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UNITED STATES NAVY

PROJECT SQUID

TECHNICAL MEMORANDUM No. PUR-5

SOME THERMODYNAMIC PROPERTIES

OF THE

NITROPARAFFINS

PRINCETON UNIVERSITY

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Clark L. Dorsey

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SOME THERMODYNAMIC PROPERTIES OF THE NITROPARAFFINS

by

Clark L. Dorsey

Louis H. Going

Dysart E. Holcomb

Project SQUID is a Program of Fundamental Research on Liquid Rocket and Pulse Jet Propulsion, for the Bureau of Aeronautics and the Office of Naval Research of the Navy Department, Contract N6 ori-104, Task Order No. 1, Designation No. NR 220 042

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SUMMARY

1. Heats of combustion and latent heats of vaporization of several straight-chain nitroparaffins have been determined experimentally. The resulting values have been used to test the accuracy of three generalized methods of predicting heats of combustion of organic compounds from a knowledge of the chemical structure of the molecules. All three methods gave values accurate to within about one percent.
2. An equation has been developed which correlates the heats of combustion of all of the nitroparaffin samples for which data are available, both from this study and in the open literature, with an average deviation of about two percent.
3. Conclusions reached by other investigators that the heats of explosion and the explosive powers of pure chemical compounds are related to the oxygen balance of the molecules have been varified and extended.

INTRODUCTION

The possible utilization of the mono- and poly-nitroparaffins as explosives, propellants, and fuel additives, coupled with their already extensive uses as solvents and chemical intermediates, is indicative of the value of experimental data concerning their thermodynamic properties.

The utility of heats of combustion, latent heats, specific heats, and pressure-volume-temperature relationships in the calculation of heat effects in chemical processes, theoretical flame temperatures, heats of explosion, theoretical thrusts for reaction engines, etc. has been stressed by many investigators. Information on these properties is of major importance in engineering practice. In cases involving the combustion of those compounds yielding such products as carbon dioxide, water, and gaseous nitrogen, the specific heats and P-V-T relationships of the products are known with high degrees of accuracy, and the major problem often becomes one of estimating or determining the heats of combustion of the compounds in their standard states.

As a step in the estimation of heat effects when accurate experimental data are lacking, the relationships between heats of combustion and chemical structure have been studied by many investigators, and there are several generalized correlations of good accuracy available in the literature. Because of the lack of experimental data on more than a few members of the nitroparaffin series, however, there is only slight evidence to substantiate the belief that these correlations can be used with any reasonable degree of certainty for the estimation of properties of the series as a whole. Additional information on the thermodynamic properties of the nitroparaffins may be used to test the available correlations and, possibly, to aid in developing new and better relationships.

A conclusion reached in the recent Arthur D. Little, Inc. "Report on Study of Pure Explosive Compounds" that, from the viewpoint of explosives, the most desirable molecules include those containing only carbon, hydrogen, and the nitro group lends increasing importance to the present study. Data obtained in this investigation may be used to test and extend some of the conclusions reached in that report, and to analyze the nitroparaffin series from the explosives viewpoint.

It is the purpose of this investigation to determine experimentally the heats of combustion of various straight-chain members of the nitroparaffin series of organic compounds, and to investigate the correlation of these and of other derived properties so that calculations may be extended to include other members of the series for which experimental data are at present unavailable.

DEFINITION OF TERMS

The following terminologies, consistent with those ordinarily used in thermochemical work, have been adopted in this report.

1. Heat of Combustion. The heat of combustion of an organic compound containing only carbon, hydrogen, oxygen, and nitrogen is defined as the quantity of heat evolved when a unit quantity of the compound is burned in the presence of excess oxygen to yield combustion products that are in their final states of oxidation (e.g., gaseous carbon dioxide, liquid water, and gaseous nitrogen). Symbols are assigned as follows, depending on the conditions of the combustion process:

ΔE_b = the heat of combustion when the sample is burned under the standardized conditions of the bomb process (28).

ΔE_r^o = the heat of combustion at constant volume with the reactants and products in their standard states at 25°C and one atmosphere pressure.

ΔH_r^o = the heat of combustion at constant pressure with the reactants and products in their standard states at 25°C and one atmosphere pressure.

The ordinary units for heats of combustion are either kilocalories per gram-mol (kcal/mol) or kilocalories per kilogram (kcal/kg).

2. Latent Heat of Vaporization. The latent heat of vaporization is defined as the quantity of heat necessary to completely vaporize a unit quantity of pure liquid at constant temperature and pressure. In this report the latent heat is calculated at 25°C and at a total pressure corresponding to the vapor pressure of the pure compound at that temperature. The units employed for latent heats are kcal/mol.

3. Vapor Pressure. The vapor pressure of a pure liquid compound

is defined as the pressure at which vapor and liquid are in equilibrium at a given temperature. In this investigation the units of vapor pressure are millimeters of mercury.

4. Heat of Formation. The standard heat of formation, ΔH_f^0 , is defined as the quantity of heat evolved when a unit quantity of compound in its standard state is formed from the elements in their standard states in a reaction beginning and ending at 25°C and one atmosphere total pressure. Unless preceded by a positive sign, values of ΔH_f^0 tabulated in this report should be taken as negative in order to be consistent with thermodynamic nomenclature. The units of this quantity are ordinarily taken as kcal/mol.

5. Heat of Explosion. The heats of explosion, ΔE_e , given in this report are defined as the quantities of heat liberated when unit quantities of the compounds are detonated, in the absence of external oxygen, to yield detonation products. The detonation products have been calculated using the following assumptions:

- a) the carbon present in the molecule is oxidized to carbon monoxide.
- b) the hydrogen present is oxidized to gaseous water.
- c) the carbon monoxide is further oxidized to carbon dioxide.
- d) if insufficient oxygen is present to accomplish all of the above reactions, they will take place in the above order.

The validity of the above assumption is discussed in the Arthur D. Little, Inc. report (14).

Numerical values used in converting heats of combustion to heats of explosion have been taken from this report (14). The units for heats of explosion have been taken as either kcal/mol or kcal/kg.

6. Oxygen Balance. Oxygen balance (O.B.) has been calculated as the negative of one hundred times the weight of external oxygen required for the complete combustion of unit weight of a compound to carbon dioxide, water, and nitrogen. In the form of an equation (14):

$$\text{O.B.} = \frac{-(2x + 1/2y - z)}{M} 1600 \quad \dots\dots\dots(1)$$

where

x = the number of carbon atoms in the molecule

y = the number of hydrogen atoms in the molecule

z = the number of oxygen atoms in the molecule

M = the molecular weight of the compound

7. Explosive Power. Explosive power (P) has been calculated as the ratio of the Berthelot product for a compound to the same product for TNT as a reference standard. With the Berthelot product defined as the heat of explosion in calories per gram multiplied by the cubic centimeters of gases (measured at NTP) evolved from one gram of the compound, it is shown (14) that:

$$P = \frac{-3500 N \Delta E_e}{M^2} \quad \dots\dots\dots(2)$$

where

N = the increase in the number of moles of gas, carbon being considered as a solid.

ΔE_e = the heat of explosion, in kcal/mol, calculated to gaseous water.

M = the molecular weight of the compound.

The explosive power thus defined is expressed as a percent of the explosive power of TNT. The assumptions inherent in this definition of explosive power are discussed in the report by A. D. Little, Inc. (14).

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EXPERIMENTAL INVESTIGATIONS

A. COMPOUNDS INVESTIGATED

Samples of nitromethane, nitroethane, 1-nitropropane, 2-nitropropane, and 2,2-dinitropropane were obtained from the Commercial Solvents Corporation. These samples were purified by drying and fractional distillation.

1,1-Dinitropropane was prepared from potassium nitrite and 1-chloro-1-nitropropane following the procedure developed by Jacobson (9). The product was purified by rectification.

1,3-Dinitropropane was prepared from silver nitrite and 1,3-diiodopropane following the procedure used by McElroy (15). The product was dried and twice-distilled. The details of the preparation of this compound are given by Hass, Kispersky, and Holcomb (7).

1-Nitrobutane was prepared from silver nitrite and 1-iodobutane via the Victor Meyer reaction. The product was purified by drying and fractionation.

2-Nitrobutane was prepared by the vapor-phase nitration of butane. The sample was purified by fractionation.

