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Thermochemical studies of special propellants.

Frederick C. Damm
University of Louisville

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THERMOCHEMICAL STUDIES OF SPECIAL PROPELLANTS

A Dissertation

Submitted to the Faculty

Of the Graduate School of the University of Louisville

In Partial Fulfillment of the

Requirements for the Degree

Of Master of Arts

Department of Chemistry

By

Frederick C. Damm

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of Special Propellants

APPROVED BY READING COMMITTEE COMPOSED OF THE

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NAME OF DIRECTOR: C. C. Vernon

DATE: 9/26/46

PREFACE

The thermochemical investigations of the special propellants that are discussed in this report were carried out in the Burnside Laboratory of the E. I. du Pont de Nemours and Co., Inc., Carney's Point, New Jersey.

All of the work was done under the jurisdiction of the National Defense Research Committee for the purpose of developing new propellants with higher ballistic qualifications.

ACKNOWLEDGEMENT

I wish to make grateful acknowledgement of my
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Director of Burnside Laboratory, who has read the
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for their considerations.

Frederick C. Damm

TABLE OF CONTENTS

THERMOCHEMICAL STUDIES OF SPECIAL PROPELLANTS

INTRODUCTION

Historical Comments

In 1857, Bunsen & Schischkoff published their very important researches on gun powder. Their experiments were directed, first, to determine the nature and proportions of the permanent gases generated by the explosion of the powder; secondly, to determine the amount of heat generated by the transformation. With the aid of these experimental data they deduced, from theoretical considerations, the temperature of explosion, the maximum pressure in a closed chamber, and the total theoretical work which gun powder is capable of performing on the projectile. The powder in the experiments was not exploded, but deflagrated by being allowed to fall in an attenuated stream into a heated bulb, in which, and in the tubes connected with it, the products were collected.

The transformation, according to these experimenters, was given in a well organized scheme which consisted of the original explosive ingredients on one hand (at that time Nitre, Sulphur and Charcoal) and the residue and gas analyses on the other.

Bunsen and Schischkoff determined the number of units of heat generated by combustion, by exploding a small amount of powder in a tube immersed in water. They found

that the combustion of a gram of powder gave rise to 620 gram units of heat; and hence, they calculated that the temperature of explosion, in a closed chamber impervious to heat, was 3340°C. (5980°F.)[1].

After the introduction of smokeless powder in 1864[2], thermochemical determinations, similar to those on black powder were made on nitrocellulose and its derivatives in order to formulate an explosive that would show the highest qualifications for a propelling substance. In many cases nitroglycerin was incorporated with nitrocellulose to add more oxygen. The British have manufactured nitrocellulose-nitroglycerin propellants (commonly called cordite) for several decades. Propellant research, which includes formulating mixtures of new ingredients, granulating the mixture of ingredients in various forms, testing the final products for their burning characteristics, and determining their thermochemical properties, has been carried out by many the world over. It is to be emphasized that this field of research has been a continued process.

Numerous thermochemical tables have been formulated in order that they may be used theoretically for calculating thermochemical reactions. Milus[3], in 1935, found that thermochemical constants calculated from thermochemical data on heats of formation from the literature could not be relied upon for accurate work, since discrepancies existed in published values, especially for nitrocellulose. His research on the thermochemical properties of nitrocellulose

and various smokeless powder ingredients was an important contribution to those who were working on new compositions for propellants.

In 1940, with an inevitable war facing our country, our government inaugurated the National Defense Research Committee of the Office of Scientific Research and Development Council. Under its jurisdiction several research stations were established to carry on an extensive research program in order to improve the propellants that were to be used in our war machinery. Improved compositions were in order that would give high velocities, low breech pressures, with a minimum of barrel erosion and flash.

The thermochemical investigations in this report were designed to aid in the development of new propellants; new compositions that would give lower heats of explosion, greater gas volumes, and lower flame temperatures than those compositions that are commonly used.

Heat of Explosion

Most chemical reactions either liberate or absorb heat. However, it is a characteristic for all chemical explosive reactions to liberate heat, making the external heat effect (commonly called Q) a positive quantity.

Employing the simple form of energy balance,

$$Q - W = \Delta E$$

where Q = external heat effect

W = work done

ΔE = internal energy

If the explosion occurs in a closed chamber, or calorimeter bomb, where there cannot be any external work, then

$$W = 0$$

and

$$Q = \Delta E$$

All the heat liberated is absorbed by the system and, consequently, there is a corresponding rise in temperature. The heat of explosion of a propellant can readily be determined by burning it inside a closed chamber and then measuring the amount of heat expelled. Since its potential energy is transformed almost completely to heat, it is usually accepted that the term "heat of explosion" of a propellant may be used in lieu of its potential.

In a constant volume process

$$\int_{T}^{T_o} C_v dT = \Delta E$$

where C_V = mean specific heat of the powder gases

T_o = adiabatic flame temperature

T = ambient temperature

and the rise in temperature may be computed if values of the heat capacity at constant volume of the products of explosion are known.

In order to determine the true quantity of heat or rational heat generated by the explosive material at the adiabatic flame temperature it is necessary to deduct from the observed heat of explosion the amount of heat liberated by the products formed during the process of cooling from the adiabatic flame temperature, which is usually above 2000°C., to the ambient temperature. Since these explosions take place between 2000°C - 3000°C., only the water-gas equation is applied in the determination of the dynamic equilibrium of the gases. While methane is the most common compound formed during the progress of cooling, the powders with relatively low flame temperatures may form ammonium bicarbonate, ammonium hydroxide, and free ammonia. A deduction must also be made for the heat evolved on condensation of water during cooling of the product gases.

Having found the rational and specific heats of the gases present immediately after the explosion, the isochoric temperature of the explosion can be calculated from the following relations:

$$T_e = \frac{H}{C_v} \qquad (1)$$

where:

T_e = Isochoric temperature of explosion in degrees centigrade.

H = Rational heat in calories per gram.

C_v = Specific heat of the products of the explosion at constant volume.

MATERIALS AND METHODS

Apparatus

The apparatus necessary for measurements and analyses is similar to that of Milus (Milus, P. R., "Thermochemical Examination of Nitrocellulose" Industrial and Engineering Chemistry, 29, 492 (1937) and that of Kincaid and Dailey (OSRD Report No. 1578 by Kincaid, J. F. and Dailey, B. P., "Thermochemical Examination of a Number of Commercial Propellants", Explosives Research Laboratory, Bruceton, Pa., 1943).

Calorimetric Bomb

The calorimetric bomb (Figure I) used in the following calorimetric measurements has a chamber capacity of 75 c.c., is made of Rezistal 4 stainless steel, and is designed to withstand a pressure of 30,000 p.s.i. It consists of a bomb chamber proper, firing head, and a gas outlet tube. The firing head is threaded into the bomb proper and sealed by a copper gasket. An insulated firing pin extends through the firing head, being sealed on the interior end with a bakelite cone, a fiber washer, and a neoprene washer, and insulated on its exterior end by a rubber washer and a piece of rubber tubing. The position of the outlet tube and needle valve makes the bomb easy to manipulate for evacuation and the expulsion of the gases.

