THE HEAT OF COMBUSTION

OF

CYANOGEN

By

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I. INTRODUCTION

In modern chemical thermodynamics it is possible to evaluate the entropies of substances by the application of the third law to measurements of heat capacity, heats of fusion and transition, etc., down to low temperatures, as well as from statistical calculations, utilizing spectroscopic and other molecular data. Combination of these values of entropy with experimentally determined heats of formation will yield values for the free energies of formation of many substances on which it is not possible to make equilibrium measurements. This new source of free-energy data places a great demand upon accurate thermochemical data, as was recently pointed out by Rossini [1].[1]

The existing data on the heat of combustion of cyanogen are those of Dulong in 1838 [2], Berthelot in 1879 [3], Thomsen in 1886 [4], von Wartenberg and Schütza in 1933 [5], and McMorris and Badger in 1933 [6]. These investigations yield the values 275, 264, 259.4, 261.3, and 251.4 kilocalories per mole, respectively (see Section VII of this paper).

Because of the discordance in these values, a determination of the heat of cyanogen was undertaken in the Thermochemical Laboratory of the National Bureau of Standards.

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[1]The figures in brackets throughout the text designate the literature references listed at the end of this paper.

II. UNITS OF ENERGY AND MOLECULAR WEIGHTS

The unit of energy used in this investigation is the
NBS international joule, which is based on standards of the
international ohm, the international volt, and the mean
solar second, as maintained at the National Bureau of
Standards.

The thermochemical values reported from the Thermo-
chemical Laboratory of the National Bureau of Standards are
given in international joules, the unit in which they were
measured, and, because the calorie is favored by many as the
name of the unit of energy, these data are also expressed in
terms of a conventional calorie which is defined by means of
the relation

4.1833 international joules = 1 calorie

This relation is that used by practically all American
laboratories at this time [25].

All molecular weights used in this paper were calcu-
lated from the International Atomic Weights for 1940 [7].

III.   METHOD AND APPARATUS

The calorimetric method employed in the present
investigation has been described by Rossini [8, 1], and
the method of evaluation of the uncertainty of the results
has been discussed by Rossini and Deming [9]. A complete
description of the apparatus, with subsequent improvements
or refinements, is to be found in certain papers reporting
earlier investigations of the Thermochemical Laboratory of
the National Bureau of Standards [8, 10, 11, 12]. Since
these reports are complete, only a brief description of the
method and apparatus will be given here.

In these measurements the thermal energy liberated by
a measured amount of a given chemical reaction is determined
by direct comparison with an equal, measured quantity of
electrical energy. To accomplish this there is employed a
calorimetric system subject to a definite thermal environ-
ment, and whose essential components are: (1) a measured
mass of water for the absorption of the heat evolved, (2)
a thermometer for measuring changes in the temperature of
the system, (3) a stirring mechanism to facilitate the
attainment of thermal equilibrium in the calorimeter, (4)
a suitable reaction vessel in which the given reaction may
be carried out, and (5) an electrical heating coil connected
with instruments for measuring the energy it evolves in the
calorimeter. By always operating with a calorimetric
system which is standardized for a given investigation, the

quantitative correspondence between the chemical and the electrical energy is obtained by a comparison of the temperature rise observed in two kinds of experiments which are performed. In the first kind of experiment a measured amount of chemical reaction is carried out in the reaction vessel, which brings the system from an initial temperature, t_a, to a final temperature, t_b. In an experiment of the second kind, the same calorimetric system is carried over the same temperature range, t_a to t_b, by means of a measured amount of electrical energy. The power for such an experiment is adjusted so as to produce about the same rate of temperature rise as occurs in a chemical experiment.