Trinitromethane was obtained from Prof. W. L. Gilliland of the Purdue University Department of Chemistry. The sample was not further purified.

The purity of these aforementioned samples, except 1,3-dinitropropane and trinitromethane, was estimated to be greater than 99% pure. By the use of time-temperature freezing point curves (6) the estimated purity of 1,3-dinitropropane was 98.2% and for trinitromethane was 95.6% (all on a molar basis).

Heat of combustion values taken from the literature for use in

developing the correlations of Section IV included those reported by Miller and Hunt (16) for 2,3-dimethyl-2,3-dinitrobutane, 2,2-dimethyl-1,3-dinitropropane, 2-methyl-2,3,3-trinitrobutane, 2-methyl-2,3,3-trinitropentane, and 2,2,3,3-tetranitrobutane; that reported by Roth (24) for tetranitromethane; and that reported by Rubtsov (25) for 1,1,1-trinitroethane.

The physical properties used to characterize the samples prepared in the course of this investigation are summarized in Table I.

B. EXPERIMENTAL METHODS

1. Heats of Combustion. The experimental method used in the investigations of heats of combustion was the so-called "adiabatic" method of bomb calorimetry. The equipment used was, in principle, similar to that perfected by Richards (22) and modified by Daniels (5).

The experiments were based upon the method of comparative measurements, where the effects caused by an experimental sample are compared with the effects caused by a chosen standard substance under identical conditions. In theory, as applied to heat of combustion measurements, a weighed quantity of standardized benzoic acid is burned in a calorimeter under standardized conditions to evolve a standard quantity of heat; the sample to be investigated is then burned in the same equipment, under the same conditions, to evolve the same quantity of heat; the ratio of the mass of the experimental sample to the mass of the standard substance multiplied by the heat of combustion of the standard substance gives the heat of combustion of the experimental sample.

In practice, exactly identical conditions cannot be maintained from experiment to experiment, so that the method of calculation must be modified to reduce the conditions under which each experiment is made to some arbitrarily selected standard set of conditions. This reduction has

TABLE I

PHYSICAL PROPERTIES OF THE NITROPARAFFINS INVESTIGATED

Compound	Density at 25°C g/cc' in Stable State ^a		Refractive Index n_D^{20}	
	Literature	Experimental	Literature	Experimental
Nitromethane	1.1287 ^a	1.1286	1.3818	1.3818
Nitroethane	1.045	1.0413	1.3916	1.3917
1-Nitropropane	0.997	0.9934	1.4015	1.5018
2-Nitropropane	0.985	0.9821	1.3941	1.3944
1-Nitrobutane	0.968	0.9685	1.4112	1.4108
2-Nitrobutane	0.962	0.9609	1.4036	1.4044
1,1-Dinitropropane	-	1.2610	-	1.4339
2,2-Dinitropropane	-	1.30	-	-
1,3-Dinitropropane	-	1.354	-	1.4654
Trinitromethane	1.597	1.615	-	1.4454

^a All densities from the literature, except that for nitromethane, corrected to 25°C by the Lorenz-Lorentz equation

been accomplished indirectly by basing the calculations upon the "water equivalent" of the calorimetric system, i.e. that quantity which, when added to the mass of water placed in the calorimeter, gives a sum which is numerically equal to the total heat capacity of the calorimetric system. The water equivalent of the system may be determined by experiments, under conditions substantially equal to the standard set of conditions, in which benzoic acid, standardized by the Bureau of Standards, is burned.

Final experimental values for the heats of combustion given in Table II are accepted as the average of the results of a number of experiments. Uncertainty limits are assigned to the averages using standard statistical procedures (23). The heats of formation of the products of combustion being known, the heats of formation of the experimental samples are readily calculated from their standard heats of combustion (13).

2. Latent Heats of Vaporization. The method used for the determination of the latent heats of vaporization of the liquid nitroparaffin samples involved experimental measurements of vapor pressures and liquid densities followed by application of the Clapeyron equation (13) with the assumption of ideal vapor phases. The applicability of the Clapeyron equation is based on the assumption of reversible, isothermal vaporization at a constant temperature with the vapor and liquid phases in dynamic equilibrium. This assumption was validated insofar as experimentally possible by measuring the vapor pressures at constant temperatures with samples boiling under their own vapor pressures at those temperatures.

Vapor pressures were measured using the method proposed by Pickett (20) and utilized by Hodge (8) in his earlier determinations of vapor pressures of the mono-nitroparaffins.

Selected values from the experimental vapor pressure curves are

tabulated in Table III. The calculated latent heats of vaporization are given in Table IV.

3. Units, Constants, and Uncertainties. The values for heats of combustion which are reported in this memorandum are based on the heat of combustion of United States Bureau of Standards Sample 39-f of benzoic acid as 26.4294 ± 2.6 international joules per gram mass in vacuo when the sample is burned under the standardized conditions of the bomb process (12,28).

The atomic weights of hydrogen, oxygen, carbon, and nitrogen were accepted as 1.0080, 16.0000, 12.010, and 14.008, respectively, from the 1941 Table of International Atomic Weights (3).

The conventional thermochemical calorie, as used in this report, is defined as:

$$1 \text{ calorie} = 4.1833 \text{ international joules (17).}$$

The value of the gas constant, R, was taken as 8.3128 ± 0.0008 international joules per gram-mols per degree Kelvin (19).

Limits of uncertainty were assigned to the reported values for heats of combustion and formation, using twice the estimated standard deviation of the average as the uncertainty limit (23). Insofar as they were significant, the standard deviations associated with the accepted constants and other constant factors entering into the reduction of the data were incorporated into the final overall standard deviation associated with the quantity being evaluated. Estimated one-percent uncertainty limits were assigned to the values given for latent heats of vaporization.

Accepted experiments included all except those in which a gross error had obviously been made, or in which an extraordinarily large deviation could be accounted for by purely physical means.

C. EXPERIMENTAL APPARATUS

1. The Calorimeter. Details of the calorimetric system used in the heat of combustion investigations are shown in Figures 1-4. The jacket (Figures 1 and 3) was a standard Emerson, No. 23B, Daniels jacket modified to provide for stirring of the jacket water. Water in the jacket was heated by passing a current of about five amperes at 60 volts intermittently through the water, using the circuit shown in Figure 2a to control the quantity of heat generated.

The bomb, shown in Figure 4, was a standard Parr No. 1101 nickel-chromium alloy oxygen combustion bomb with a double valve, self-sealing head.

The difference in temperature of the jacket and the water in the calorimeter can was indicated by means of a multiple-junction, differential, copper-constantan thermopile with leads to a Rubicon No. 3401-H galvanometer. As shown in Figure 1, one set of junctions were immersed in the calorimeter water, the other set in the jacket water. Each of the thermopiles contained 32 separate junctions and had a resistance of 59 ohms. The galvanometer was deflected about four millimeters per hundredth of a degree Centigrade temperature difference between jacket and calorimeter.

Temperatures changes in the calorimeter were measured by means of a Peckman-type differential thermometer calibrated by the Bureau of Standards. The temperature of the air surrounding the calorimeter was measured by a calibrated mercury thermometer.

The firing unit (Figure 2b) was designed to enable a current of three amperes at 14 volts to be impressed across the fuse wire (attached to the bomb electrodes) for a measured time interval. Standard Parr, iron fuse wire was used in all experiments.