Water Calorimeter

The water calorimeter was designed for the calorimeter bomb (Figure II). An inner cylindrical chamber,

CALORIMETER BOMB
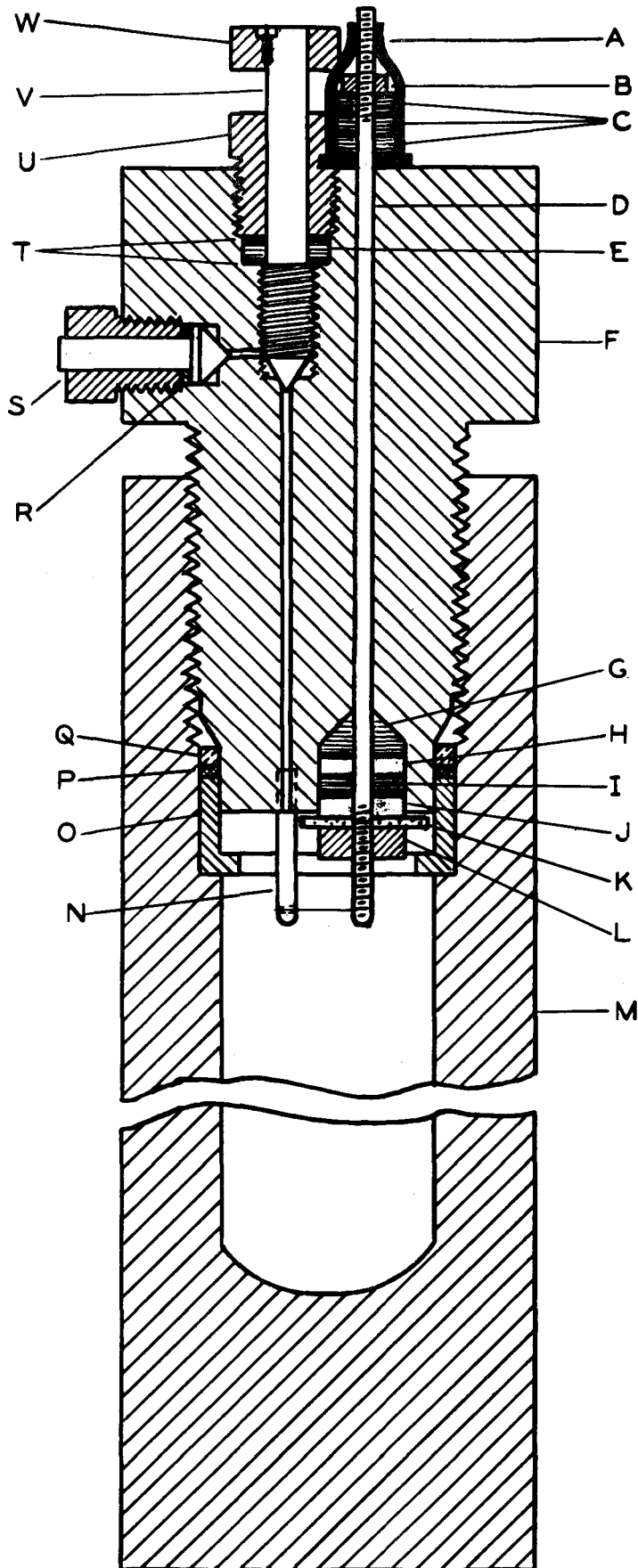
A — RUBBER TUBE

B — STEEL KNURLED NUT

C — FIBER WASHERS

D — INSULATED FIRING PIN

E — FIBER WASHER

F — FIRING HEAD

G — FIBER CONE

H — RED RUBBER WASHER

I — FIBER WASHER

J — NEOPRENE WASHER

K — ASBESTOS WASHER

L — STEEL KNURLED NUT

M — BOMB HOUSING

N — GROUND PIN

O — STEEL GASKET RING

P — LEAD GASKET

Q — COPPER GASKET

R — COPPER GASKET

S — ESCAPE PLUG & VALVE

T — BRASS WASHERS

U — VALVE SEAT

V — NEEDLE VALVE

W — STEEL HEX NUT

10-23-45

FIG. 1

WATER CALORIMETER
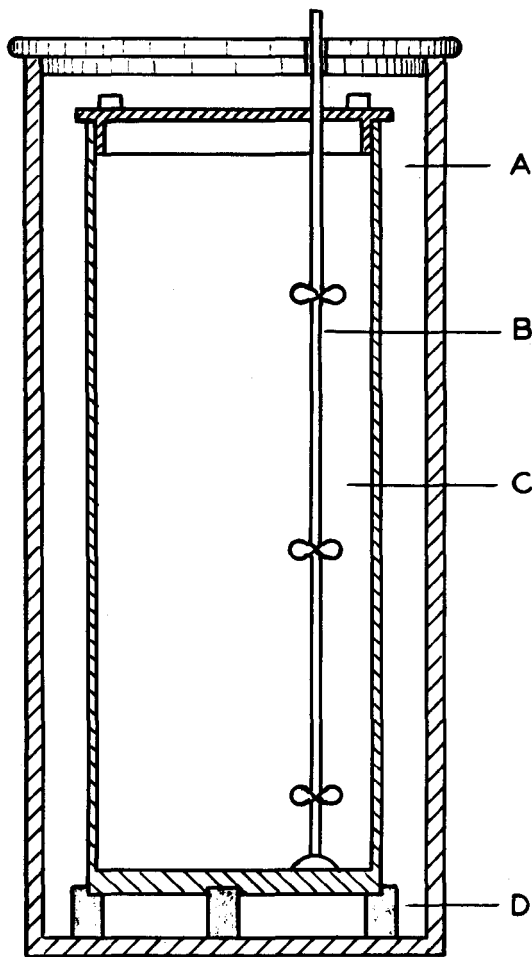
A – WATER CHAMBER

B – STIRRER

C – AIR INSULATION

D – FIBER RESTS

10-23-45

FIG. II

made of aluminum is constructed to hold the bomb and a
certain amount of water. An outer and heavier walled
aluminum cylinder insulates the system with a two inch air
space. A three propeller stirrer is connected with an
adjustable speed laboratory motor by a piece of rubber
tubing. The stirring rod rests in a bearing on the bottom
of the inner chamber with its propellers pitched and spaced
to give adequate agitation.

Ignition

A fine iron wire is wrapped around the firing
head terminals and charged with 0.2 gm. of nitrocellulose
whose heat value is known. The explosion is initiated
by the current from a storage battery. A correction
is made for the heat generated by the ignition nitrocellulose
when calculating the heat of explosion of the propellant.

Gas Measuring Equipment

The equipment used for measuring the permanent
gas volume consists essentially of two 2000 ml. vacuum
flasks, an accurate manometer, a filter tube, and a calcium
chloride tube. (Figure III) The gases in the bomb are
allowed to expand into the system after it has been evacuated
by a Hy-Vac pump. With the volume of the system known, a
volume of gas can be measured by observing the change in
pressure when it is passed into a completely evacuated
system.

Gas Sampling

A gas sampling tube, connected to a reservoir
containing an acidulated solution of sodium sulfate, is