The calibration experiments with electrical energy determine a quantity called the energy equivalent of the calorimeter, which is the average energy associated with unit temperature change of the system, when brought from t_a to t_b. The term energy equivalent is preferred [1, 9] instead of the expression "heat capacity" of the calorimeter, with which it is dimensionally equivalent. The objection to this latter designation is that it implies that the heat capacity of the calorimeter may be evaluated by a summation of the heat capacities of its component parts, which is not admissible in precise work; and hence, that the physical boundaries of the calorimetric system are known, a condition difficult to define distinctly. Furthermore, since the function of the thermometric measurements in this method is

essentially to reproduce the initial and final temperatures
of the calorimeter, knowledge of the exact magnitude of a
degree of temperature is not required. The actual tempera-
ture on the Centigrade scale is needed only to determine
the temperature at which the reaction may be said to have
taken place. The most precise measurements of calorimeter
temperatures are usually made with a platinum resistance
thermometer, by which the actual measurements are made in
terms of electrical resistance. The quantitative relation
between resistance and temperature, obtained for a given
instrument by independent calibration, is, in principle,
unnecessary in the computation of the energy equivalent of
the calorimetric system, since to the temperatures t_a and
t_b there correspond, respectively, the unique resistances
R_a and R_b. As a consequence, the value for the energy
equivalent of the calorimeter may be expressed as inter-
national joules per ohm increase in resistance of the given
platinum resistance thermometer [12].

Because of the substitutional character of this method,
systematic errors in the calorimetry tend, in general, to
eliminate themselves, since they affect both kinds of
experiments similarly. Any errors found in the thermochemi-
cal values obtained are to be expected to originate prin-
cipally in the determination of the amount of reaction and
in the measurement of the electrical energy. High precision

is obtained in this method through the use of proper calorimetric technic, and the employment of sensitive measuring devices.

The calorimeter is enclosed by (but in poor thermal contact with) a constant-temperature water jacket which is maintained at a temperature slightly above that of the calorimeter water after the reaction period. This subjects the calorimeter to a definite thermal head at all times during its operation, and Newton's law of cooling may be safely assumed in the calculation of the corrected temperature rise.

In all the calorimetric experiments of this investigation, the jacket temperature was maintained constant at 27.02° C, and the initial and final temperatures of the calorimeter were 23° and 27° C, respectively. In each experiment the observations were divided into three periods. First, over a fore period of 20 minutes, readings of the calorimeter water temperature were made every 4 minutes. Second, during a reaction period of 44 to 48 minutes, electrical energy or combustion energy was supplied to the calorimeter at a rate which brought it to the final temperature in 38 to 42 minutes, leaving a time of 6 minutes for the attainment of equilibrium in the calorimetric system. In this period, observations of the calorimeter water temperature were made every minute, and in the electrical-energy experiments readings of the current and voltage were taken every minute. Third, over an after-period of 20 minutes, readings of the calorimeter water temperature

were made every 4 minutes. Finally, the jacket temperature
was determined with the same thermometer. Separate obser-
vations on the constancy of the jacket temperature showed
that, over the period of time of a given calorimetric experi-
ment, the jacket temperature varied no more than $\pm 0.003°C$.
The substantial identity of the two kinds of experiments,
electrical and combustion, has been graphically demonstrated [8].

The method of determining that part of the temperature
rise in the reaction period which is due to the reaction
energy alone, has been explained previously [13]. In a
discussion of the type of calorimeter used in this investi-
gation, Dickinson [14] showed that, inherently, Newton's law
of cooling applies as long as the temperature difference be-
tween the jacket and the calorimeter is small (here no
greater than $4°$ C). Of greater significance is the con-
sideration that the substitutional nature of the method re-
sults in the cancellation of systematic errors. Hence, a
very accurate calculation of the corrected temperature rise
is unnecessary.

The corrections to be applied to the observed tempera-
ture rise involve in a large measure (1) the flow of energy
from the jacket to the calorimeter, (2) the energy given to
the calorimeter through stirring, and (3) the energy removed
from it due to evaporation of water from the calorimeter can.
The first of these corrections is the Newtonian heat flow,
which is proportional to the temperature difference between
the calorimeter and the jacket. The second correction is

independent of the temperature difference between the
calorimeter and the jacket, and is constant with time.
The third may be substantially expressed as the sum of two
terms; one constant, and one proportional to the temperature
of the calorimeter water (and hence to the negative of the
temperature difference between the calorimeter and the
jacket). The contribution of these effects to the change of
temperature during the fore period (a to b) of 20 minutes,
and during the after period (c to d) of 20 minutes, may be
expressed by the following equations [13]:

$$\underline{u} + \underline{k}(\underline{R}_j - \frac{R_a + R_b}{2}) = \frac{R_b - R_a}{Z_b - Z_a} \tag{1}$$

$$\underline{u} + \underline{k}(\underline{R}_j - \frac{R_c + R_d}{2}) = \frac{R_d - R_c}{Z_d - Z_c} \tag{2}$$

