 are tried until the above two quantities balance. This gives the correct value for T_0 .

The composition of the explosion products of a propellant is obtained by equating the number of gram-atoms of its constituent elements to the corresponding elements in the products of explosion. Assuming that (C), (H), (N) and (O) are the numbers of gram-atoms of these elements in one gram of propellant and that CO_2 , CO, H_2O , H_2 , N_2 are the corresponding concentrations of the products in gram-molecules per gram then:-

$$(C) = \text{CO}_2 + \text{CO} \quad (1)$$

$$(H) = 2\text{H}_2\text{O} + 2\text{H}_2 \quad (2)$$

$$(N) = 2\text{N}_2 \quad (3)$$

$$(O) = 2\text{CO}_2 + \text{CO} + \text{H}_2\text{O} \quad (4)$$

Equations (1) and (4) are connected by the water gas equilibrium relationship

$$\frac{\text{CO} \times \text{H}_2\text{O}}{\text{H}_2 \times \text{CO}_2} = K_0 \quad (5)$$

where K_0 is the equilibrium constant at T_0 °K.*

Note: The nomenclature used for the equilibrium constants is that employed in A.R.E. Report No.25/49 (7) and values of specific heats and equilibrium constants used in the calculations in this report were taken from that report.

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By eliminating CO, H₂O and H₂ from equations (1), (2), (4) and (5) a quadratic expression for CO₂ is obtained, the solution being

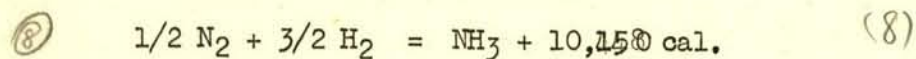
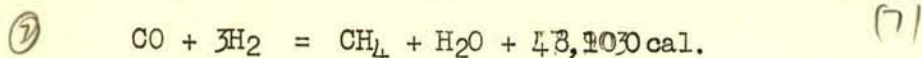
$$\textcircled{6} \quad \text{CO}_2 = \frac{-x \pm \sqrt{x^2 + 4(K_0-1)(C)[(O)-(C)]}}{2(K_0-1)} \quad (6)$$

$$\text{where } -x = K_0(H/2) + K_0(C) - (K_0-1)(O)$$

Substitution of CO₂ in equations (1) to (4) gives the concentrations of the other gases viz: CO, H₂O, H₂, N₂.

The above derivation assumes that the only products of explosion formed are CO₂, CO, H₂O, H₂, N₂. If any other products are formed the equations (1) to (4) are not strictly true. When T₀ is greater than 2,700°K. appreciable but small quantities of dissociation products are formed. These are small compared with the major products of explosion and can be estimated by methods of approximation (1).

When T₀ is below 2,500°K. appreciable quantities of methane and ammonia can be formed. These gases are in equilibrium with the other products of explosion according to the reversible reactions.



In order to calculate the products of explosion it would be necessary to obtain a solution to the following equations:-

$$(C) = \text{CO}_2 + \text{CO} + \text{CH}_4 \quad (9)$$

$$(H) = 2\text{H}_2\text{O} + 2\text{H}_2 + 4\text{CH}_4 + 3\text{NH}_3 \quad (10)$$

$$(N) = 2\text{N}_2 + \text{NH}_3 \quad (11)$$

$$(O) = 2\text{CO}_2 + \text{CO} + \text{H}_2\text{O} \quad (12)$$

$$K_0 = \frac{\text{CO} \times \text{H}_2\text{O}}{\text{CO}_2 \times \text{H}_2} \quad (13)$$

$$K_7 = \frac{\text{CO} \times (\text{H}_2)^3}{\text{CH}_4 \times \text{H}_2\text{O}} \quad (14)$$

$$K_8 = \frac{\text{NH}_3}{(\text{N}_2)^{1/2} \times (\text{H}_2)^{3/2}} \quad (15)$$

Such a solution would be very complex and it was therefore decided to extend the approximation method used for the minor products of explosion to calculate the concentration of methane and ammonia, using the quadratic solution (equation (6)) for the major products. The atomic composition of one gram of propellant was worked out in the usual way. A value of T₀ was chosen and concentrations of CH₄ and NH₃ at this temperature estimated. A new set of atomic concentrations (C)', (H)' and (N)' was then obtained by subtracting the number of gram-atoms of carbon, hydrogen and nitrogen