- A. CONSTANT LEVEL CONTROL
- B. CALORIMETER STIRRER
- C. BECKMAN THERMOMETER
- D. CALORIMETER
- E. JACKET
- F. JACKET STIRRER
- G. BOMB
- H. WATER INLET
- J. THERMEL LEADS
- K. FIRING LEADS
- L. HEATER LEADS

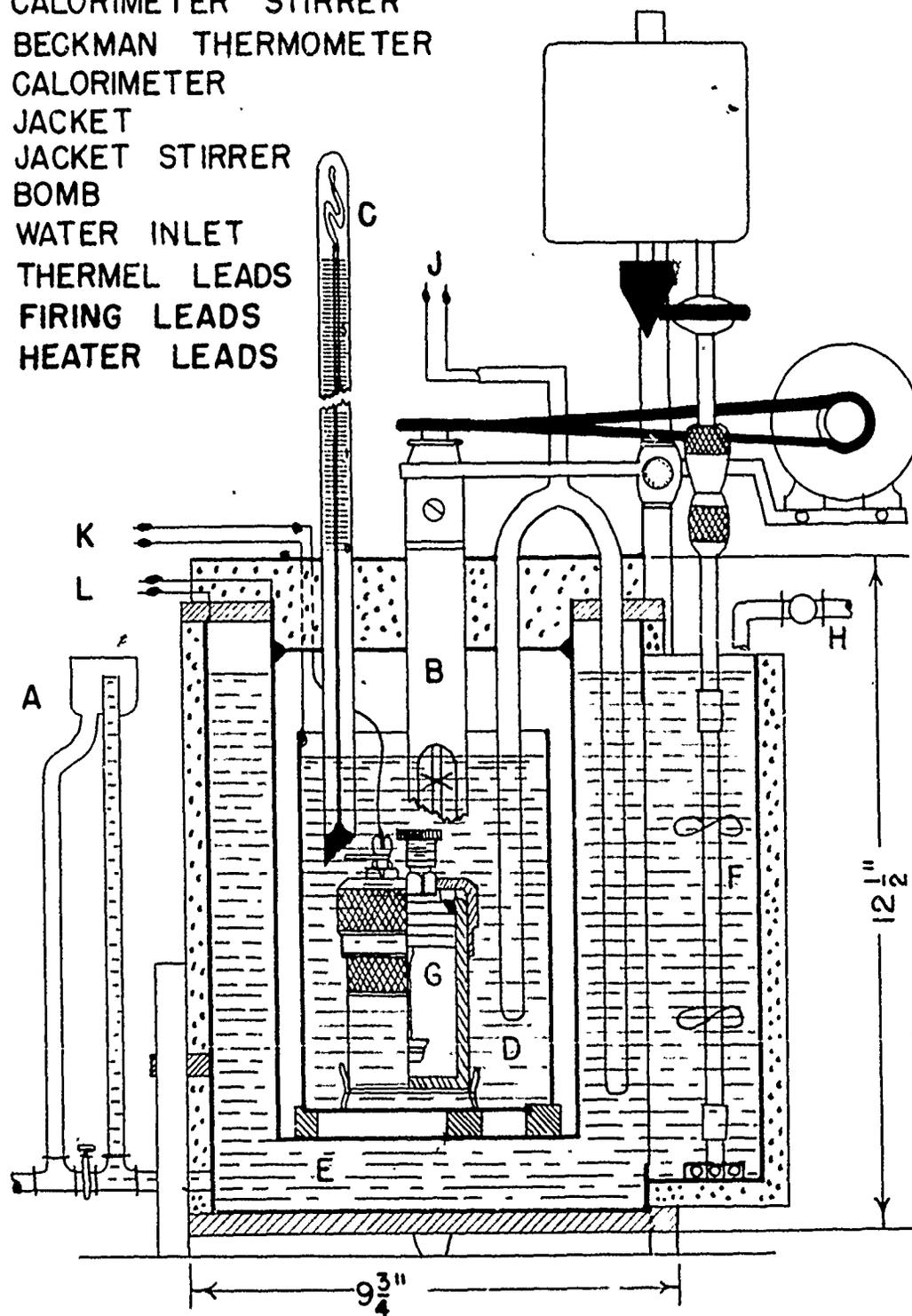


FIG. 1. SCHEMATIC DIAGRAM OF APPARATUS

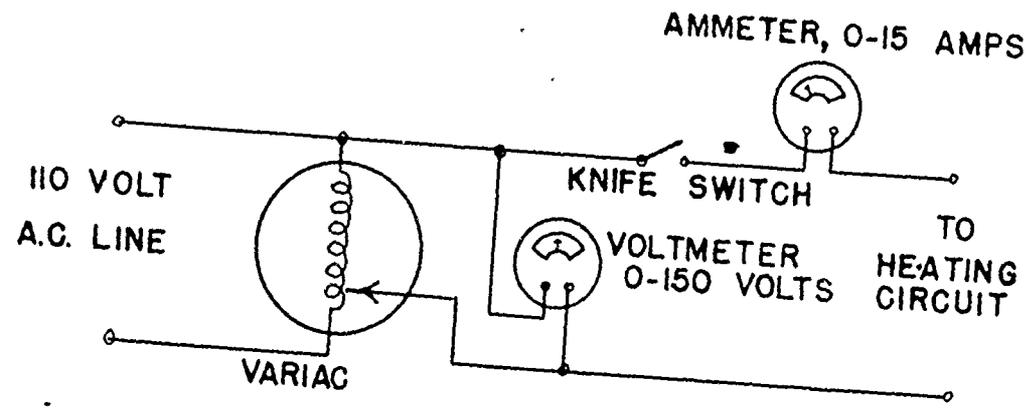


FIG. 2a. WIRING DIAGRAM FOR HEATER

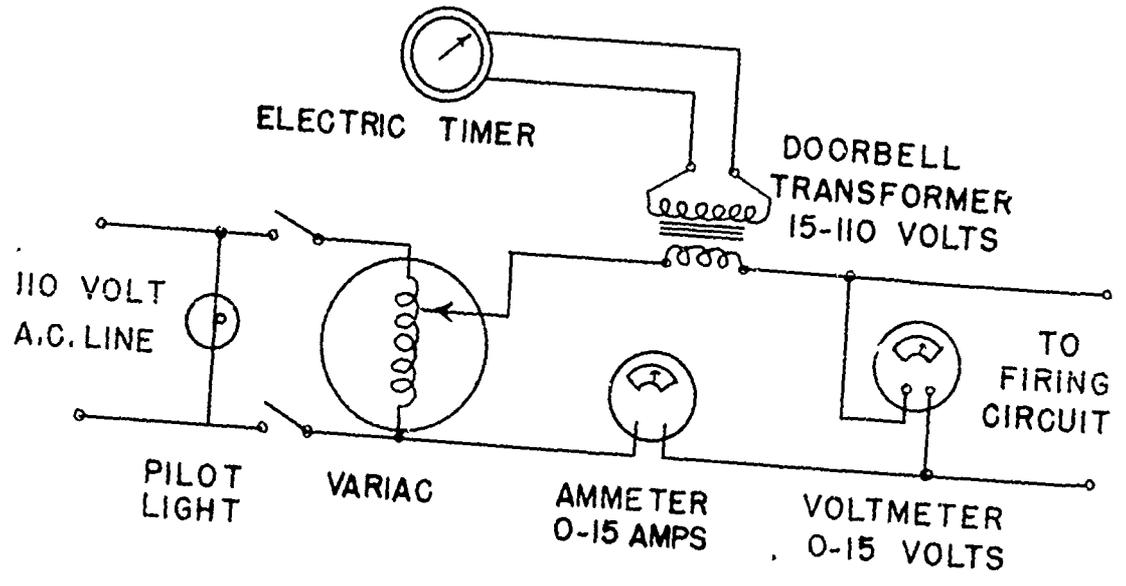


FIG. 2b. WIRING DIAGRAM FOR FIRING CIRCUIT

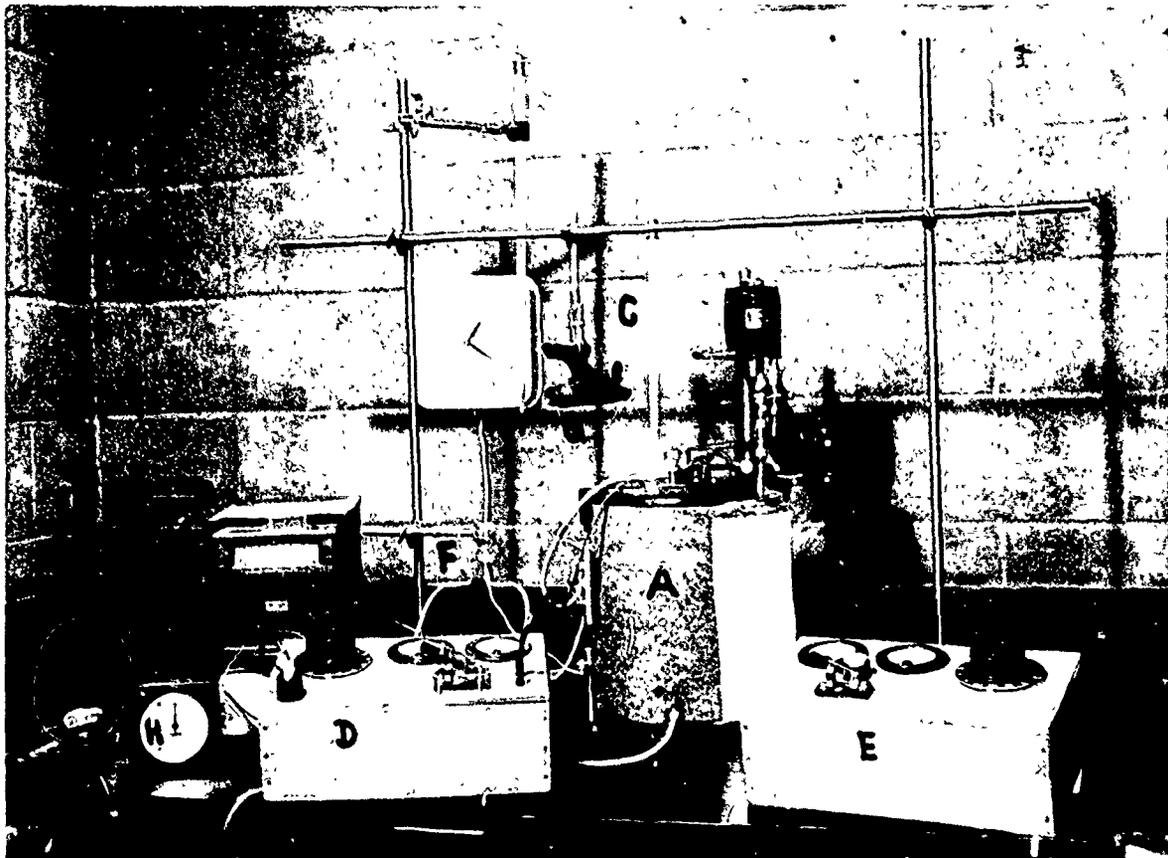


Fig. 3 - The Calorimeter Assembly

- A. Calorimeter
- B. Galvanometer
- C. Thermometer
- D. Firing Controls
- E. Heater Controls
- F. Constant Level Controller
- G. Telescope
- H. Electric Stopwatch

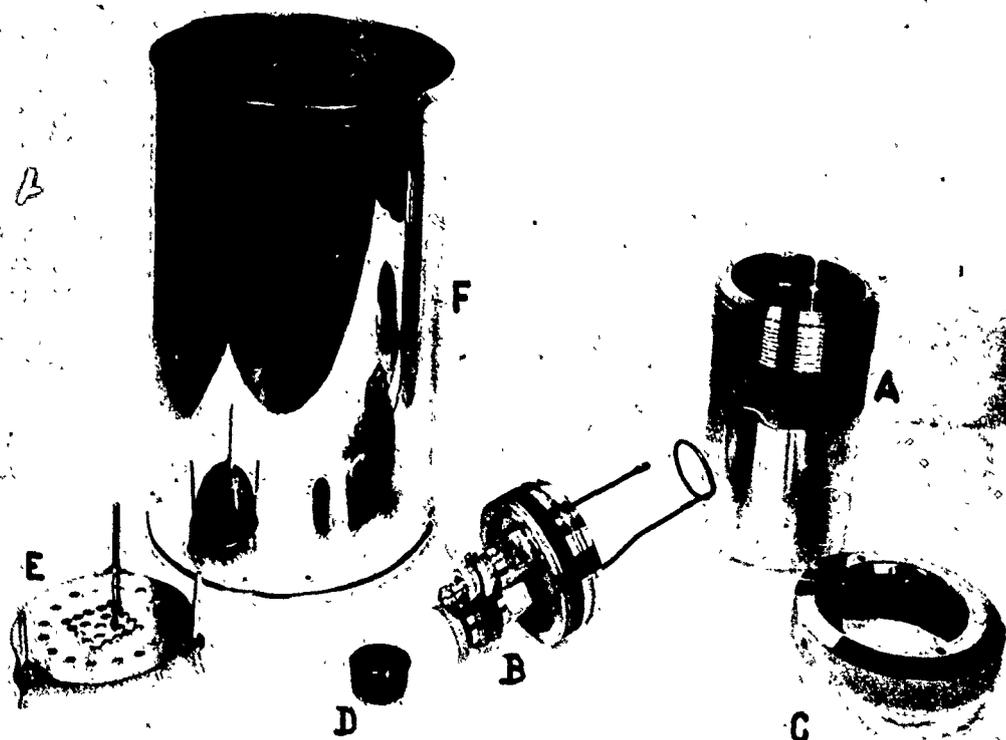


Fig. 4 - Bomb and Calorimeter Can

- A. Bomb Cylinder
- B. Bomb Head
- C. Screw Cap
- D. Combustion Cup
- E. Bomb Support Bracket
- F. Calorimeter Can

2. Vapor Pressure Apparatus. The apparatus used for measurements of vapor pressure was identical with that described by Pickett (20) with the exception of the modifications described below.

Temperatures were measured by calibrated mercury thermometers. Magnifying lenses were used in estimating the temperatures to within 0.01°C in the range from $0-50^{\circ}\text{C}$, and to within 0.1°C in the range from $50-150^{\circ}\text{C}$. The thermometer bulbs were covered with cloth wicks, and were immersed in the sample so that the wick dipped into the liquid while the bulb itself was surrounded by vapor.

In order to initiate vaporization of the sample when the total pressure in the system approached the vapor pressure of the sample, provisions were made to introduce dry nitrogen just below the surface of the sample through a small capillary tube.

A Zimmerli gage was used to measure the pressure in the system. The difference in the height of mercury in the two working legs of the gage was estimated to within 0.01 mm by means of a cathetometer.

RESULTS

A. HEATS OF COMBUSTION AND FORMATION

The heats of combustion determined experimentally in this investigation are shown in Table II. Statistical properties (1) of the experimental data are summarized in Table III. Heats of formation have been calculated (13) from the standard heats of combustion, ΔH_T° , using 94.052 kcal/mol as the standard heat of formation of gaseous carbon dioxide (21) and 68.317 kcal/mol as the standard heat of formation of liquid water (27).