$\underline{R}_j$ is the jacket temperature (constant to ± 0.0003 ohm through-
out an experiment) and $\underline{R}$ (with its appropriate subscript,
designating the time, $\underline{Z}$, of observation) is the temperature
of the calorimeter water expressed in ohms on the platinum
thermometer; $\underline{k}$ is the proportionality factor in ohms per
ohm-minute, for that contribution which is proportional to
the head of temperature (the first correction and part of the
third); and $\underline{u}$ is the net constant contribution in ohms per
minute (the second correction and the constant part of the
third).

During the reaction period, the observed temperature change is $R_o - R_b$, and the contribution of all effects is expressed by the equation:

$$\Delta R_{corr} + u(Z_c - Z_b) + k(R_j - \overline{R}_{b,c})(Z_c - Z_b) = R_c - R_b \qquad (3)$$

The symbols here have the same meaning as above, and also ΔR_{corr} is that part of the temperature rise which is due to the reaction energy alone; while $\overline{R}_{b,c}$ is the average calorimeter temperature during this period, computed from the temperature observations taken every minute, by means of the trapezoidal rule. This calculation is necessary because the relation between temperature and time in the reaction period is not linear.

The corrected temperature change is, then

$$\Delta R_{corr} = (R_c - R_b) - u(Z_c - Z_b) - k(R_j - \overline{R}_{b,c}) \qquad (4)$$

For convenience in the calculations, the last two terms of the right hand member of equation (4) are designated U and K, respectively. The observations in the fore and after period give data which permit the simultaneous solution of equations (1) and (2) to give values for u and k. These, in turn, are used in equation (4) to compute ΔR_{corr}.

In order to correct the slightly varying amounts of water weighed into the calorimeter can to a common mass (that of the standard calorimetric system of the investigation), the heat capacity of water at 25° C was taken as 4.1879 international joules per gram-degree C [15], and was appropriately converted to joules per gram-ohm on the platinum thermometer employed.

In this investigation the calorimeter and other apparatus were the same as used previously in the Thermo-chemical Laboratory [3, 10, 11, 12], and, for burning cyanogen, there was employed the same reaction vessel used in the determination of the heat of formation of water [8].

IV. CHEMICAL PROCEDURE

1. Preparation and Purity of the Materials

(a) Cyanogen.

After a review of the methods for the preparation of
cyanogen, the most direct means of generation appeared to be
the thermal decomposition of silver cyanide to metallic
silver and cyanogen gas. A method similar to that of Cook
and Robinson [16] was used, as described by Ruehrwein and
Giauque [17]. Silver cyanide was precipitated from a satu-
rated aqueous solution of silver nitrate by the addition of
a slight excess of an aqueous solution of potassium cyanide
(78 percent by weight). The silver cyanide was filtered,
washed free of excess cyanide, and dried in an oven at
130° C for 15 hours. The material was a brown powder.

The silver cyanide was transferred to a 3-liter flask
which was placed in an electric furnace. This generating
flask was then sealed to a purifying system which consisted
of a vacuum-jacketed still designed for low-temperature
operation, a differential manometer for measuring the purity
of the cyanogen, suitable collecting bulbs of various
capacities, and a 1-liter brass bottle for the storage of the
purified product.

With all the connections completed, the system was
evacuated to a pressure of 10^{-5} mm. The furnace containing
the reaction vessel was gradually heated to 380° C to decom-
pose the silver cyanide. A virtually even distribution of

temperature in the generating flask was obtained by packing iron pellets around it. The cyanogen was collected by condensation in a receiving bulb refrigerated with a slush composed of a 50-percent mixture of chloroform and carbon tetrachloride cooled by the addition of solid carbon dioxide. (For brevity this is referred to as "carbon dioxide slush.") In all, about 350 ml of liquid cyanogen was collected.