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contained in those estimated concentrations from the total in the propellant. Thus

$$(C)' = (C) - CH_4$$

$$(H)' = (H) - 4CH_4 - 3NH_3$$

$$(N)' = (N) - NH_3$$

Substituting these values in equation (6) we obtain a value for CO_2 and since

$$(C)' = CO_2 + CO$$

$$(H)' = 2H_2O + 2H_2$$

$$(N)' = 2N_2$$

it is possible to obtain values for CO_2 , CO , H_2O , H_2 and N_2 . By substituting these values in equations (14) and (15) corresponding equilibrium values for CH_4 and NH_3 are obtained. Approximation is continued until the estimated and derived values for CH_4 and NH_3 agree at the temperatures under investigation.

It is then necessary to balance the heat of explosion of the propellant with the heat content of the products and continue in this way until the true values of T_0 , CH_4 and NH_3 are arrived at.

4.2. Correction for Compressibility.

The physical and chemical data usually employed in calculating flame temperatures and force constants are those for zero pressure. At gun pressures i.e. ca. 20 tons/square inch deviations from the gas laws occur and in order to achieve accuracy it is necessary to apply a correction for compressibility.

The method of correction and tables used in the present report are described in A.R.D. Theoretical Research Report 8/43 (Comer's Tables) (2). The quantities to which these corrections have been applied are the water gas equilibrium constant, the internal energy of the propellant gases and the pressure. The expressions used to obtain these quantities are given in the following paragraphs. The quantity V is the volume of unit mass gas and is the reciprocal of the density. In the calculations of force constant described in the report the density corresponding to maximum pressure has been taken as 0.35 gm./cc. For conditions at the point of shot ejection the value was 0.13 or 0.15 gm./cc. depending on the gun.

4.2.1. Water Gas Equilibrium Constant.

The value of the water gas equilibrium constant at a density of V^{-1} gram/cc. and temperature $T^{\circ}K$. is given by:

$$/K' = K_0 T$$

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$$K = K_0 T \left\{ \frac{-n \Delta B}{V} - \frac{n^2}{V^2} \frac{\Delta C}{2} \right\}$$

$$\text{where } \Delta B = B_{CO} + B_{H_2O} - B_{CO_2} - B_{H_2}$$

$$\text{and } \Delta C = C_{CO} + C_{H_2O} - C_{CO_2} - C_{H_2}$$

values for ΔB and $\frac{\Delta C}{2}$ are given in the tables.

4.2.2. Internal Energy.

The internal energy of 1 gram of propellant **gases** at a density V^{-1} gm./cc. and temperature $T^\circ K$ is given by

$$E = \Sigma CO.E_{CO,0} + \frac{n}{V} \Sigma E_{CO,1} + \frac{n^2}{V^2} \Sigma CO.E_{CO,2}$$

where $E_{CO,1}$ and $E_{CO,2}$ etc. are given in the tables and $\Sigma CO.E_{CO,0}$ is the internal energy at zero pressure obtained by multiplying the mean specific heat of the propellant gases between 300 and $T^\circ K$. by the temperature interval ($T-300$).

4.2.3. Pressure.

The pressure of propellant gas at a density V^{-1} gm./cc.

$$P = 0.5384 \frac{nT}{V} \left(1 + \frac{B}{V} + \frac{nC}{V^2} \right) \text{ tons/square inch}$$

$$\text{where } B = \Sigma CO.B_{CO}$$

$$\text{and } C = \Sigma CO.C_{CO}$$

4.2.4. Co-volume.

The co-volume η is given by the expression

$$P(V - \eta) = n RT$$

$$\text{i.e.} \quad = V - \frac{nRT}{P} \text{ cc./gm.}$$

$$= V - \frac{\lambda_0}{P}$$

where λ_0 is in tons/square inch/gm./cc.

P is in tons/square inch.

4.3. Force Constant λ_0 .

This is the product of the pressure and the corresponding volume of unit mass and is given by the formula

$$\lambda_0 = P.V = nRT_0$$

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where n = Number of gram.molecules per gram of propellant

R = Universal Gas Constant

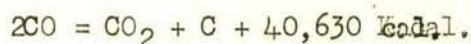
T_0 = Adiabatic Flame Temperature

λ_0 is 14.91 $n T_0$ inch tons/lb.

or 0.5384 $n T_0$ tons/square inch/gm./°C.