PERMANENT VOLUME MEASURING SYSTEM

A — HY-VAC PUMP

B — CALORIMETER BOMB

C — CALCIUM CHLORIDE TUBE

D — FILTER TUBE

E — GAS RESERVOIRS

F — MANOMETERS

A

B

C

D

E

F

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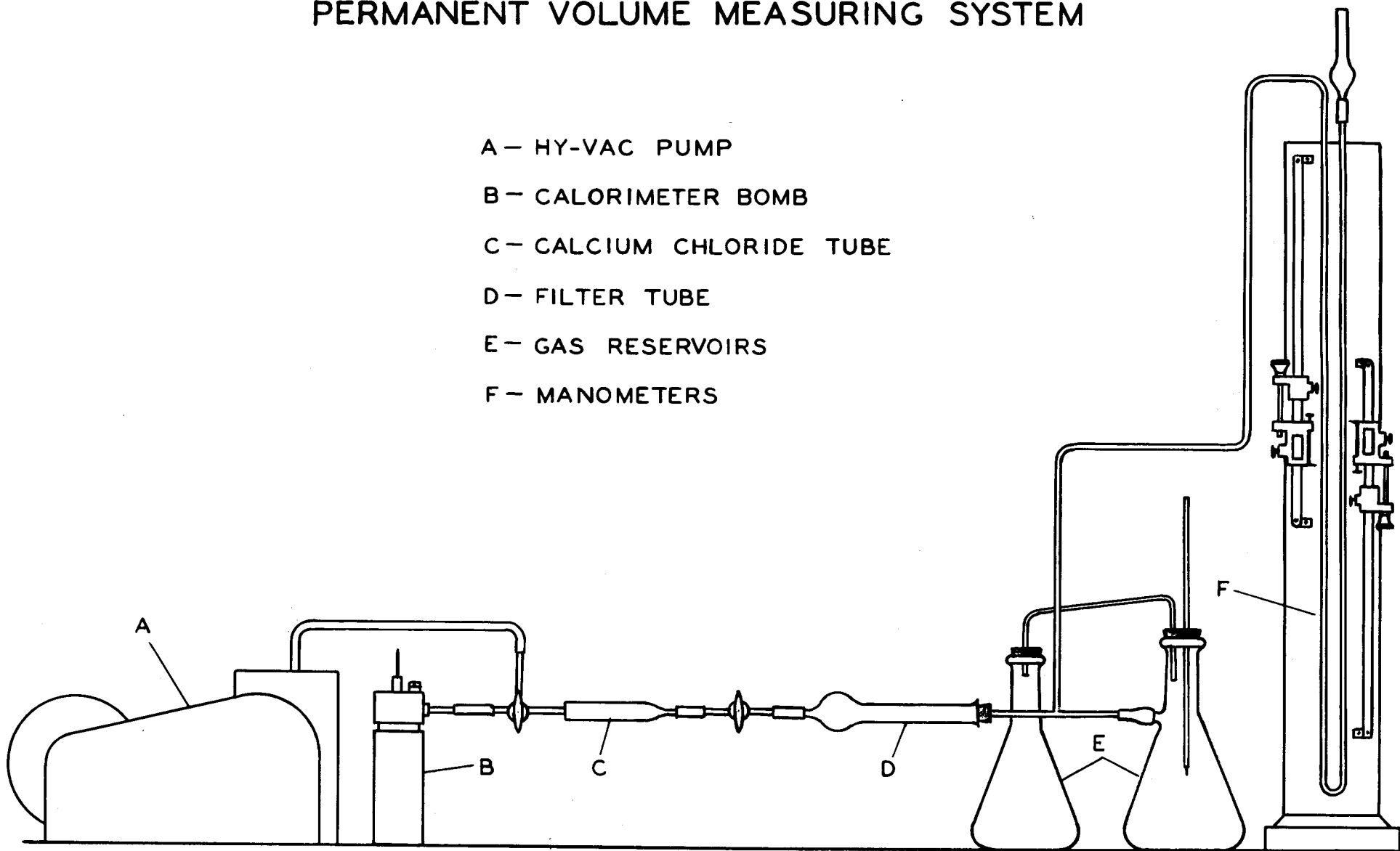
evacuated by the auxiliary evacuating system and the gases allowed to enter from the permanent reservoir. (Figure iv).

Thermometry

The measurement of the change in temperature, when a charge of powder is fired in the calorimeter, is made by means of a Beckman thermometer, graduated in $0.01^{\circ}C$ and estimated to the nearest $0.001^{\circ}C$ with a magnifier. The best results are obtained when the mercury column in the thermometer is set about two degrees below room temperature, if a $4 - 5^{\circ}C$ rise is anticipated, and the water for the calorimeter cooled a little below the zero point of the thermometer. After the stirrer is started and the system allowed to reach equilibrium, a change in temperature with respect to time is observed and recorded. When the rate of temperature change becomes constant the bomb is fired. At the end of ten minutes the temperature is recorded and as cooling takes place the change in temperature with respect to time is again secured. From these data and extrapolations the total rise in temperature is calculated. (Fig. VII).

The data taken and the method of calculating the heat of explosion are given below.

Let: T_1 = temperature of calorimetric system at the time of firing in $^{\circ}C$.

$$\Delta T = (T_2 - T_1)$$

$T_2 = T_e + T_c$ = corrected temperature after firing

T_e = temperature of final reading

APPARATUS FOR GAS SAMPLING
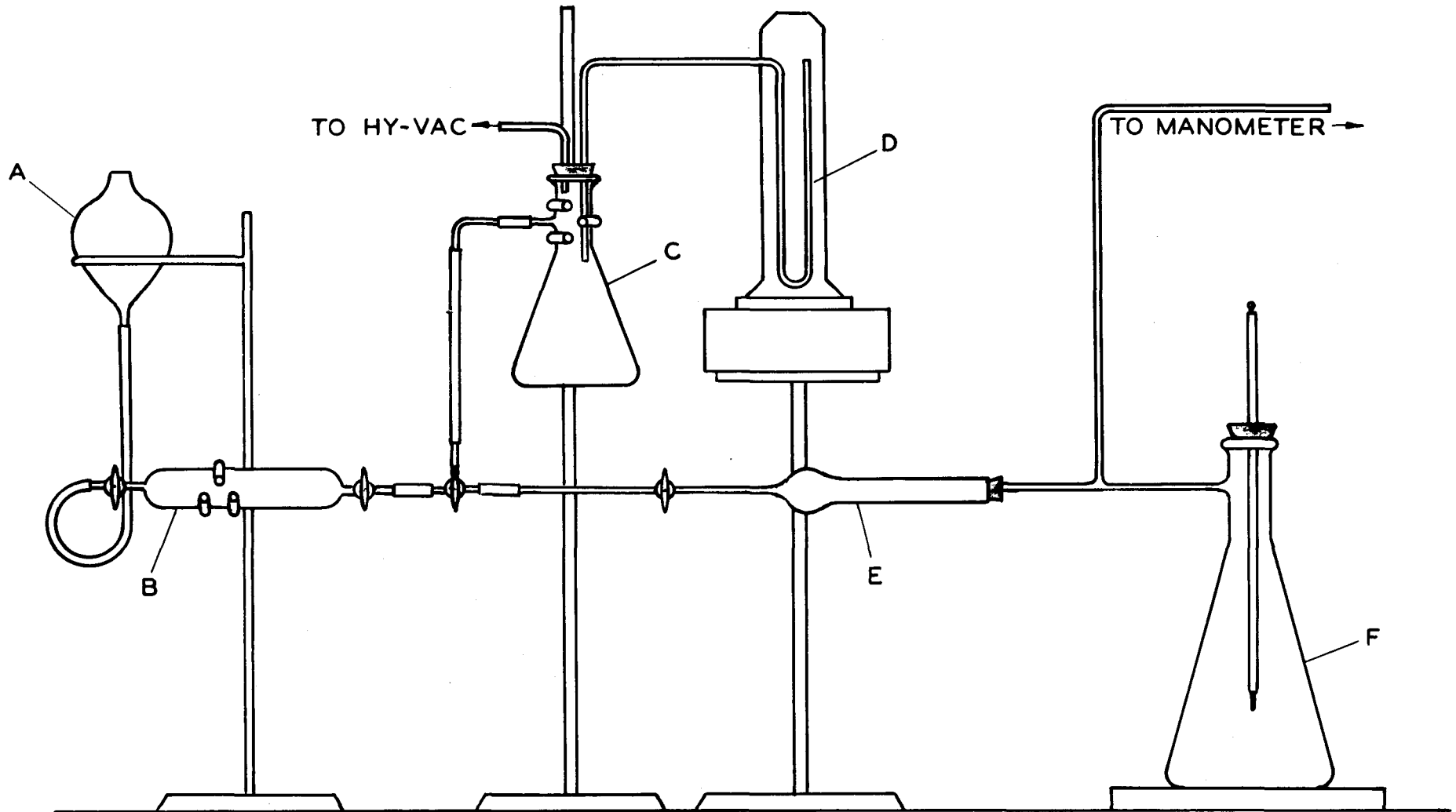
A — ACIDULATED SODIUM SULFATE RESERVOIR

B — SAMPLING BULB

C — VACUUM RESERVOIR

D — MANOMETER

E — FILTER TUBE

F — GAS RESERVOIR

TO HY-VAC

TO MANOMETER

10-23-45

$$T_c = c \, (t_e - t_r) = \text{temperature correction}$$

c = average cooling correction in $^\circ$C per min.

t_e = time (in min.) of last reading

t_f = time (in min.) of firing

If: H_{ex} = heat of explosion in calories per gram

Q = total calories from the explosion $\mp$ W_e xΔT

q = calories from igniter

Then:

$$H_{ex} = \frac{Q - q}{\text{Wt. of Sample}}$$

Determination of the Water Equivalent of the Calorimeter

The water equivalent of the calorimetric system,
W_e in the previous paragraph, is defined as its capacity
to take up heat in comparison with water. The water equivalent
of the calorimetric system is 1580 calories per one degree
rise in temperature. This was determined by an electrical
method, in which an electrical heating coil was placed inside
the bomb and a sufficient amount of heat was emitted in two
minutes to raise the temperature of the system 3 to 4°C.
By converting joules to calories, the average of ten
determinations gave 1580 calories with 850 gms. of water;
a mean deviation of 0.42%, an extreme variation of 1.46%,
and extreme deviation from the mean 0.84%.