B. VAPOR PRESSURES AND LATENT HEATS OF VAPORIZATION

Selected points from the experimentally determined vapor pressure-temperature curve are listed in Table IV. The precision of these data is better than five parts in one thousand, and the experimental values compare excellently with the data published by Hodge (8).

Values of the latent heats of vaporization at 25°C, calculated from the experimental vapor pressure data, are tabulated in Table V. Estimated one-percent uncertainty limits have been assigned to the calculated values.

C. TESTS OF PUBLISHED CORRELATIONS

Table VI compares the experimental values for heats of combustion, ΔH_T° , with the values predicted by three generalized correlations of heats of combustion or formation with chemical structure.

The correlation by Kharasch (12), developed for the estimation of heats of combustion of organic liquids, has been used without supplementary data except in the case of solid 2,2-dinitropropane, where it has been necessary to add a correction for the heat of fusion of the compound. The heat of fusion value used was 1.03 kcal/mol, approximated

from data obtained during the time-temperature freezing points tests for purity.

The method developed by Anderson, Beyer, and Watson (2), correlating heats of formation in the ideal gaseous state with chemical structure, necessitates the use of experimental or estimated latent heats in converting the results to heats of combustion of the compounds in their ordinary states. Latent heats determined in the present investigation have been used in applying the necessary corrections.

The values of ΔE_b estimated by the method developed in the Arthur D. Little, Inc. "Report on Study of Pure Explosive Compounds (Part II)", have been corrected to standard heats of combustion, ΔH_r° , by addition of terms to allow for the changes in the pressure-volume products during the combustions (13). ΔE_b has been assumed equal to ΔE_r° since the percentage error is small enough to be negligible.

D. CORRELATION OF HEAT OF COMBUSTION WITH OXYGEN BALANCE

Figure 5, plotted from data in Table VII, shows the essentially linear relationship between oxygen balance (as defined in Section II) and the heat of combustion under bomb conditions, ΔE_b . The points are numbered to correspond with the nomenclature of Table VII.