4.4. Deposition of Carbon.

Under certain circumstances conditions can occur for the deposition of carbon according to the reaction



The equilibrium constant of this reaction is

$$K_9 = \frac{[p(CO)]^2}{p(CO_2)} \quad (\text{in the presence of graphite})$$

where $p(CO)$ and $p(CO_2)$ are partial pressures.

In order to ascertain whether conditions for carbon deposition are present, the value of the fraction $\frac{[p(CO)]^2}{p(CO_2)}$ is calculated from the partial

pressures of carbon monoxide and carbon dioxide in the barrel gases. This is obtained from the concentration in gram-molecules per gram by multiplying by a factor (1) thus :-

$$\frac{[p(CO)]^2}{p(CO_2)} = \frac{(CO)^2}{CO_2} \times \frac{82.06 T}{V}$$

where T is the temperature in °K

and V is the volume of unit mass of barrel gas.

If the value of this fraction is less than the equilibrium constant at the same temperature then the partial pressure of carbon monoxide in the gases is below the equilibrium value and there is no deposition of carbon.

If, on the other hand, the calculated values give value of $\frac{[p(CO)]^2}{p(CO_2)}$ in

excess of the equilibrium constant, then conditions for carbon deposition do occur.

5. CONDITIONS AT THE MUZZLE.

The previous paragraphs refer to conditions at maximum pressure. When the shot has reached the muzzle the temperature and pressure are both lower. Conditions at the muzzle can be calculated by allowing for the energy imparted to the shot and the heat lost to the gun barrel.

5.1. Work Done on Shot.

The work done on the shot by unit mass of gas is given by the formula:

/11.1

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$$11.1 \frac{(V)^2}{(1,000)} \cdot \frac{W + C/3}{C} \text{ cal. /gm.}$$

where V = muzzle velocity in ft./sec.

W = shot weight in lb.

C = charge weight in lb.

Example: Q.F. 3 inch/70 cal. A.A. gun.

Chamber capacity	370 cubic inches
Calibre	3 inch
Shot travel	70 x 3 = 210 inch
Shot weight	15 lb.
Charge weight	10 lb.
Velocity	3,400 feet per second

$$\begin{aligned} \text{Work done} &= 11.1 \frac{(3,400)^2}{(1,000)} \times \frac{15 + 3.33}{10} \\ &= 11.1 \times (3.4)^2 \times 1.833 \\ &= 11.1 \times 11.56 \times 1.833 \\ &= 235.2 \text{ calories per gram. of propellant} \end{aligned}$$

5.2. Density at Muzzle.

The density of the gas when the shot is about to be ejected from the barrel can be calculated from the charge weight and the total volume of the gun. Thus :-

$$\begin{aligned} \text{Density} &= 27.68 \cdot \frac{C}{V} = \frac{27.68 \times 10}{1854.4} \\ &= 0.14926 \\ &= 0.15 \text{ gm./cc. approx.} \end{aligned}$$

5.3. Heat Loss at Muzzle.

In the calculations made in this report it was assumed that the loss of heat to the barrel was 5 per cent. of the total heat of explosion of the propellant.

5.4. Calculation of Gas Composition and Temperature at the Muzzle.

The procedure for obtaining the gas composition at the muzzle is similar to that already outlined for a density of 0.35 gm./cc., an estimate of the flame temperature being first made and the corresponding gas composition calculated. In this case, however, the heat content of the gases obtained from the product of the flame temperature and the mean specific heat of the gases must be equated to the heat of explosion less the energy imparted to the shot and the heat lost to the barrel. This is best seen in the detailed calculation for propellant F.527/155 in the 3 inch/70 calibre gun given in Appendix II.

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6. THE PROPELLANTS UNDER INVESTIGATION.

The compositions of the propellants under investigation are given in Table 1. Compositions F.527/155 and F.428/180 are of the same nominal flame temperature (1950°K), that for both F.527/156 and F.428/181 being 1700°K. Propellants of the F.527 series, however, contain 60 per cent. of picrite whereas those of the F.428 series have no picrite but contain much more dibutyl phthalate as a coolant. Composition F.487/47 is of the picrite type but contains diethylene glycol dinitrate in place of nitroglycerine. This last composition was included since it was the only propellant of this calorimetric level which had actually been fired in a gun.