Methane Formation

Since methane is formed during the process of
cooling, it is a secondary reaction and its heat of formation
must be considered when calculating rational heat and total
gas volume.

$$CO + 3H_2 = CH_4 + H_2O + 58,900 \text{ calories}$$
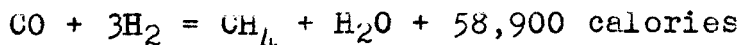
At 25°C., and considering water as a liquid, the heat of formation of CO is 26.9, CH_4 18.4, and H_2O 67.4 kilo calories. If the gas analysis shows "X" cc. of methane per gram at S.T.P. then,

$$\frac{58900 \ X}{22400} = \text{methane correction in cal./gm. of powder} \quad (2)$$

By inspection it is seen that the formation of methane causes a decrease in the total gas volume, consequently, a correction must be applied to the total gas volume measurement in order to determine the mole fractions of the gases before cooling has taken place. To make the correction, the volume "X" of methane formed is subtracted from the volume of H_2O and added to the volume of CO and H_2 as "X" and 3 "X", respectively.

Calibration of The Permanent Volume Measuring System

The exact volume of a 1000 ml. round bottom flask was determined by filling it with water and weighing it at a known temperature. Several of these determinations gave a mean of 1103 ml. at 20°C.

The system was evacuated to a vacuum of 0.1 mm. of mercury. The calibrated flask, with its air under atmospheric pressure, was connected to the evacuated system and its gases allowed to expand into the system. The total volume of the system was determined by the increase in pressure.

If:
p_1 = pressure in system (if any)

p_2 = final pressure in system

p_3 = atmospheric pressure in calibrated flask

V_1 = zero volume of system

V_3 = volume of calibrated flask

m = change of mercury in manometer in cm.

k = cross-sectional area of manometer tube $(.0442 \text{ cm.}^2)$

Then:

$$p_1 V_1 + (p_3 - p_2) V_3 = (V_1 + mk) p_2 \qquad (3)$$
$$V_1 = 4538 \text{ ml.}$$

Experiments

A weighed amount of the explosive, sufficient to give a loading density of 0.07 gm./cc., is placed in the calorimeter bomb. The ignition wire is attached to the firing head and charged with a carefully weighed piece of fibrous nitrocellulose (13.4%N), approximately 0.2 gm. After the firing head is screwed into position the bomb is evacuated with a Hy-Vac pump. It is then placed in the calorimeter and the stirrer set into position. A weighed amount of water, adjusted to approximately two degrees below room temperature, is introduced to the calorimeter by means of a glass funnel. A Beckman thermometer is set into position and the stirrer started. During the first five minutes the system approaches a steady state; the temperature is recorded at one minute intervals until the difference between successive readings is the same. When the bomb is fired a continuous rise in temperature is observed for at least ten minutes. Readings are resumed when the system

begins to cool and continued until a constant rate of cooling is obtained for ten consecutive minutes. (See Figure VII in appendix).

Determination of Permanent Gas Volume

The bomb is removed from the calorimeter and attached to the permanent volume measuring system, which has previously been evacuated with a Hy-Vac pump. The heights of the right and left mercury columns of the manometer are read with a vernier scale to the nearest 0.1 mm. The gases inside the bomb are then released gradually into the system. After an equilibrium in pressure has been established between the bomb and the rest of the system, the temperature of the gas is recorded and the mercury columns read, in order to determine the change in pressure.

If R_1 and L_1 are the first manometer readings and R_2 and L_2 are the readings after the gases are introduced, then:

$(R_1 + L_1) - (R_2 + L_2)$ = pressure of the gases in the system.

Letting:

V = volume of the permanent gases at standard temperature and pressure in cm.^{3}.

V_s = volume of the system in cm.^{3}.

m = $(L_1 - L_2)$ or change of mercury in the manometer in cm.

k = cross-sectional area of manometer tubing in cm.^{2}

- 12 -

p = pressure in the system at equilibrium in mm. Hg.

T = room temperature in °C.

t = temperature of the gases in °C.

0.14 = correction factor for expansion of mercury.

then:

$$Vs.t.p. = \frac{(Vs + mk)\ P \times 273}{760 + .14T)\ (273 + t)} \qquad (4)$$

$$\frac{Vs.t.p.}{Wt.\ of\ charge\ in\ gms.} = permanent\ gas\ volume\ in\ cc./gm$$

Water Determination

After the permanent gas volume has been measured, the gas reservoirs are shut-off from the rest of the system and the calcium chloride tube disconnected. The bomb and the previously weighed tube are left connected and raised to the height of a tripod stand into a two liter metal beaker. The disconnected end of the calcium chloride tube is connected to an auxiliary evacuating system, in which is attached a small manometer (Figure V) and the system gradually evacuated by a Hy-Vac pump. When the manometer no longer shows a change under reduced pressure, water is poured around the bomb and heated to 70°C. Evacuation is continued until the manometer shows no change. The calcium chloride tube is disconnected, reweighed, and the amount of water absorbed is calculated by difference.

W_g = weight of water in gms.

W_i = weight of water from ignition N/C

then:

$$\frac{(Wg - Wi)\ 22,400}{18 \times wt.\ of\ charge} = H_2O\ in\ cc./gm. \qquad (5)$$