Non-condensible gases were removed from the cyanogen by melting, freezing with carbon dioxide slush, and evacuating. This operation was repeated three times. The cyanogen was then transferred to the still pot.

The still was packed with glass helices, and arranged for low-temperature distillation, in the usual way, by having as an integral part of it a partial condenser at the top. This was formed by a Dewar return from the vacuum jacket (which extended above the column proper) to the ring seal joining it to the center tube. This served as a container in which the refrigerant was placed. Solid carbon dioxide was added to the slush from time to time in the course of the distillation in order to maintain the temperature of the condenser constant, at -24.00° C. The cyanogen in the still was boiled for 2 hours with total reflux of the material to the column, and with a rate of liquid return to the pot of about 5 ml per minute (adjusted by varying the energy input to the still pot). The vapor pressure of cyanogen at -24° C is about 650 mm of mercury. The actual distillation was then

carried out with the liquid return rate kept constant, and
the take-off rate set at about 30 ml per hour, giving a re-
flux ratio of about 10 to 1.

By distillation in this manner, the material was divided
into the following fractions: I, 50 ml; II, 5 ml; III,
120 ml; IV, 5 ml; V, 120 ml, VI, 5 ml; and VII, a residue of
about 45 ml. The fore cut, fraction I, and the residue,
fraction VII, were discarded. The 5-ml fractions, II, IV, and
VI, constituted the material to be used for differential vapor
pressure measurements, in order to determine the purity of the
240-ml of material in fractions III and V, which constituted
the desired product of this purification process.

The purity of the cyanogen was determined by means of
differential vapor-pressure measurements on the 5-ml fractions
collected for this purpose, according to the method of
Shepherd [18], but not using the micrometric manometer-read-
ing devices used by him. For this purity test, an isothermal
distillation is carried out. The vapor pressure of a small
portion of the distillate, collected near the beginning of
the distillation, is compared differentially with that of an
equal fraction taken at the middle, and towards the end of the
distillation. The difference in composition of any two
fractions may be expressed by applying Raoult's law. Let $\underline{A}$
and $\underline{B}$ identify the members of a two-component system com-
prising the fraction, $\underline{p}_A^o$ and $\underline{p}_B^o$ their respective vapor
pressures in the pure state, and $\underline{x}_A$ and $\underline{x}_B$ their mole

fractions in a given mixture. Then, if p is the total vapor pressure of the mixture, by Raoult's law,

$$p = p_A^o x_A + p_B^o x_B \qquad (5)$$

Since $x_A = 1 - x_B$,

$$p = p_A^o + x_B(p_B^o - p_A^o) \qquad (6)$$

This condition applies to each fraction, and identifying any two under comparison by the prime and second superscript,

$$p' = p_A^o + x_B'(p_B^o - p_A^o) \qquad (7)$$

$$p'' = p_A^o + x_B''(p_B^o - p_A^o) \qquad (8)$$

Subtracting equation (8) from equation (7)

$$p' - p'' = (x_B' - x_B'')(p_B^o - p_A^o) \qquad (9)$$

The quantity $p' - p''$ is the measured difference in vapor pressure, and $x_B' - x_B''$ is the difference in the mole fraction of B in the two samples. For convenience these terms are written Δp and Δx, respectively. Equation (9) then becomes

$$\Delta x_B = \Delta p/(p_B^o - p_A^o) \qquad (10)$$

If the component B occurs as an impurity in A, the difference in purity between two fractions is given by equation (10). The limitations of this method are: (1) it is not suited for azeotropic mixtures, (2) the identity of the impurity must be known in order to evaluate $p_B^o - p_A^o$, (3) for polycomponent systems, the operation is more complicated, involving measurements at more than one temperature, and (4) in order to be sensitive, $p_B^o - p_A^o$ must be reasonably large.

Factors contributing to the sensitivity of the measurements are: (1) efficient rectification, whereby the separation of the material into its components is intensified, and (2) making the cuts selected for comparison a very small fraction of the total.