7. DESCRIPTION OF WORK.

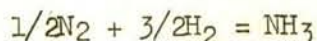
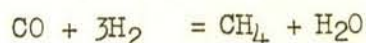
Calculations of the true flame temperature and force constant have been carried out for propellant compositions F.527/155, F.527/156, F.428/180 and F.428/181. The results are summarised in Table 2. Calculations have also been made of the 'nominal' flame temperature and corresponding force constant obtained by neglecting both compressibility corrections and the formation of methane and ammonia. In addition, another series of calculations gave figures for the same quantities when correcting for compressibility but ignoring methane and ammonia formation. The results are given in Tables 3 and 4 respectively.

In order to see whether conditions for carbon deposition occur when the shot has reached the muzzle, calculations of the conditions at the muzzle were made for compositions F.527/155 and F.428/180 in the Q.F. 3 inch/70 cal. A.A. gun and for F.428/181 and F.487/47 in the Q.F. 17 pounder gun. The results of these are summarised in Table 6. The characteristics of these two guns are given in Table 5.

A specimen calculation is given in Appendix II as an example in detail for composition F.527/155 both at a density of 0.35 and under muzzle conditions.

8. DISCUSSION OF RESULTS.

8.1. From the tables it will be seen that appreciable quantities of methane and ammonia are formed although conditions for the deposition of carbon do not exist at a density of 0.35 gm./cc. Since the syntheses of methane and ammonia according to the reactions



are exothermic, the flame temperatures of the explosion products will be higher than if the calculation is made without taking their formation into account. The total gas volume on the other hand is smaller since in both reactions the volume of the products is half that of the reaction gases. The results obtained from individual propellants are considered in detail below.

F.527/155 gives an adiabatic flame temperature of 2,045°K. compared with 1942.4°K. in Table 3, whilst the force constant is increased from 1474.5 to 1493.2 inch tons/lb., i.e. about 1.3 per cent.

/F.428/180

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F.428/180 has a corrected adiabatic flame temperature of 2050°K . compared with 1950°K . whilst the force constant increases from 1435.6 to 1453.4 - about 1.5 per cent.

F.527/156 the value for T_0 is 1905°K . compared with 1702°K . uncorrected, the force constant increasing from 1317.9 to 1380.8 inch tons/lb. - 4.8 per cent.

F.527/181 gives T_0 1915°K . compared with 1700°K . the force constant increasing from 1301.0 to 1346.9 inch tons/lb. - 3.5 per cent.

8.2. Deposition of Carbon.

Conditions for the deposition of carbon do not occur under conditions of maximum pressure but it will be seen in Table 6 that carbon deposition conditions are present in the case of compositions F.428/180 and F.428/181 when the shot has reached the muzzle.

9. ACKNOWLEDGMENTS.

The authors are indebted to Dr. H.H.M. Pike of the Armament Research Establishment for valuable advice during the course of this investigation.

10. BIBLIOGRAPHY.

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M.No.27/51.
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APPENDIX I

TABLE 1

Propellant Composition

Type	Number	Picrite	G.C.	N.G.	D.E.G.N.	Carbamite	D.B.P.	T _c , °K. (nominal)
Picrite - N.G. Series.	F.527/155	60	20	8.86	-	2.64	8.5	1950
	F.527/156	60	20	6.38	-	2.64	10.98	1700
	F.428/180	-	65	15.4	-	2.0	17.6	1950
Non-Picrite N.G.Series.	F.428/181	-	65	13.1	-	2.0	19.9	1700
Picrite-DEGN Series.	F.487/47	60	20	-	7.9	2.64	9.46	1700