- 13 -

DETERMINATION OF WATER CONDENSATION

TO HY-VAC
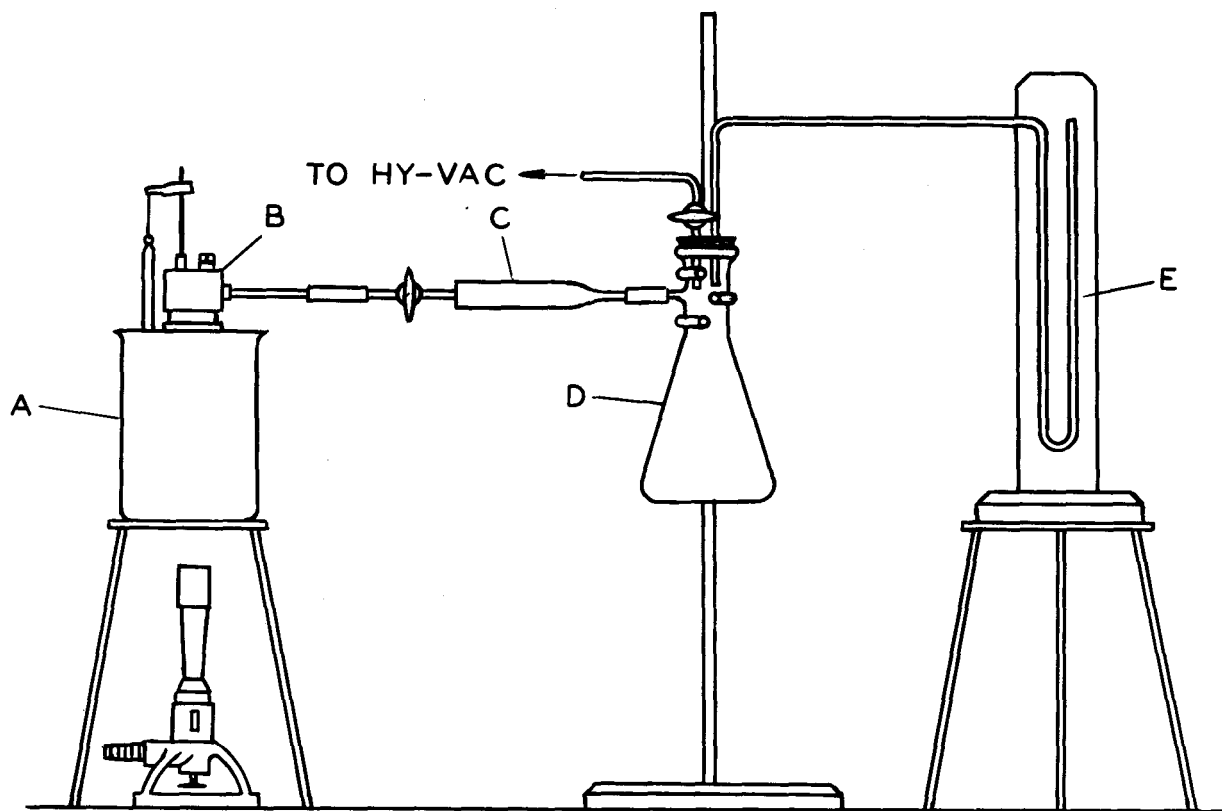
A — METAL BEAKER

B — CALORIMETER BOMB

C — CALCIUM CHLORIDE TUBE

D — VACUUM RESERVOIR

E — MANOMETER

10-23-45

FIG. V

Residue Analysis

If a qualitative examination reveals a residue it may
be necessary to make quantitative determinations. In most
cases only ammonium bicarbonate is present in sufficient
quantity to warrant a determination.

In the cases of cooler powders, i.e. in the proximity
of or below 2000°C., appreciable quantities of ammonium
bicarbonate, ammonium hydroxide, and free ammonia may be
formed during the process of cooling. The amount of heat
liberated by these reactions is subtracted from the observed
heat of explosion in the calculation of rational heat.

Determination of Carbonates

After the gases are released from the bomb it is
opened and washed down with 50 c.c. of barium chloride 0.1 N.
The precipitate is washed and scrubbed from the bomb with several
portions of hot water into a beaker. The precipitate is cooled
and filtered, ignited in a 800°C oven, cooled, and weighed
as barium carbonate.

Determination of Ammonia Present As Ammonium
Bicarbonate and Ammonium Hydroxide

When the gases have been released from the bomb it
is opened and immediately washed down with a 1% hydrochloric
acid solution. The acidified solution is transferred to a
round bottom flask, made alkaline with an excess of 3% sodium
hydroxide solution, and immediately connected to a vertical
air condenser. The ammonia liberated on heating is bubbled
into 50 ml. of standardized 0.1 N hydrochloric acid. The

excess acid is back-titrated with standard 0.1 N sodium hydroxide with methyl red as an indicator. If the ammonia as ammonium chloride and the carbonate as barium carbonate are in proportion to their equivalent weights, the residue is considered to contain only ammonium bicarbonate. An excess of ammonia is calculated as ammonium hydroxide.

Determination of Free Ammonia

If ammonia is present in the permanent gas volume its quantity is determined by bubbling the gases through an absorption column containing standard 0.1 N hydrochloric acid and back-titrating the excess acid with standard 0.1 N sodium hydroxide with methyl red as an indicator.

Determination of Hydrogen Sulfide

When the bomb has been fired and cooled, the volume of permanent gases is allowed to bubble through an absorption column containing a standardized solution of 0.1 N iodine solution mixed with 0.1 N hydrochloric acid in equal proportions. Any hydrogen sulfide in the gases will be converted to hydriodic acid and free sulfur. The excess iodine is back-titrated with a standardized solution of 0.1 N sodium thiosulfate, employing starch as an indicator. The excess hydrochloric acid is back-titrated with a standardized solution of 0.1 N sodium hydroxide. (This method is used to determine various other sulfides).

Gas Analyses

The reservoir containing the permanent gases is sampled by means of an evacuated sampling bulb (Figure IV), to

- 15 -

which is attached a reservoir containing acidulated sodium sulfate. The bulb is transferred to the gas analyzer and the gases analyzed for carbon dioxide, carbon monoxide, hydrogen, methane, and nitrogen according to standard procedure.

Calculation of The Temperature of Explosion

In order to calculate the temperature of explosion it is necessary to know:

1. The heat of explosion in cal./gm.

2. The heat liberated by all the constituents formed on cooling.

3. Water of condensation.

4. Water - gas reaction shift.

5. Rational heat.

6. Total gas volume (corrected for methane formation).

7. Gas analysis of the permanent gases.

$$\frac{\text{Rational heat}}{\text{Mean Specific heat of the gases from Room T to T of Explosion}} = \text{temperature of explosion}$$

Discussion

Contribution of Butyl Stearate to the Heat of Explosion of Butyl Stearate RDX Mixtures

Thermochemical analyses of several RDX compositions containing butyl stearate showed appreciable differences between observed and calculated values of heats of explosions. In other words, the summation of the heats of explosion of their ingredients did not coincide with actual values obtained from the compositions.

In an effort to explain these discrepancies, several combinations of butyl stearate and RDX, containing from 2 to 15% of the stearate were examined calorimetrically. The percent of butyl stearate in the mixtures was plotted against the heat of explosion value of butyl stearate. A curve, almost exponential, was drawn, showing that the cooling effect of butyl stearate in RDX decreases as its percentage increases. (Figure VI). Consequently, if the heat of explosion is taken from this chart when calculating the heat of a propellant containing butyl stearate and RDX, the results are practically identical with those obtained calorimetrically.

Thermochemical Analyses of Several RDX and Albanite Compositions

Preliminary thermochemical analyses were made on a sample of pure tetryl and three nitrocelluloses of different nitrogen contents in order to verify the calibration of the calorimetric and gas measuring equipment.

Table I shows the composition of each propellant tested and chemical analyses of its ingredients.

Several of the most widely used military propellants were tested first and the results compared favorably with the determinations made by others on these compositions.

Finally, experimental RDX and Albanite powders, manufactured at Burnside Laboratory, and several Albanite and experimental compositions submitted by the Explosives Research Laboratory, Bruceton, Pa. were analyzed and their thermochemical characteristics determined. The results from

CONTRIBUTION OF BUTYL STEARATE TO THE HEAT OF EXPLOSION
OF BUTYL STEARATE – RDX MIXTURES
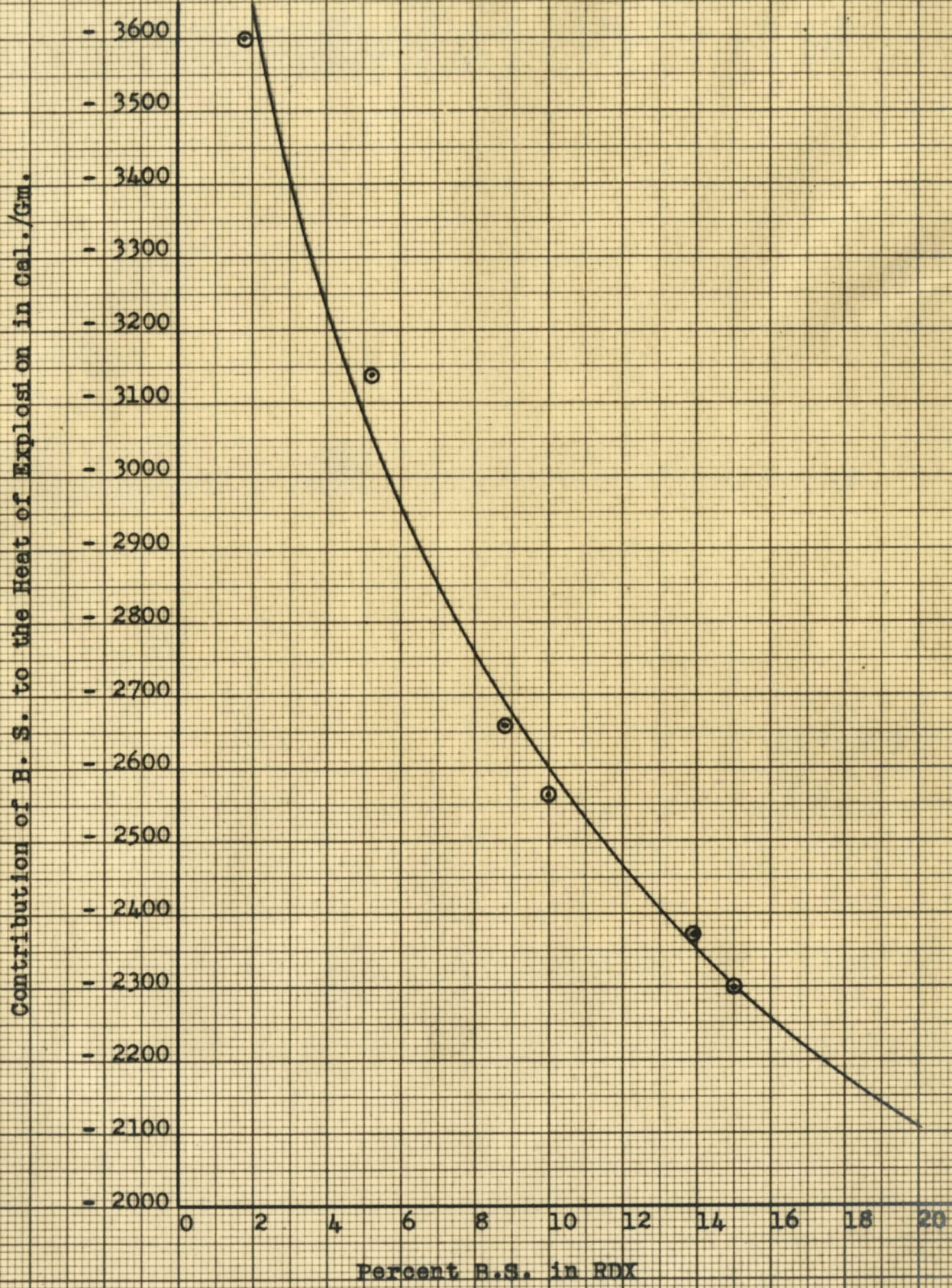
Contribution of B. S. to the Heat of Explosion in Cal./Gm.