The measurements on the cyanogen were taken over a temperature range of -24.8° to -23.3° C, representing a vapor pressure of the material from 650 to about 700 mm of mercury. The observed difference in vapor pressure between the fore fraction II and the middle fraction IV, and between the fore fraction II and the tail fraction VI was 0.0±0.5 mm of mercury. This measurement of differential vapor pressures, and the lack of any reported side reactions in the thermal decomposition of silver cyanide, establish the purity of the cyanogen for the purpose of determining its heat of combustion. A lot of cyanogen prepared in a similar way was found by Ruehrwein and Giauque [16] to contain impurities to the amount of 0.00005 mole fraction, as determined by calorimetric measurement of the premelting below the normal temperature of fusion.

The purified cyanogen was then transferred to a 1-liter brass bottle for storage, and for introduction to the calorimeter as needed. To test the effect of the gas when in contact with the substances it would encounter (other than glass) in the course of the investigation, a small amount of cyanogen was generated in a glass bulb in which

had been placed small pieces of copper, brass, and steel, as well as a smear of stopcock grease. After ten months of storage, no effect on the materials was observed.

(b) Oxygen.

The oxygen (prepared commercially from liquid air) used for the combustion of the cyanogen was purified by passage through a tube of combustion glass containing copper oxide, and maintained at a temperature of about 600° C. It then passed successively through Ascarite (a commercial mixture of sodium hydroxide and asbestos), anhydrous magnesium per-chlorate, and phosphorus pentoxide.

2. Purity of the Combustion Reaction

The cyanogen, previously dried by passage of the gas through anhydrous calcium sulfate, was burned in an atmos-phere of purified oxygen in the calorimeter reaction vessel. The combustion was initiated by passing an electric spark across the ends of platinum wires at the tip of the burner. The flame burned quietly in the reaction chamber.

Substances other than carbon dioxide and nitrogen in the products of combustion would be oxides of nitrogen and carbon monoxide. After about fifty ignitions of the cyanogen, with combustions of varying duration, including those of the calorimetric observations, no significant deposit of carbon was observed in the reaction vessel.

Because nitrous oxide itself supports combustion and since the combustion of the cyanogen occurred in a flame in

the presence of about 50 percent excess oxygen, the possibility of the presence of nitrous oxide as an impurity in the combustion reaction appeared to be very remote. The other oxides of nitrogen are acidic, and, mixed with oxygen or air, are completely absorbed in alkali solutions (nitric oxide will oxidize under these conditions [19]). Dennis and Nichols [20] report that methods for the detection of nitric oxide appear to be influenced by the higher oxides, if present.

For the detection of any nitrogen oxides, the effluent gas from a combustion of cyanogen in the calorimeter reaction vessel was passed through a solution of sodium hydroxide, and any nitrogen oxides absorbed were reduced to ammonia with Devarda's alloy. This was distilled off, and the distillate was tested with Messler's reagent. It was calculated that the formation of 10^{-4} moles of nitrogen peroxide per mole of carbon dioxide would result in a calorimetric error of 0.0002 percent in the resulting heat of combustion, and a stoichiometric error of 0.01 percent in determining the amount of reaction. Control tests showed that amounts of nitrogen of this order of magnitude, present as an equimolal mixture of nitrate and nitrite, could be readily detected in this way. In five combustion experiments, fixed nitrogen was found in amounts varying up to 2 percent of the total amount in the cyanogen burned. Attempts to reduce this by

varying the flame velocity of the combustion, by substitution of a different reaction vessel, or by changing the technic of ignition were unsuccessful, or gave difficulty in securing ignition.

It was thus necessary to determine quantitatively for each calorimetric combustion, the nitrate and nitrite present in the Ascarite used for the absorption of carbon dioxide from the reaction. The volumetric method for determining nitrate, of Kolthoff, Sandell, and Moskovits [21], which depends on the reduction of nitrate with ferrous sulfate, using ammonium molybdate as a catalyst, was found to be unsatisfactory in the presence of nitrite. No other method was available for determining nitrate directly, so that it was necessary to estimate the nitrate by difference of nitrite from total fixed nitrogen, as determined by reduction to ammonia by Devarda's alloy, and direct titration of the ammonia when distilled off. Nitrite was determined on a separate portion of the sample by oxidation with potassium permanganate [22]. The adopted procedure for the nitrogen analysis follows.