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TABLE 2

Composition	F.527/155	F.428/180	F.527/156	F.428/187
Nominal flame temperature °K.	1950	1950	1702	1700
True flame temperature °K.	2045	2050	1905	1915
Gas Composition in gm.mol./gm.				
CO ₂	0.000802	0.001182	0.000800	0.001175
CO	0.016341	0.025268	0.016523	0.025334
H ₂ O	0.005753	0.004849	0.004948	0.004239
H ₂	0.012191	0.011177	0.011819	0.010594
N ₂	0.013075	0.004085	0.012765	0.003955
CH ₄	0.000630(1.29%)	0.000900(1.89%)	0.001550(3.19%)	0.001780(3.77%)
NH ₃	0.000180(0.37%)	0.000090(0.189%)	0.000210(0.432%)	0.000094(0.19%)
Total gas.gm.mol./gm.	0.048972	0.047551	0.048615	0.047171
$\left[\frac{p(\text{CO})}{p(\text{CO}_2)} \right]^2$	19718.0	30,627.6	18,536	24,89.1
K ₉	54,450	52,481	25,550	26,160
Whether carbon deposition at this density	No	No	No	No
True force constant λ_0	1493.2	1453.4	1380.8	1346.9
Pressure tons/square inch	27.82	27.3	25.88	25.21
Co-volume cc./gm.	0.92	0.93	0.93	0.93

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TABLE 3

Calculated Flame Temperatures and Force Constants at Density 0.35 gm./cc.
Uncorrected for Compressibility, Methane and Ammonia

Composition	F.527/155	F.428/180	F.527/156	F.428/181
Nominal flame temperature °K.	1942.4	1950	1702.2	1700.4
Total gas volume gm.mol./gm.	0.050912	0.049375	0.0519255	0.050825
Force Constant in inch-tons/ lb.	1474.5	1435.64	1317.86	1288.54

TABLE 4

Calculated Flame Temperature and Force Constants at Density 0.35 gm./cc.
Corrected for Compressibility, but not for Methane and Ammonia

Composition	F.527/155	F.428/180	F.527/156	F.428/181
Flame temperature °K.	1959.3°	1973.1°	1721.3°	1716.9°
Calculated total gas volume in gm.mol./gm.	0.050912	0.049378	0.0519255	0.050825
Force Constant in inch-tons/ lb.	1487.3	1452.6	1332.6	1301.0

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TABLE 5

Data for QF 17 pdr. and QF 3 inch 70 Cal. A.A. Guns

Characteristic	Gun	
	3-inch 70 cal.	17-pdr.
Calibre	3 inches	3 inches
Shot Travel	70 x 3 = 210 inches	204 inches
Chamber Capacity	370 cubic inches	300 cubic inches
Shot Weight	15 lb.	17 lb.
Charge Weight	10 lb.	8.25 lb.
Muzzle velocity	3,400 f.s.	2,900 f.s.
Pressure (copper)	22½ tons	20 tons
" (true)	27 "	24 "
Total volume of gun	1854.4 cubic inches	1742 cubic inches
Density at muzzle	0.15	0.13
Work done on shot in calories per gram of propellant	235.2	223.1

TABLE 6

Gas Compositions and Flame Temperature at Muzzle

Composition	F. 527/155	F. 428/180	F. 487/47	F. 428/181
Gun	3 inch/10 cal.	3 inch/10 cal.	17 pdr.	17 pdr.
Density in gm./cc.	0.15	0.15	0.13	0.13
Flame Temperature °K.	1508.5°	1565	1465	1512
Pressure in tons/square inch	6.64	6.73	5.37	5.23
Gas Composition in gm.mols./gm.				
CO ₂	0.002319	0.002976	0.002560	0.003780
CO	0.013340	0.021980	0.012789	0.020545
H ₂ O	0.005726	0.004550	0.005219	0.003818
H ₂	0.009327	0.008551	0.008291	0.006722
N ₂	0.013105	0.004039	0.012919	0.003980
CH ₄	0.002120 (4.6%)	0.002394 (5.4%)	0.003400 (7.5%)	0.003964 (9.25%)
NH ₃	0.000120 (0.26%)	0.000054 (0.12%)	0.000110 (0.24%)	0.000044 (0.10%)
n = gas volume	0.046058	0.044544	0.045288	0.042853
$\left[\frac{p(\text{CO})}{p\text{CO}_2} \right]^2$	1424.9	3147.7	988.3	1801.8
K ₉	1626.25	2986.6	1128.0	1628.5
Carbon Deposition	Nil	Slight	Nil	Slight

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APPENDIX II

Calculation of T_0 and λ_0 etc. for Composition F.527/155 at a
Density of 0.35 gm./cc.

Composition of Propellant in gm.atoms/gm.