E. CORRELATIONS OF EXPLOSIVE PROPERTIES

Figures 6, 7, and 8, compiled from the data of Table VII, have been constructed in the manner used in the Little Report (14) to show the effects of oxygen balance and heat of combustion on the explosive properties of the compounds. The broken lines in the figures indicate extrapolated portions of the curves. The points are numbered to correspond with the nomenclature of Table VII.

TABLE II
SUMMARY OF RESULTS
HEATS OF COMBUSTION AND FORMATION OF THE NITROPARAFFINS

Compound	Standard State	$-\Delta E_b$ kcal/mol	$-\Delta E_f^0$ kcal/mol	$-\Delta H_f^0$ kcal/mol	ΔH_f kcal/mol
Nitromethane	liquid	175.87 ± 0.18	175.70 ± 0.18	175.25 ± 0.18	-21.28 ± 0.18
Nitroethane	liquid	325.79 ± 0.30	325.57 ± 0.30	325.42 ± 0.30	-33.48 ± 0.31
1-Nitropropane	liquid	481.33 ± 0.61	481.07 ± 0.61	481.22 ± 0.61	-40.05 ± 0.61
2-Nitropropane	liquid	477.60 ± 0.17	477.34 ± 0.17	477.49 ± 0.17	-43.78 ± 0.17
1-Nitrobutane	liquid	637.47 ± 0.32	637.16 ± 0.32	637.61 ± 0.32	-46.03 ± 0.32
2-Nitrobutane	liquid	633.89 ± 0.36	633.58 ± 0.36	634.02 ± 0.36	-49.61 ± 0.36
1,1-Dinitropropane	liquid	447.65 ± 0.33	447.22 ± 0.33	446.33 ± 0.33	-40.78 ± 0.34
1,3-Dinitropropane	liquid	434.92 ± 0.33	434.48 ± 0.33	433.59 ± 0.33	-53.51 ± 0.33
2,2-Dinitropropane	solid	443.56 ± 0.64	443.12 ± 0.64	442.24 ± 0.64	-44.87 ± 0.64
Trinitromethane	liquid ^a	112.62	112.10	109.58	+12.63

a Only one experiment was performed.

TABLE III
 STATISTICAL PROPERTIES OF EXPERIMENTAL DATA ON
 HEATS OF COMBUSTION

No.	Compound	Number of Runs	\bar{X} cal/g	σ' cal/g	$\sigma_{\bar{x}}$ cal/g	$\sigma_{\bar{x}}$ cal/g
1	Nitromethane	3	2881.10	2.60	1.50	2.00
2	Nitroethane	4	4339.88	4.05	2.03	4.05
3	1-Nitropropane	4	5402.54	6.81	3.40	6.81
4	2-Nitropropane	5	5360.63	2.11	0.94	1.88
5	1-Nitrobutane	4	6181.86	3.12	1.56	3.12
6	2-Nitrobutane	4	6147.07	3.51	1.76	3.51
7	1,1-Dinitropropane	4	3338.34	2.49	1.25	2.49
8	1,3-Dinitropropane	3	3243.38	2.09	1.21	2.42
9	2,2-Dinitropropane	5	3307.84	5.34	2.39	4.78
12	Trinitromethane	1	745.6	-	-	-

\bar{X} = Statistical average of experimental values
 σ' = Estimated standard deviation of the population
 $\sigma_{\bar{x}}$ = Estimated standard deviation of the average

TABLE IV
VAPOR PRESSURES OF THE NITROPARAFFINS

Temperature °C	Vapor Pressure, millimeters of mercury						
	Nitromethane	Nitroethane	2-Nitropropane	1-Nitropropane	2-Nitrobutane	1-Nitrobutane	1,1-Dinitropropane
10	16.12	8.52	7.05	3.96	2.79	1.23	-
20	27.89	15.65	12.99	7.52	5.48	2.50	-
25	36.26	20.89	17.27	10.00	7.46	3.50	-
30	46.67	27.41	22.65	13.48	10.01	4.82	-
40	75.21	46.20	38.11	23.24	17.29	8.85	-
50	117.1	74.55	61.32	38.41	28.63	15.49	1.62
60	178.2	113.2	95.22	61.17	46.18	26.00	3.27
70	262.7	173.9	143.6	94.32	71.67	42.08	6.37
80	377.7	254.2	211.0	140.9	106.2	65.58	11.10
90	530.2	361.1	299.1	204.5	158.8	99.5	18.7
100	730.4	499.4	416.4	289.5	228.1	145.8	30.50
110	-	676.6	564.2	401.2	318.8	207.1	48.88
120	-	-	-	545.1	436.5	292.5	-
130	-	-	-	728.2	584.1	399.4	-
140	-	-	-	-	760.0	533.8	-
150	-	-	-	-	-	696.0	-

TABLE V

LATENT HEATS OF VAPORIZATION OF THE NITROPARAFFINS

Compound	Latent Heat of Vaporization at 25°C kcal/mol
Nitromethane	9.09 ± 0.09
Nitroethane	9.94 ± 0.10
1-Nitropropane	10.37 ± 0.10
2-Nitropropane	9.88 ± 0.10
1-Nitrobutane	11.61 ± 0.12
2-Nitrobutane	10.48 ± 0.10
1,1-Dinitropropane	14.93 ± 0.15

TABLE VI

COMPARISON OF EXPERIMENTAL HEATS OF COMBUSTION
WITH VALUES PREDICTED BY SEVERAL GENERALIZED CORRELATIONS

Compound	Standard State	Standard Heat of Combustion at 25°C, - ΔH_f° kcal/mol				Little ^c
		Experimental	Kharasch	Anderson et al. ^a		
Nitromethane	liquid	175.3	169.5	168.5	167.7	
Nitroethane	liquid	325.4	325.9	325.6	322.7	
1-Nitropropane	liquid	481.2	482.4	482.3	477.5	
2-Nitropropane	liquid	477.5	482.4	481.4	477.5	
1-Nitrobutane	liquid	637.6	638.9	638.2	632.5	
2-Nitrobutane	liquid	634.0	638.9	637.7	632.5	
1,1-Dinitropropane	liquid	446.3	443.2	438.0	434.8	
1,3-Dinitropropane	liquid	433.6	443.2	-	434.8	
2,2-Dinitropropane	solid	442.2	442.2 ^b	-	434.8	
Trinitromethane	liquid	109.6	91.1	-	82.4	
Average deviation from experimental value, % ^d			0.95	1.08	1.28	

a Values corrected from ideal gas state using best available data.

b Value corrected from liquid state using best available data.

c Values corrected from - ΔE_f° to - ΔH_f° .

d Excluding trinitromethane.

TABLE VII
EXPLOSIVE PROPERTIES OF THE NITROPARAFFINS
(Calculated from Experimental Data)

.No.	Compound	Oxygen Balance %	- ΔE_e		- ΔE_b kcal/kg	Power % of TNT
			kcal/mol	kcal/kg		
1	Nitromethane	-39.3	63.1	1034	2881	178.0
2	Nitroethane	-95.8	18.8	250	4340	58.2
3	1-Nitropropane	-134.6	11.4	128	5403	30.1
4	2-Nitropropane	-134.6	7.7	86.4	5361	20.4
5	1-Nitrobutane	-163.0	4.7	45.5	6182	10.8
6	2-Nitrobutane	-163.0	1.1	10.7	6147	2.5
7	1,1-Dinitropropane	-59.6	96.3	718	3338	131.1
8	1,3-Dinitropropane	-59.6	83.5	622	3243	113.8
9	2,2-Dinitropropane	-59.6	92.2	687	3308	125.6
10	2,3-Dimethyl-2,3-dinitrobutane	-127.1	27.6	157	5110	34.3
11	2,2-Dimethyl-1,3-dinitropropane	-108.5	38.5	237	4606	51.3
12	Trinitromethane	-37.1	107.3	711	746	78.4
13	1,1,1-Trinitroethane	-4.9	277.6	1680	1777	187.0
14	2-Methyl-2,3,3-trinitrobutane	-65.6	110.7	524	3381	99.5
15	2-Methyl-2,3,3-trinitropentane	-83.2	58.1	263	3944	54.0
16	Tetranitromethane	-49.0	106.2	543	543	58.1
17	2,2,3,3-Tetranitrobutane	-20.2	350.3	1470	2460	194.5