After weighing the carbon dioxide absorption tube used to determine the amount of cyanogen combustion, the stopcocks were removed, and the barrels were carefully cleaned of stopcock grease, using ether. The layers of phosphorus pentoxide and magnesium perchlorate were removed, and traces of this material adhering to the glass were carefully

washed out with a jet of distilled water played in such a
manner as to avoid wetting any of the Ascarite. The
asbestos plugs over the Ascarite were removed, and as much
material was was loose (including the asbestos plugs) was
transferred to a beaker. The remaining material was
leached out with water, with all washings being added to
the beaker. This solution was quantitatively filtered
through a Büchner funnel, and the filtrate was transferred
to a 200 ml volumetric flask, which was then filled to the
mark with water. From this amount of solution, 100 ml was
pipetted out for the nitrite determination, and the remain-
ing material, plus washings from the pipette, was used for
the estimation of the total nitrogen.

For the titration of nitrite, 30 ml of 0.017 molar
potassium permanganate was added from a burette to an Erlen-
meyer flask. This was diluted to 75 ml with water, and then
25 ml of 18 $\underline{N}$ sulfuric acid was added. The 100-ml sample was
added to this from a pipette, with the flask being cooled in
tap water. The cold solution was then treated with standard
0.04 molar sodium oxalate until decolorized, an integral
amount of oxalate being added. The end point of the titration
was reached by the further addition of the permanganate, with
the solution heated to 50 to 60° C before the addition of
the last few drops. For each determination the permanganate
equivalent of the oxalate was determined in the same manner,
and the color blank on the end point was determined in each

ease by the addition of permanganate to 25 ml of the 18 $\underline{N}$ sulfuric acid, diluted to the same volume as the solution being titrated, until the color matched that selected as the end point in the regular titrations. The reactions involved were

$$5\ \overline{NO}_2 + 2\ \overline{MnO}_4 + 6\ H^+ = 5\ \overline{NO}_3 + 2\ Mn^{++} + 3\ H_2O \qquad (11)$$

$$2\ \overline{MnO}_4 + 5\ \overline{C_2O_4} + 16\ H^+ = 2\ Mn^{++} + 8\ H_2O + 10\ CO_2 \qquad (12)$$

By converting the permanganate consumed by the nitrite into the equivalent amount of oxalate, the primary standard used, then 1 mole of oxalate is equivalent to 1 mole of nitrite.

The total fixed nitrogen was determined from the remaining alkali solution obtained from the Ascarite. This was reduced for one hour with 2 g of Devarda's alloy in a Kjeldahl still, and then the ammonia was distilled into 50 ml of 0.05 $\underline{N}$ sulfuric acid, which was back-titrated with 0.05 $\underline{N}$ sodium hydroxide.

In these determinations it was necessary to know: (1) the completeness of the absorption of the oxides of nitrogen, (2) the completeness of their determination, and (3) the effect of small amounts of cyanogen. To test the first premise, a combustion of cyanogen was run for 4 minutes under the same conditions as in the calorimetric experiments. The reaction vessel was connected to an absorption tube charged with Ascarite, and this in turn was connected to a gas-washing bottle fitted with a fritted glass bubbler, and filled with 10 percent (by weight) sodium hydroxide solution. This

solution was examined for nitrogen by reduction and treatment with Nessler's reagent, as described above. None was detected in a test which would have shown the presence of less than 0.01 mg, which amount was estimated to be 1 part in 400 of the nitrogen actually fixed in a combustion carried out under these conditions.

Control tests were then run on samples of 35 g of Ascarite (the amount used in all absorptions) to which was added amounts of sodium nitrate and sodium nitrite which were equal in magnitude to those actually found in the calorimetric combustion. As an average of three such experiments in which there were added 0.002668 moles of sodium nitrite and 0.000482 moles of sodium nitrate, there were found, ny the determinations described above, 0.002662 moles of nitrite and 0.003129 moles of nitrogen. While no attempt was made to purify the control samples of nitrite and nitrate, the results indicate that the method of determination was sufficiently accurate for this investigation.