Per cent Compositions	C	H	N	O	Cal.Val.
Picrite 60	0.005772	0.023076	0.023076	0.011538	432.0
G.C. 20	0.004264	0.005222	0.001886	0.007326	204.0
N.G. 8.86	0.0011713	0.001952	0.0011713	0.003513	153.28
D.B.P. 8.50	0.004891	0.006727	-	0.001223	-161.50
Carb. 2.64	0.001675	0.001970	0.000197	0.000098	-55.44
	0.017773	0.038947	0.026330	0.023698	572.34

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Water Gas Equilibrium Constant.

From Corner's Tables.

$$K(T) = K_0(T) \exp. \left[\frac{-n}{V} B - \frac{n^2}{2V^2} C \right]$$

$$= K_0(T) \exp. \left[- \frac{0.048335}{2.857} B \frac{n^2}{V^2} \cdot \frac{C}{2} \right]$$

$$= K_0(T) \exp. [0.016918. 32.9 + 0.0002862 \times 382]$$

$$= K_0(T) \exp. (0.5566 + 0.1093)$$

$$= K_0(T) \exp. (0.6659)$$

$$\text{i.e. } K = K_0(T) e^{0.6659}$$

$$= K_0(T) \times 1.946$$

$$K = 4.990 \times 1.946$$

$$= 9.7123$$

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Calculation of Gas Composition and Flame Temperature

	Assuming that	$\left\{ \begin{array}{ll} T & 0.2050 \\ CH_4 & 0.000630 \\ NH_3 & 0.000180 \end{array} \right.$
$C' = 0.1773 - 0.000630$		0.017143 gram atoms/gram
$H' = 0.038947 - 0.002520 - 0.000540$		0.035887 " " "
$N' = 0.026330 - 0.000180$		0.026150 " " "
$O' = 0.023698$		0.023698 " " "
$O - C' = 0.023698 - 0.017143$		0.006555 " " "
$H/2 = 0.035887/2$		0.017944 " " "
$-x = 9.7123 \times 0.017944 + 9.7123 \times 0.017143 - 8.7123 \times 0.023698$ $= 0.174277 + 0.166507 - 0.206464$ $= 0.134320$		
$CO_2 = \frac{-0.134320 \pm \sqrt{(0.134320)^2 + 34.849 \times 0.017143 \times 0.006555}}{17.425}$ $= \frac{-0.134320 \pm \sqrt{(0.0180419 + 0.0039161)}}{17.425}$ $= \frac{-0.134320 \pm \sqrt{0.021958}}{17.425}$ $\frac{-0.134320 \pm 0.14819}{17.425} = \frac{0.01387}{17.425}$ $= 0.000796 \text{ gm. mol./gm.}$		

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CO ₂		0.000796 gm. mol./gm.
CO	0.017143 - 0.000796	0.016347 " " "
H ₂ O	= 0.006555 - 0.000796	0.005759 " " "
H ₂	= 0.017944 - 0.005759	0.012185 " " "
N ₂	= 0.026150/2	0.013075 " " "

Checking the value for the water gas equilibrium constant

$$K \text{ (check)} = \frac{0.016347 \times 0.005759}{0.000796 \times 0.012185} = \frac{0.000094142}{0.0000096993} = 9.706 \text{ (cf. 9.712)}$$

Checking calculated CH₄ against estimated value

$$\begin{aligned} \text{CH}_4 &= \frac{3.533 \times 10^{-8} \times 0.016347 \times (0.012185)^3 \times 3.4667 \times 10^9}{0.005759} \\ &= \frac{3.533 \times 1.6347 \times 1.80916 \times 3.4667 \times 10^{-4}}{5.759} = 0.000629 \text{ (cf. 0.000630)} \end{aligned}$$

Checking calculated NH₃ against estimated value

$$\begin{aligned} \text{NH}_3 &= 2.029 \times 10^{-5} \times (0.013075)^{1/2} \times (0.012185)^{3/2} \times 5.888 \times 10^4 \\ &= 2.029 \times 0.11434 \times 0.0013448 \times 5.888 \times 10^{-1} = 0.0001837 \text{ (cf. 0.000180)} \end{aligned}$$

Mean Specific Heat of Gases between 300° and 2050°K.