FIG. 5
 HEATS OF COMBUSTION VS. OXYGEN BALANCE
 FOR THE NITROPARAFFINS

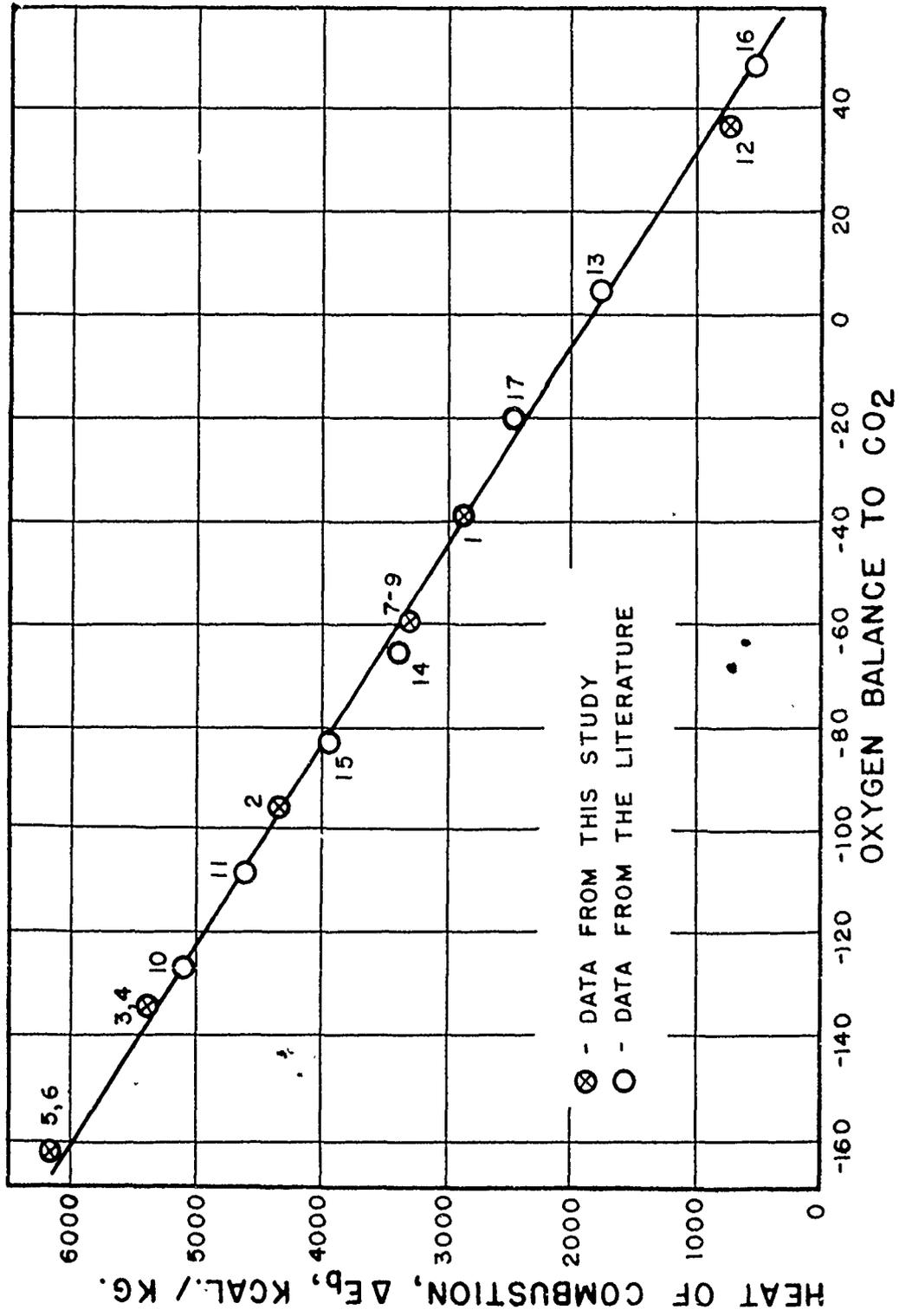
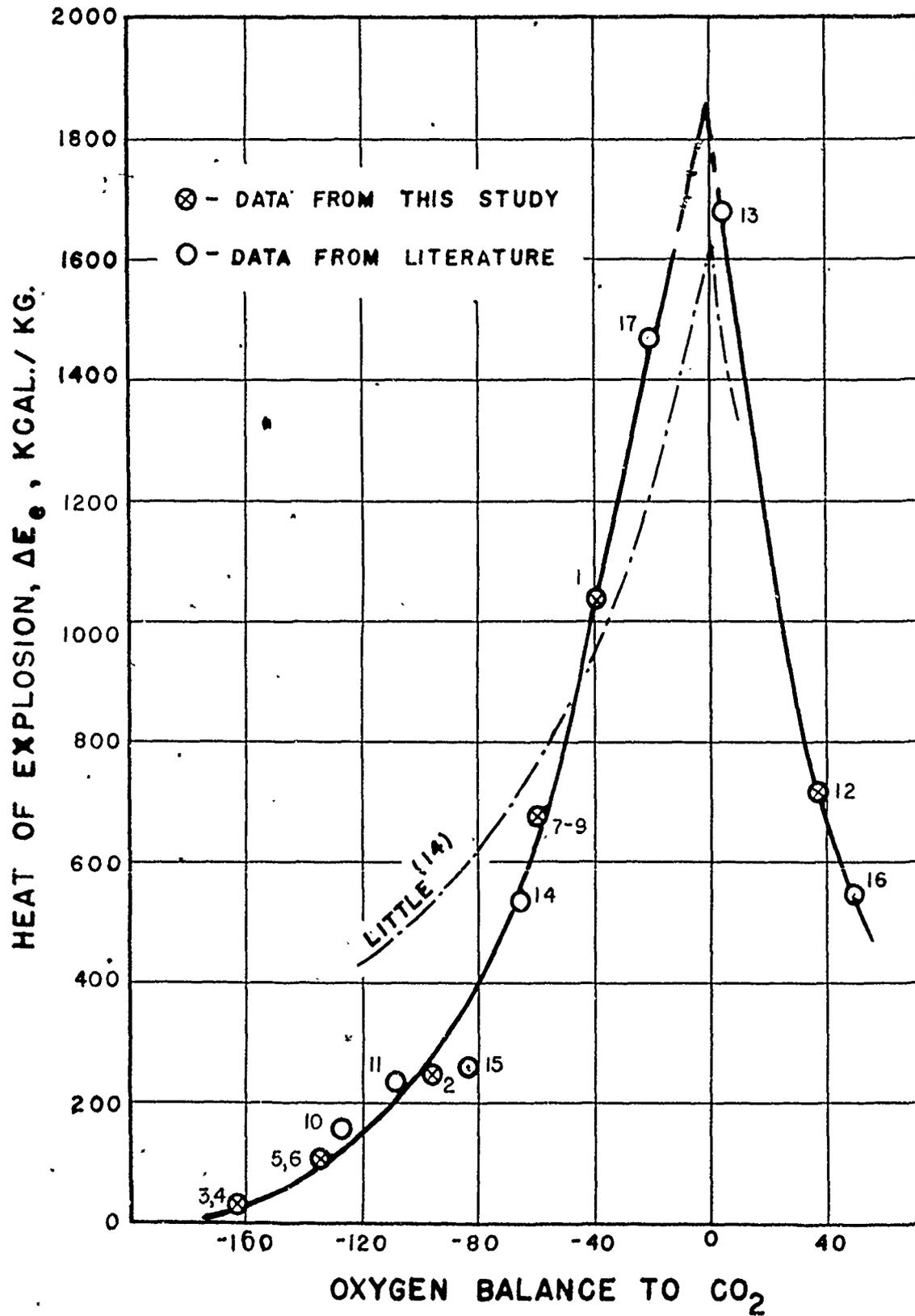


FIG. 6
HEAT OF EXPLOSION VS. OXYGEN BALANCE
FOR THE NITROPARAFFINS



ERRATA

The points for trinitromethane (No. 12) in Figures 7 and 8 are incorrectly plotted.

In Figure 7, the coordinates should be:

$$\text{O.B.} = + 37.1$$

$$P = 78.4$$

In Figure 8, the coordinates should be:

$$- E_b = 746$$

$$P = 78.4$$

These changes do not alter the conclusions that are drawn from these data.