Percent B.S. in RDX

10-23-45

Fig. VI

these experiments, as shown in Tables II and III, indicated that RDX propellants of the compositions designated as CC1 and CC2 gave an appreciably greater gas volume, per gram of powder, than did the FNH and NH cannon powders, while no great difference existed between their rational heats. The flame temperatures of the RDX powders examined cover the range from 2100 to $3000^\circ C$. This covers the field from cool, flashless cannon powder to a hot rifle composition.

It will be noted that the Albanite sample VC-66EX which represented powder granulated for the Navy 6"/47 Gun gave a lower adiabatic flame temperature than Cordite N/P/M, OC-172-EX, also made for this gun. Both contained 1.5% K_2SO_4. Both of these powders have lower flame temperatures than FNH (85-10-5), represented by VG-10397. The Pyro powder, VG-10648, gave a still higher flame temperature. The order of increasing temperature is also that of increasing flash tendency in cannon. It is interesting to note that there is very little difference between the rational heats of Albanite, Cordite N and FNH. That of Pyro is somewhat higher.

The calculated values given for the heats of explosion and flame temperatures were computed from the data contained in the thermochemical tables of the October 1944 OSRD monthly report on Contract OEMsr-881 from California Institute of Technology - Investigations of Double Base powders. In cases of the cooler powders these values did

not compare favorably with experimental results because of the large calorimetric corrections involved in compensating for the heats of formation of various substances formed when the hot gases are cooled to room temperature.

SUMMARY

Thermochemical analyses have been made on a number of propellant compositions, both service and experimental, as an aid in the study of flash, interior ballistics, and barrel erosion. Heats of explosions and gas compositions were obtained, experimentally, through the employment of a calorimeter bomb, gas measuring and analyzing equipment. Rational heats and flame temperatures were calculated from the observed data on 19 samples of military and experimental compositions, including Albanite, RDX powders, Cordite N/P/M, and single-base propellants. The results obtained strongly indicate that actual calorimetric measurements are necessary in order to determine the true heat of explosion and flame temperature. In some instances it was found that the calculated values, obtained from the summation of the thermal data of the individual ingredients, diverged to an appreciable extent from the values observed when in combination with one another. Further investigations showed that the extent of the combustion of the cooling agents and the state of the corresponding oxygen balance seemed to explain this phenomenon. This is clearly illustrated in connection with the relatively cool RDX compositions, where the cooling effect per gram of butyl stearate depends upon its quantity in the mixture. Thermochemical data are tabulated for some experimental RDX and Albanite compositions.

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A TYPICAL THERMOCHEMICAL CALCULATION

Determination of the Heat of Explosion
Wt. of Sample   4.7096 gms.

Wt. of ignition 0.2132 gm.   Wt. of $CaCl_2$ tube 54.7385 gm.

Time (in min.)	Temperature (in C°)	Temperature change (in C°)
1	1.218	+0.006
2	1.224	+0.006
3	1.230	+0.006
4	1.236	----- $T_1 = 1.242°$
5	fired	-----
6	-----	-----
7	-----	-----
8	-----	-----
9	-----	-----
10	-----	-----
11	-----	-----
12	-----	-----
13	-----	-----
14	-----	-----
15	-----	-----
16	-----	-----
17	-----	-----
18	-----	-----
19	4.302	-----
20	4.300	-0.002
21	4.297	-0.003
22	4.293	-0.004
23	4.289	-0.004
24	4.286	-0.003
25	4.283	-0.003
26	4.281	-0.002
27	4.279	-0.002 $T_e = 4.279$

$$\frac{0.023}{8} = 0.003°/min.$$

$$c = 0.003°/min.$$

$$t_e = 27$$

$$T_c = c(t_e - t_f) = 0.003 (27-4) = 0.069°C$$

$$T_2 = T_e + T_c = 4.279 + 0.069 = 4.348°C$$
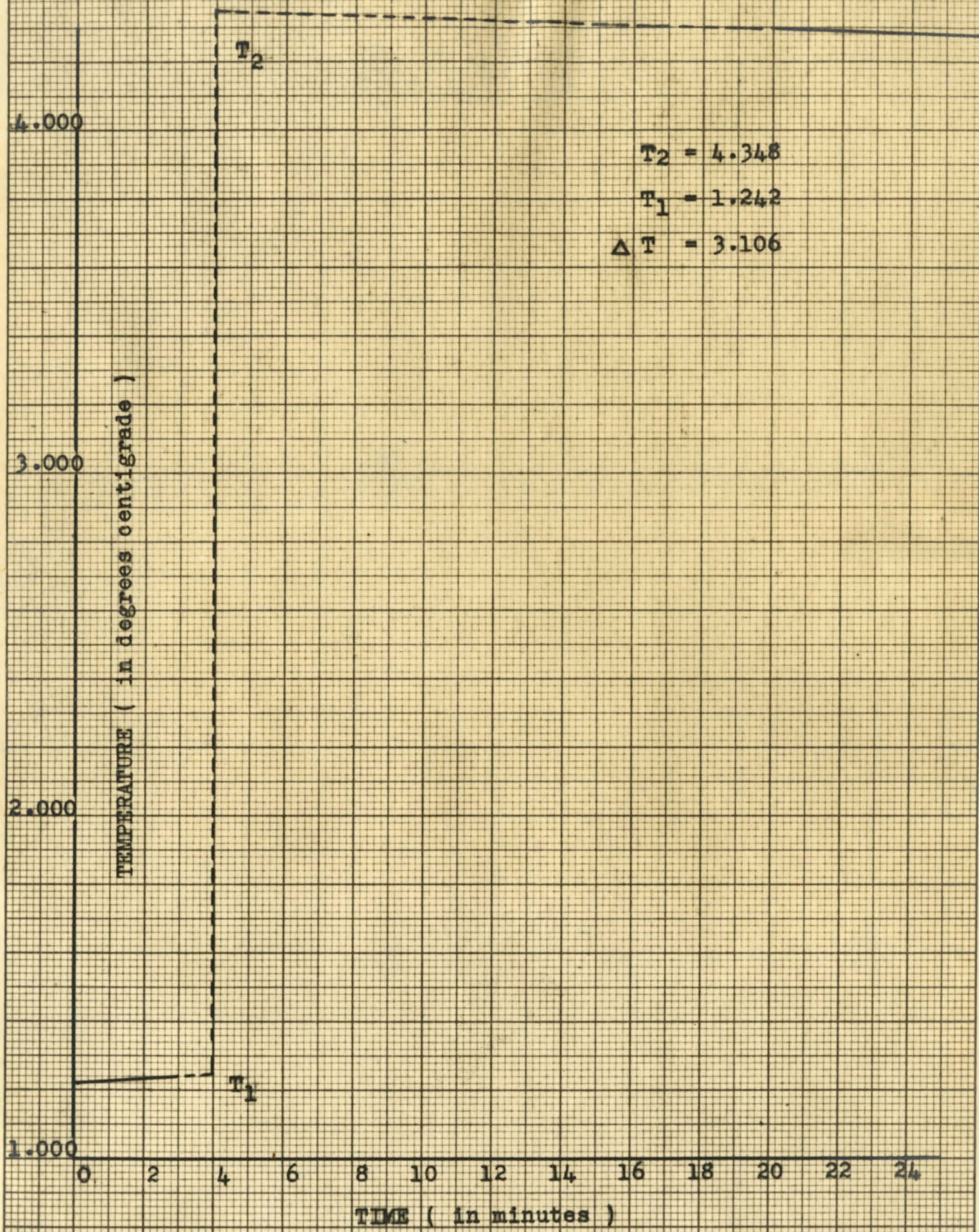
Fig. VII