CO ₂	0.000796 x 10.889	= 0.008676
CO	0.016347 x 6.004	= 0.098147
H ₂ O	0.005759 x 8.294	= 0.047765
H ₂	0.012185 x 5.467	= 0.066615
N ₂	0.013075 x 5.923	= 0.077443
CH ₄	0.000630 x 15.529	= 0.009783
NH ₃	0.000180 x 11.828	= 0.002129

$$\underline{0.31056 \text{ cal./gm./}^\circ\text{C.}}$$

Heat content of gases between 300 and 2050°K.

$$= 1750 \times 0.31056 = 543.48 \text{ cal./gm.}$$

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Heat of Formation of Gases.

CO ₂	0.000796 x 94,052	74.87
CO	0.016347 x 26,711	436.64
H ₂ O	0.005759 x 57,504	331.17
CH ₄	0.000630 x 17,307	10.90
NH ₃	0.000180 x 10,150	<u>1.83</u>

855.41 cal./gr..

Heat of formation of propellant 319.9 " "

Heat of explosion of propellant 535.51 " "

Correcting T₀ for Compressibility. (2)

	n	E ₁ /100	(E ₂ /10 ⁴)		
CO ₂	0.000796	-742	-0.59063	230	0.17512
CO	0.016347	-47	-0.76831	34	0.55589
H ₂ O	0.005759	-782	-4.5038	35	0.20157
H ₂	0.012185	+72	+0.87732	3	0.03656
N ₂	0.013075	-47	-0.6145	34	0.44455
CH ₄	0.000630	-52	-0.03276	37	0.02331
NH ₃	<u>0.000180</u>	-52	<u>-0.00936</u>	37	<u>0.00666</u>
	0.048972		-5.6408		1.4445

$$\begin{aligned}\text{Correction} &= \frac{n}{V} E_1 + \left(\frac{n}{V}\right)^2 \cdot E_2 \\ &= \frac{0.048972}{2.8571} \times (-5.641) + \frac{n^2}{V^2} \cdot 1.444 \times 10^4 \\ &= 0.01714 \times (-5.641) + 0.00029379 \times 10^4 \times 1.4441 = -9.67 + 4.25 \\ &= -5.42\end{aligned}$$

$$E \text{ corr.} = 543.48 - 5.42 = 538.06$$

$$\text{Calculated} = 535.56$$

$$\text{Difference} = 2.5 \text{ cal.}$$

$$\text{Temperature correction} = 5^\circ \text{ approx.}$$

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Pressure at Density 0.35 gm./cc.

$$P = 0.5384 \times 0.048972 \times 2045 \times 0.35 \left(1 + \frac{B}{V} + \frac{nC}{V^2} \right) \\ = 18.8720 \left(1 + B/V + nC/V^2 \right)$$

		B		C	
CO ₂	0.000796	50.4	0.04012	1062	0.8453
CO	0.016347	32.65	0.5337	165	2.6973
H ₂ O	0.005759	1.7	0.00979	172	0.9905
H ₂	0.012185	16.0	0.19496	15	0.1828
N ₂	0.013075	32.65	0.42690	165	2.1574
CH ₄	0.000630	35.8	0.02255	181	0.1140
NH ₃	0.000180	35.8	<u>0.00644</u>	181	<u>0.0326</u>
			<u>1.23446</u>		<u>7.0199</u>

$$\frac{B}{V} = 1.23456 \times 0.35 = 0.4321$$

$$\frac{nC}{V^2} = 0.048972 \times (0.35)^2 \times 7.0199 = 0.042113$$

$$\therefore 1 + \frac{B}{V} + \frac{nC}{V^2} = 1.474213$$

$$\therefore P = 1.474213 \times 18.8720$$

$$= 27.82 \text{ tons/sq. inch}$$

Force Constant.

$$\lambda_0 = 14.91 \times 2045 \times 0.048972$$

$$= 1493.2 \text{ inch-tons/lb.}$$

Percentages of Minor Products.

$$CH_4 = \frac{0.000630}{0.048973} \times 100 = 1.29\%$$

$$NH_3 = \frac{0.000180}{0.048972} \times 100 = 0.37\%$$

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Carbon Deposition.

$$\frac{(CO)^2}{CO_2} = \frac{(0.016347)^2}{0.000796} = \frac{0.000267224}{0.000796} = 0.33571$$

Converting to partial pressures

$$\left[\frac{p(CO)}{pCO_2} \right]^2 = 0.33571 \times 82.06 \times 2045 \times 0.35$$

$$= 29,360$$

Now the value of K_p at 21,045 = 54,450

Therefore there is no deposition of carbon in this case.