FIG. 7
EXPLOSIVE POWER VS. OXYGEN BALANCE FOR THE NITROPARAFFINS

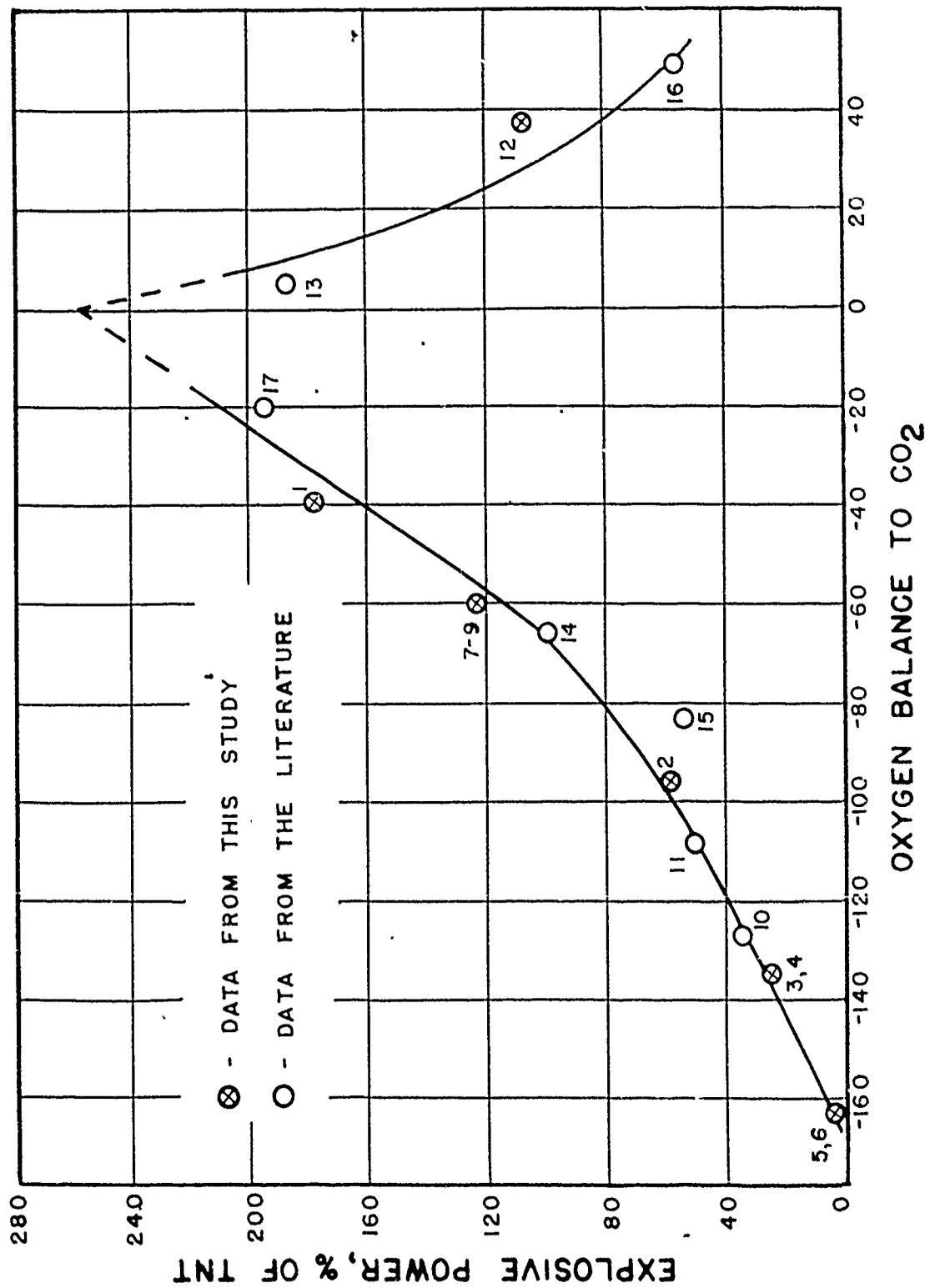
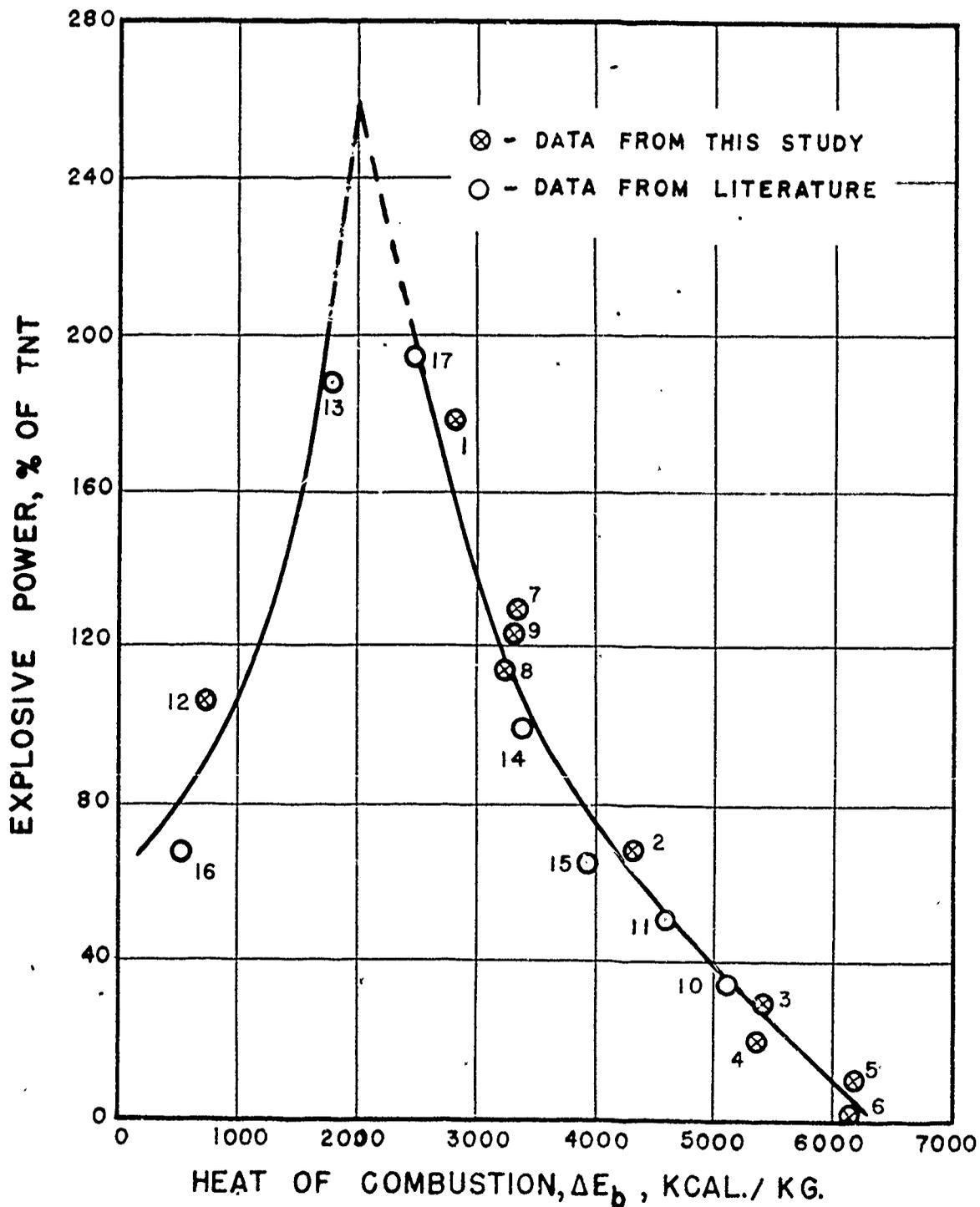


FIG. 8
 HEAT OF COMBUSTION VS. EXPLOSIVE POWER
 FOR THE NITROPARAFFINS



DISCUSSION OF RESULTS

A. EXPERIMENTAL MEASUREMENTS

Heats of combustion values as recorded in the literature to which the present experimental values may be compared are those for nitromethane (4), nitroethane (4), 1-nitropropane (26), and 2,2-dinitropropane (14). The value for nitromethane as determined in this work is about 5 kcal/mol higher than the average of the three available literature values. This difference is possibly due to impurities in the samples used by the earlier investigators (1890-1910). No reason can be advanced why the value of 2,2-dinitropropane as determined in this investigation is 16 kcal/mol higher than the value cited in the Little Report because the actual source of those data is unknown to the writers. The experimental values for the other two compounds compare well with the literature values.