$$T = T_2 - T_1 = 4.348 - 1.242 = 3.106$$

$$Q = W_e \times T = 1580 \times 3.106 = 4907.5 \text{ calories}$$

$$q = .2132 \times 1082 = 230.7 \text{ cal. (Ht. of Explos. of 13.45\%N}$$
$$\text{N/C} = 1082)$$

$$\text{Hex} = \frac{Q-q}{\text{Wt. of sample}} = \frac{4907.5 - 230.7}{4.7096} = 993.0 \text{ cal./gm.}$$

Determination of Permanent Gas Volume

If:
$$V_b = \text{vol. of bomb in ml., then:}$$

$$V_{s.t.p.} = \frac{(V_s + V_b + mk)\ (L_1 - L_2) + (R_1 - R_2)\ 273}{(760 + 0.14T)\ (273 + t)}$$

$$t = 29.0°C$$

$$(L_1 - L_2) + (R_1 - R_2) = 764.5 \text{ mm Hg.}$$

$$V_{s.t.p.} = \frac{(4538 + 73 + 16.7)\ 764.4 \times 273}{(760 + 3.5)\ 302.0} = 4188.0 \text{ cc.}$$

Correcting for gases from igniters at 713 cc/gm of N/C.

$$\frac{4188.0 - 152.0}{4.7096} = 856.9 \text{ cc/gm. S.T.P.}$$

Determination of Water of Condensation

Difference in weights of $CaCl_2$ tube = 55.2071 - 54.7385 = 0.4686 gm. Water of condensation from ignition N/C = 0.0288 gm.

$$0.4686 - 0.0288 = 0.4398 \text{ gm.}$$

$$\frac{0.4398 \times 22,400}{18 \times 4.7096} = 116.2 \text{ cc/gm. S.T.P.}$$

Gas Analysis

Composition	%	cc/gm.
CO_2	12.4	106.3
CO	39.5	338.5
H_2	23.1	197.9
CH_4	0.1	0.9
N_2	24.9	213.4

Calculation of the Temperature of Explosion

	CO_2	CO	H_2	CH_4	N_2	H_2O
Anal. cc./gm	106.3	338.5	197.9	0.9	213.4	116.2
Corr. for CH_4	106.3	339.4	200.6	---	213.4	115.3
Gm. mole/gm.	0.0047	0.0151	0.0089		0.0095	0.0051

Estimated $T°C$ at 3010° $k* = 7.33$

$$k = \frac{(CO + X)\ (H_2O + X)}{(CO_2 - X)\ (H_2 - X)}$$

$$7.33 = \frac{(339.4 + X)\ (115.3 + X)}{(106.3 - X)\ (200.6 - X)} = \frac{39{,}133 + 454.7X + X^2}{21{,}324 - 306.9X + X^2}$$

$$\begin{array}{r} 7.33X^2 - 2{,}250X + 156.304 \\ -X^2 - \quad 455X - \quad 39{,}133 \\ \hline 6.33X^2 - 2{,}705X + 117{,}171 \end{array}$$

$$X = \frac{2{,}705 \pm \sqrt{7{,}317{,}025 - 2{,}966{,}770}}{12.66}$$

$$X = 49.0 \text{ cc.}$$

$$= 0.0022 \text{ gm. mole.}$$

Corrections:

	CO_2	CO	H_2	N_2	H_2O
Gm. mole	0.0025	0.0173	0.0067	0.0095	0.0073
Mole.heat	11.70	6.33	5.93	6.27	9.24
Specific heat	0.0293	0.1095	0.0397	0.0596	.0676 = 0.3057

Water of Condensation: H_2O (vap.) = H_2O (liq.) + 9900 cal.
        Correction = 51 cal.
Water-Gas Reaction Shift: $CO + H_2O = CO_2 + H_2 + 9800$ cal.
        Correction = 21 cal.
Methane Formation: $CO + 3H_2 = CH_4 + H_2O + 58{,}700$ cal.
        Correction = 2 cal.
        Total Corrections 74 cal./gm.
Heat of Explosion (993 cal./gm.) - 74 cal/gm. = Rational heat
                                              = 919 cal./gm.

From Equation (1)

Temperature of Explosion = $\dfrac{919 \text{ cal./gm.}}{0.3057}$ = 3006°C

* (k is the equilibrium constant taken from tables by Lewis & van Elbe - JACS, 57 (1935) 612-14)

TABLE I

Composition of the Various Propellants Studied

Sample No.	Type	NC	NG	NGD	RDX	DINA	DBP	DBT	Cent.l	Tri-acetin	DPA	DBT(1)	BS(2)	Cryo-lite	Butyl NENA	TNEB(3)	K₂SO₄	T.V.	V.S.
VO-10648	5°/38 Pyro	93.96	-----	-----	-----	-----	-----	-----	-----	-----	0.98	-----	-----	-----	-----	-----	-----	5.06	-----
VO-10397	FNH (85-10-5)	83.26	-----	-----	-----	-----	4.93	9.85	-----	-----	1.00	-----	-----	-----	-----	-----	0.98	----	0.31
VO-7967	NH (87-10-3)	87.16	-----	-----	-----	-----	2.88	9.96	-----	-----	0.98	-----	-----	-----	-----	-----	-----	----	1.51
VA-5386	IMR 4814	88.09	-----	-----	-----	-----	-----	8.57	-----	-----	0.63	-----	-----	-----	-----	-----	0.73	----	-----
OC-172-EX	N/P/N	18.40	18.60	53.80	-----	-----	-----	-----	7.30	-----	-----	-----	-----	0.32	-----	-----	1.52	0.8	-----
EX 6079	CC1	37.93	-----	-----	48.96	-----	-----	-----	-----	-----	0.50	-----	12.21	-----	-----	-----	-----	0.4	-----
EX 6080	CC2	36.17	-----	-----	52.20	-----	-----	-----	-----	-----	0.50	-----	10.73	-----	-----	-----	-----	0.4	-----
EX 6081	CC - Special	38.17	-----	-----	52.28	-----	-----	-----	3.81	-----	0.45	-----	4.50	-----	-----	-----	0.39	0.4	-----
VB-10751W	CC - Special	47.98	-----	-----	40.02	-----	-----	-----	-----	-----	0.50	-----	4.59	-----	-----	-----	0.4	-----	-----
EX 6082	CR2	55.79	-----	-----	35.28	-----	-----	5.67	-----	-----	0.50	1.92	-----	-----	-----	-----	0.44	0.4	-----
EX 6083	CR3	35.61	-----	-----	54.90	-----	-----	7.52	-----	0.77	0.50	-----	-----	-----	-----	-----	0.30	0.4	-----
VC-96-EX	Albanite	18.51	-----	53.25	-----	18.49	3.80	-----	1.24	-----	-----	-----	-----	-----	-----	-----	4.29	0.42	-----
VC-66-EX°	Albanite	20.00	-----	55.00	-----	19.50	4.00	-----	1.50	-----	-----	-----	-----	-----	-----	-----	1.50	-----	-----
UG-11625°	(ERL) Albanite	20.00	-----	55.00	-----	19.50	4.00	-----	1.50	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
UG-11451°	(ERL) Experimental	25.60	-----	55.00	-----	8.50	-----	oil 9.4	1.50	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
UG-11454°	(ERL) Experimental	20.80	-----	55.00	-----	8.50	-----	-----	1.50	-----	-----	-----	-----	-----	14.2	-----	-----	-----	-----
UG-11455°	(ERL) Experimental	20.80	-----	55.00	-----	8.50	-----	-----	1.50	-----	-----	-----	-----	-----	14.2	-----	-----	-----	-----
UG-11456°	(ERL) Experimental	21.75	-----	55.00	-----	8.05	-----	-----	1.50	-----	-----	-----	-----	-----	13.7	-----	-----	-----	-----
UG-11457°	(ERL) Experimental	23.00	-----	55.00	-----	7.50	-----	-----	1.50	-----	-----	-----	-----	-----	-----	12.7	-----	-----	-----