Co-volume.

$$V. - \eta = \frac{nRT}{P} = \frac{0.048972 \times 2045 \times 0.5384}{27.82}$$

$$\frac{1.1}{0.35} - \eta = \frac{53.92}{27.82} = 1.938$$

$$\therefore \eta = 2.857 - 1.938$$

$$= 0.92 \text{ cc./gm.}$$

F.527/155 in QF 3 inch/70 cal. A.A. Gun - Condition at Muzzle.

Assuming $T_0 = 1500^\circ K$; $CH_4 = 0.002120$; $NH_3 = 0.000120$

$$K_9 = K_0 \times e^{26104} \text{ i.e. } K_9 = 1.2983 \times 2.718 = 3.5288$$

By a calculation similar to that carried out on p. 17 the gas composition is found to be CO_2 0.002319, CO 0.012340, H_2O 0.005726, H_2 0.0093275, N_2 0.013105, $CH_4 = 0.002120$, $NH_3 = 0.000120$.

Then using the mean specific heat of the gases between 300° and $1500^\circ K$, the heat content of the gas can be calculated.

Mean Specific Heat between 300° and $1500^\circ K$.

$$CO_2 \quad 0.002319 \times 10.278 \quad = \quad 0.023835 \text{ cal./gm./}^\circ K.$$

$$CO \quad 0.013340 \times 5.741 \quad = \quad 0.076585 \quad " \quad " \quad "$$

$$H_2O \quad 0.005726 \times 7.589 \quad = \quad 0.043455 \quad " \quad " \quad "$$

$$H_2 \quad 0.0093275 \times 5.228 \quad = \quad 0.048764 \quad " \quad " \quad "$$

$$N_2 \quad 0.013105 \times 5.654 \quad = \quad 0.074096 \quad " \quad " \quad "$$

$$CH_4 \quad 0.002120 \times 13.672 \quad = \quad 0.028985 \quad " \quad " \quad "$$

$$NH_3 \quad 0.000120 \times 10.546 \quad = \quad 0.001266 \quad " \quad " \quad "$$

$$0.046058 \quad 0.296986 \quad " \quad " \quad "$$

Heat Content of gases at $1500^\circ K$. $0.296986 \times 1200 = 356.38 \text{ cal./gm.}$

Correction for compressibility = 6.74 cal./gm.

Corrected value = 349.64 cal./gm.

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Heat of formation of gases.

CO ₂	0.002319 x 94,052	=	218.11 cal./gm.
CO	0.013340 x 26,711	=	356.32 " "
H ₂ O	0.005726 x 57,504	=	329.27 " "
CH ₄	0.002120 x 17,307	=	36.69 " "
NH ₃	0.000120 x 10,150	=	<u>1.32</u> " "
			941.61 " "

Heat formation of propellant 319.9 " "

∴ Heat of formation of gases - Heat of formation of propellant = 621.71 cal./gm.

Heat loss to barrel (5 per cent) 31.08 "

∴ Energy of shot 235.2 "

Energy remaining in gas 355.43 "

Now value obtained assuming T_c = 1500 349.64 "

Difference = 5.79 "

$$\frac{5.79}{.343} = 17^{\circ}\text{C.} \therefore \text{Correction} = \frac{17}{2} = 8.5^{\circ}\text{C.}$$

∴ True value for T_c = 1508.5°K.

Deposition of Carbon.

From the calculated figures for the gas consumption

$$\frac{(\text{CO})^2}{\text{CO}_2} = \frac{(0.013340)^2}{0.002319} = \frac{0.00017796}{0.002319} = 0.076738$$

$$\left[\frac{p(\text{CO})}{p\text{CO}_2} \right]^2 = 0.076738 \times 82.06 \times 0.15 \times 1508.5 = 1424.9$$

$$K_9 = 1626.25$$

∴ 1424.9 is less than K₉ and ∴ there is no carbon deposition.

The value for the pressure corresponds to 6.64 tons/square inch.

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