The vapor pressure measurements of this investigation resulted in values which checked almost exactly with the values published by Hodge (8) for all of the compounds, except 1,1-dinitropropane, for which vapor pressure measurements were made. The calculated value for the latent heat of vaporization of nitromethane is about 0.6 percent lower than the value reported by Jones and Giaque (11); the calculated value for nitroethane checks very well with the value reported by Berthelot and Matignon (4). The fact that values of latent heats calculated from vapor pressure measurements seem to differ significantly from true experimental values may indicate that the deviations can be traced partly to the difficulty of obtaining the slope of the vapor pressure curves to more than three significant figures.

B. CORRELATIONS OF HEATS OF COMBUSTION

1. Methods of Group Contributions. The results of the three empirical methods of estimating heats of combustion are shown in Table VI for comparison with the experimentally determined values. The agreement between the values determined from the empirical methods and the experimental values is as would be expected after considering the empirical nature of the methods.

The method of Kharasch (12) is designed to correlate heats of combustion of organic compounds in the liquid state at 18°C. Assuming negligible change in ΔH_f° from 18°C to 25°C, the only auxiliary data necessary in constructing the table was in the case of solid 2,2-dinitropropane, where the heat of fusion had to be considered. It should be noted that the method makes no allowance for differences in the heats of combustion of isomers; however, since the average values for the nitro-paraffin isomers have a maximum deviation from the individual values of only about 1.7 percent, with an average deviation of about 0.8 percent, this is no great disadvantage when an error of estimate of a few percent is allowable.

Although the method devised by Anderson, Beyer, and Watson (2) appears to differentiate between isomers in the right direction, it, like the bond energy correlations of Pauling (18), correlates heat effects in the ideal gaseous state, thus necessitating the estimation of latent heats in order to convert the values to ordinary states. Errors in the measurement of these latter quantities will tend to increase the error in the estimate of the final heat of combustion.

Since heats of vaporization and fusion are included in the calculations leading to tabulated values for bond and group contributions in the

Little Report (14), it might be expected that the error inherent in the method there reported would be slightly greater than the error in the other two methods. Actually, in most cases, the latent heat terms are small enough in comparison with the final heat of combustion values that reasonable errors in the former have a relatively small net effect on the estimated values of the latter.

Where errors of estimate on the order of one percent are allowable, the method advanced in the Little Report is probably the most convenient of the three methods since it requires fewer numerical manipulations.

2. Heats of Combustion from Oxygen Balance. Inspection of the relationship in Figure 5 between heat of combustion, ΔE_b , and oxygen balance indicates that an apparently linear relationship exists over the range of compounds included in the correlation. As oxygen balance does not differentiate between isomers, heats of combustion of isomers were averaged before plotting the data of Table VI.

An equation of the form:

$$- \Delta E_b = (1792.3) - (26.418) (\text{O.B.}) \quad \dots\dots\dots (3)$$

fits the relationship shown in Figure 5 with an average deviation between experimental and calculated values of 2.1 percent of the experimental value. Since the value of ΔE_b for trinitromethane is based on only one experimental measurement using a sample containing 4.4 percent of an unidentified impurity, it has been excluded in the calculation of the constants of the equation.

Equation (3) may be placed in the more convenient form:

$$- \Delta E_b = 1792.3 + 42269 \left(\frac{2x + 1/2 y - z}{M} \right) \quad \dots\dots\dots (4)$$

where

ΔE_b = the heat of combustion under bomb conditions in kcal/kg

x = the number of carbon atoms in the molecule

y = the number of hydrogen atoms in the molecule

z = the number of oxygen atoms in the molecule

M = the molecular weight of the nitroparaffin

Since ΔE_b and ΔE_p are not significantly different compared with the error in the equation itself, the two terms may be assumed identical for purposes of estimation, and ΔH_p^0 may be calculated from the estimated value of ΔE_b by use of the relationship (13):

$$\Delta H_p^0 = \Delta E_b^i + \Delta nRT \quad \dots\dots\dots (5)$$

where

ΔH_p^0 = the standard heat of combustion at constant pressure, kcal/mol.

ΔE_b^i = ΔE_b in units of kcal/mol

Δn = the mols of gaseous products less the mols of gaseous reactants, per mol of nitroparaffin

R = the gas constant, kcal/mol, °K

T = the absolute temperature, °K

When referring the reaction to 25°C, the above equation takes the form:

$$\Delta H_p^0 = \Delta E_b^i + 0.5928\Delta n \quad \dots\dots\dots (6)$$

It should be recalled that both ΔE_b and ΔH_p^0 are inherently negative for the cases under consideration.

C. CORRELATIONS OF EXPLOSIVE PROPERTIES

1. Heat of Explosion vs. Oxygen Balance. Figure 6, constructed from the data of Table VII, has been plotted for comparison of the experi-

mental relationship, between ΔE_o and oxygen balance, with the relationship predicted by the idealized curve of Figure 33, p. 220 of the Little Report (14). The "idealized curve", correlating heats of explosion of all organic explosives for which data were available, although following the same general pattern as the present relationship, deviates appreciably from the present data on the nitroparaffins. Instead of a maximum heat of explosion of about 1630 kcal/kg predicted by the Little curve, it appears that a maximum of about 1850 kcal/kg would be attained by a nitroparaffin in zero oxygen balance. It should be recalled, as pointed out in the Little Report, that the indication of a maximum heat of explosion at zero oxygen balance is not strictly correct due to the assumptions made in the calculations of ΔE_o . Other investigators have concluded that "while the zero point may not be the exact maximum point, it will be close to it, and (the maximum) will not be either at very low balances or in the region of positive balance". Little (14) states that Roth has estimated that the maximum occurs at an oxygen balance of about -3.

2. Correlations of Explosive Power. Figures 7 and 8, constructed from the data of Table VII, have been modified after Figure 37, p. 253 of the Little Report (14). Explosive power has been calculated as described in this memorandum in Item 7, Definition of Terms. Keeping in mind the limitation of the oxygen balance-heat of explosion relationship discussed directly above, it appears that the maximum explosive power to be expected of a nitroparaffin is about 260 percent of that for TNT, and that this power will occur with a nitroparaffin having a heat of combustion, ΔE_b , of about -1800 kcal/kg.

CONCLUSIONS

1. The heats of combustion of six mononitroparaffins and three dinitroparaffins, including three sets of isomers, have been experimentally determined with an average precision of one part in one thousand. A single experimental value has been obtained for the heat of combustion of trinitromethane (Table II).

2. Latent heats of vaporization of six mononitroparaffins and one dinitroparaffin have been calculated (Table V), from experimental vapor pressure measurements. The estimated error in the latent heats (Table IV) is one percent.

3. Three methods of estimating the heats of combustion of organic compounds from knowledge of their chemical structures have been shown to be applicable to the nitroparaffins investigated with an error of estimate of about one percent (Table VI). Although the method of Kharasch (12) gives the smallest error estimate, and the method of Anderson, Beyer, and Watson (2) is the only one to differentiate between the heats of combustion of isomers, the method proposed in the Little Report (14) requires fewer numerical calculations and gives results which do not differ significantly from those given by the other methods when accuracy on the order of a few percent is allowable.

4. The heats of combustion of the nitroparaffins have been shown to be a linear function of the oxygen balance of the molecules (Figure 5), and an equation has been derived which relates these two variables with an average error of estimate of about two percent.

5. The correlation of heat of explosion with oxygen balance that is developed in the Little Report has been varified and extended to apply to the nitroparaffin series with much better accuracy (Figure 6).

There are indications that the maximum explosive power to be expected of a nitroparaffin will be about 260 percent of that of TNT (Figure 7), and that this power will occur with a nitroparaffin having a heat of combustion of about -1800 kilocalories per kilogram (Figure 8) and an oxygen balance close to zero.

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