° Nominal Compositions
(1) DBT = Dibutyl Tartrate
(2) BS = Butyl Stearate
(3) TNEB = Trinitroethylbenzene

TABLE II

Heats of Explosion, Rational Heats, and Isochoric Temperature of Explosion

Sample	Type	Heat of Explosion cal/gm	Explosion T°C.	Rational Heat cal/gm	Calorimetric Corrections						Calculated from Composition*	
					CH₄ (form)	H₂S (form)	H₂O (cond.)	H₂O - Gas Shift	NH₄HCO₃ (form)	Total Corrections	Heat of Explosion cal/gm	Explosion T°C
N/C	12.60% N	962	2832	864	4	----	72	22	----	98	954	2798
N/C	13.13% N	1044	3065	940	2	----	74	38	----	114	1037	3065
N/C	13.45% N	1082	3160	963	4	----	74	45	----	123	1061	3101
	Tetryl	944	3125	871	24	----	35	14	----	73	——	----
VG-10048	Pyro	808	2307	712	13	----	64	17	2	96	819	2293
VG-10397	85-10-5	744	2287	665	4	----	41	21	13	79	720	2287
VG-7967	87-10-3	776	2365	703	4	----	49	15	5	73	765	2342
VA-5356	IMR 4814	875	2640	791	4	----	55	25	----	84	880	2632
OC-172 EX	N/P/M	779	2227	671	10	----	59	9	30	108	732	2171
EX 6079	CC-1	755	2139	673	20	----	40	3	19	82	725	2192
EX 6080	CC-2	787	2263	721	5	----	42	8	11	66	775	2338
EX 6081	CC-Special	841	2450	772	15	----	42	18	5	80	828	2439
VE-10751W	CC-Special	845	2632	790	5	----	35	15	----	55	854	2614
EX 6082	CR-2	920	2730	837	4	----	50	29	----	83	947	2774
EX 6083	CR-3	936	3008	922	2	----	51	21	----	74	1042	3029
VC-96 EX	Albanite	757	2089	611	24	10	71	15	26	146	730	2028
VC-66 EX	Albanite	781	2161	674	4	2	68	9	24	107	670	2092
UG-11635	Albanite	796	2257	708	4	----	55	8	21	88	——	----
UG-11481	Flashless Experimental	782	2127	690	6	----	61	4	21	92	——	----
UG-11484	Flashless Experimental	795	2218	695	10	----	59	4	27	100	——	----
UG-11485	Flashless Experimental	811	2234	710	10	----	66	3	22	101	——	----
UG-11486	Flashless Experimental	807	2158	685	10	----	70	3	39	122	——	----
UG-11487	Flashless Experimental	771	2175	672	10	----	59	0	30	99	——	----

* Calculated from thermochemical tables in the monthly report, "Investigations of Double Base Powder," by Dr. Linus Pauling, California Institute of Technology.

TABLE III

Products of Explosion

Sample	Type	D**	Volume Measurements S.T.P.			Permanent Gas Composition in Percent							Residue Analyses NH₄HCO₃
			Perm. Vol. cc/gm.	H₂O (cond.) cc/gm.	Total Vol. cc/gm.	CO₂	CO	H₂	CH₄	N₂	NH₃	H₂S	gm/gm.
N/C	12.60% N	0.08	747	163	910	21.4	41.6	22.7	0.2	14.1	----	----	----
N/C	13.13% N	0.08	726	166	892	25.2	41.3	18.3	0.1	15.1	----	----	----
N/C	13.45% N	0.08	713	169	882	28.3	36.5	19.3	0.2	15.7	----	----	----
	Tetryl	0.08	900	39	939	6.0	53.4	15.3	0.9	24.4	----	----	----
VG-10648	Pyre *	0.08	839	113	952	12.0	49.6	25.6	0.6	12.0	0.2	----	0.0016
VG-10397	85-10-5	0.07	875	93	968	12.7	50.1	25.1	0.2	11.9	----	trace	0.0194
VG-7967	87-10-3	0.07	871	111	982	11.2	51.8	23.6	0.2	13.2	----	----	0.0076
VA-5386	IMR 4814	0.08	813	124	937	17.3	46.0	22.8	0.2	13.7	----	trace	trace
OC-172-EX	N/P/M	0.07	787	129	916	6.4	33.9	25.5	0.5	32.9	----	0.8	0.0433

RDX COMPOSITIONS

Sample	Type	D**	Perm. Vol. cc/gm.	H₂O (cond.) cc/gm.	Total Vol. cc/gm.	CO₂	CO	H₂	CH₄	N₂	NH₃	H₂S	NH₄HCO₃ gm/gm.
EX 6079	CC-1*	0.07	966	90	1056	3.1	47.0	29.1	0.8	20.0	trace	----	0.0274
EX 6080	CC-2	0.07	987	96	1083	4.6	45.0	30.3	0.2	19.9	trace	----	0.0155
EX 6081	CC-special	0.07	953	95	1048	8.0	41.9	27.7	0.6	21.8	trace	trace	0.0027
VE-10751-W	CC-special	0.07	926	80	1006	8.0	46.4	25.8	0.2	19.6	----	----	----
EX 6082	CR-2	0.07	872	112	984	12.8	41.4	24.8	0.2	20.7	----	trace	----
EX 6083	CR-3	0.07	854	115	969	12.4	39.5	23.1	0.1	24.9	----	trace	----

NITROGUANIDINE - DINA COMPOSITIONS

Sample	Type	D**	Perm. Vol. cc/gm.	H₂O (cond.) cc/gm.	Total Vol. cc/gm.	CO₂	CO	H₂	CH₄	N₂	NH₃	H₂S	NH₄HCO₃ gm/gm.
VC-96-EX	Albanite	0.07	796	158	954	3.3	31.0	26.8	1.2	32.1	----	5.6	0.0373
VC-66-EX	Albanite	0.07	811	154	965	6.4	31.6	27.0	0.2	33.9	----	0.8	0.0372
UG-11625	Albanite	0.07	799	124	923	5.8	34.4	27.5	0.2	31.8	----	----	0.0313
UG-11481	Flashless Experimental	0.07	796	139	935	4.0	31.3	30.0	0.3	33.4	----	----	0.0313
UG-11484		0.07	807	134	941	4.6	36.8	26.5	0.5	31.6	----	----	0.0396
UG-11485	"	0.07	780	150	930	5.4	37.9	23.6	0.5	32.6	----	----	0.0322
UG-11486	"	0.07	802	158	960	4.1	35.4	26.6	0.5	33.4	----	----	0.0570
UG-11487	"	0.07	777	134	911	3.8	37.1	24.3	0.5	34.3	----	----	0.0433

* Contains a trace of ammonium hydroxide in the condensed water.
** D equals loading density.