To determine the effect of small amounts of unburned cyanogen on the determination, an absorption tube was charged with Ascarite; and cyanogen, flowing at the rate used in the calorimetric experiments, was passed into the absorber for 30 seconds. No efflux of gas from the tube was observed, indicating complete absorption of the cyanogen -- a fact necessary to establish in the determination of carbon monoxide, as explained later. The increase in mass of the

tube was 0.0383 g. The Ascarite from this tube was then
treated as in the ordinary analytical determinations, and
it was found that the absorbed cyanogen had no effect on
the titer of either the permanganate or the standard sulfuric
acid used in the analysis.

In order to determine any carbon monoxide formed in the
combustion, the affluent gas from the carbon-dioxide ab-
sorption tube was passed through a combustion tube of Corn-
ing 172 glass packed with copper oxide and maintained at a
temperature of about 600° C. The connections were all glass.
Since no oxides of nitrogen and no cyanogen passed through the
carbon-dioxide absorption tube, any increase in mass of a
second similar tube, connected to the exit end of the com-
bustion tube, would be due to carbon monoxide oxidized to
carbon dioxide. This point was established by running a com-
bustion in the regular manner. The exit gas from the reaction
vessel was passed through two Ascarite tubes connected direct-
ly in series, and joined to a third connected at the exit end
of the combustion tube. The increase in mass of the first
tube was 0.5535$_8$ g, that of the second was 0.0004$_2$ g, while
that of the third, representing carbon monoxide, was
0.0418$_2$ g. An analysis of the contents of this third tube
for nitrogen gave negative results. Finally, an experiment
was performed in which the cyanogen, flowing at the rate used
in the combustion experiments was passed directly through two
absorption tubes connected in series. The system was then
swept with dry oxygen. The increase in mass of the first tube

was 0.0397$_3$ g, and that of the second was 0.0001$_2$ g. These experiments indicate that neither unburned cyanogen nor oxides of nitrogen passed through the first absorption tube.

3. Determination of the Amount of Reaction

In these experiments, the amount of reaction was determined from the mass of carbon dioxide formed in the reaction, by correcting the observed increase in mass of the absorber for the amounts of impurities found by analysis in each combustion, and also for a small amount of cyanogen remaining unburned during each ignition and extinction process. The estimation of this latter quantity will be considered later (see Section V of this paper).

The absorbers were of the usual U-tube type, fitted with ground-glass connecting joints, and were charged with Ascarite, backed with anhydrous magnesium perchlorate and phosphorus pentoxide. All weighings were corrected to vacuum. To the observed increase in mass of the absorption tube connected directly to the reaction vessel, there was added the increase in mass of the second absorption tube, connected to the first through the copper-oxide combustion tube (giving the carbon monoxide burned to carbon dioxide). From this there was subtracted the masses of nitrogen oxides determined in the nitrogen analysis (present as nitrate and nitrite), as well as the average mass of unburned cyanogen produced per experiment. This result gave the total mass of carbon dioxide representing the amount of reaction. One mole (44.010 g) of carbon dioxide was taken as one-half mole of cyanogen.

V. CALORIMETRIC PROCEDURE

1. Electrical-Energy Experiments

The energy source for the electrical-energy experiments was a storage battery of 40 volts. The power input into the calorimeter was determined by measuring (1) the potential drop across the heating coil and (2) the potential drop across a standard resistance through which passed the same current which flowed through the heating coil (plus a small calculable amount which shunted through the potential coils connected in parallel with it). These voltages were measured on a White double potentiometer having a range of 100,000 microvolts. The sensitivity of these measurements was such that 1 mm on the galvanometer scale (1 m distant from the galvanometer) was approximately equivalent to 0.75 microvolts. The scale readings were estimated to 0.1 mm. It was found (as in the previous experience of the Thermochemical Laboratory [2]) that the variation of the current and voltage was small enough to permit the calculation of the energy input as the product of the time, the average current, and the average voltage.

The time of the experiments was measured by second impulses relayed from the master clock of the National Bureau of Standards. For sending the current through the heating coil for a given, known length of time, there was employed the apparatus of Johnston [23], which was actuated by the timing relay. This apparatus is equipped with a means of

Table 1. Calorimetric results of the electrical-energy
experiments for cyanogen.

Experiment	ΔR[1]	k	K	U	Electrical energy[2]	Mass of calorimeter	Electrical energy equivalent of calorimeter system[3]	Deviation
	ohms	min⁻¹	ohms	ohms	int j	g	int j/abs. ohm	j/ohm
1	0.397063	0.001914	0.015268	0.000145	58,335.8	3602.60	152,384.1	0.0
2	.394055	.001911	.015463	.000057	57,743.1	3603.85	152,384.1	0.0
3	.399372	.001914	.015184	.000057	58,580.5	3603.06	152,367.5	-16.6
4	.393121	.001911	.015556	.000018	57,640.7	3607.53	152,359.1	-25.0
5	.392779	.001928	.015643	.000136	57,434.4	3599.71	152,357.9	-26.2
6	.393040	.001912	.015471	.000004	57,461.8	3596.16	152,350.0	-34.1
7	.398601	.001916	.015259	.000033	58,389.0	3599.36	152,356.2	-27.9
8	.396923	.001953	.015340	.000453	58,045.2	3599.52	152,437.4	+53.3
9	.395293	.001919	.015477	.000176	57,938.9	3604.35	152,435.3	+51.2
10	.394791	.001924	.015534	.000172	57,780.0	3600.86	152,408.9	+24.8

Mean 152,384.1

Standard deviation of the mean . . . . ±10.3

[1] The average temperature of the calorimeter was 24.98° C for experiment 4; 24.99° C for experiments 2, 5, and 6; 25.00° C for experiments 9 and 10; and 25.01° C for experiments 1, 3, 7, and 8.

[2] The time of electrical-energy input was 2280.00 seconds in each experiment.

[3] For 3600.00 g of water and an average temperature of 25.00° C.

reversing connections, so that starting and stopping the flow of current are accomplished by the same mechanical operation of the switch, cancelling out its time lag. During periods when the current was not flowing through the heating coil of the calorimeter, it was sent through an equal, external, stabilizing resistance.

The data of the electrical-energy experiments for this investigation are given in table 1. The various quantities have the same significance as above (section III). The standard deviation of the average value of the electrical-energy equivalent for these experiments is ±0.007 percent.

2. Correction Experiments

In the calorimetric combustion experiments, it was necessary to take account of the following sources or sinks of energy, which were not present in the experiments with electrical energy: (1) the spark energy, which is the energy introduced into the calorimeter when the reaction is initiated by passing an electric spark across the ends of platinum wires at the tip of the burner in the reaction vessel; and (2) the gas energy, which is the energy added to or taken from the calorimeter by the inflowing oxygen and cyanogen entering the calorimeter at a temperature different from the average temperature, with respect to time, of the calorimeter.

The spark energy was determined calorimetrically by passing the spark across the tip of the burner, with oxygen in the reaction vessel. The temperature of the calorimeter,

Table 2. Experiments determining the spark energy.

Experiment	Time of sparking	Energy of sparking	Spark energy
	seconds	j	j/sec
1	48	101.1	2.11
2	48	102.0	2.13
3	48	99.5	2.07
4	48	97.6	2.03
5	48	97.0	2.02
Average			2.07

Standard deviation of the mean   ± 0.02

for these experiments, was slightly below that of the jacket
and the time of sparking was about three times that employed
in a regular combustion experiment. The product of the re-
sulting small temperature rise of the calorimeter and the
energy equivalent gave the amount of this sparking energy.
The results of five experiments on the evaluation of the
spark energy are given in table 2.

The gas energy was calculated from the known heat
capacities of the gases, and the difference between their
temperature (taken as that of the air near the connecting
tubes leading to the reaction vessel) and the average
temperature, with respect to time, of the calorimeter. For
this purpose, the heat capacities of oxygen and cyanogen
were taken as 29.2 and 44.6 joules per degree-mole, respec-
tively [24].

As mentioned in section IV, besides the impurities in
the combustion, which were determined and accounted for in
each case by chemical analysis, another stoichiometric cor-
rection was necessitated by a small amount of cyanogen which
remained unburned during the ignition and extinction
processes, and which was absorbed by the carbon-dioxide ab-
sorption tube. The value of this correction was deduced from
a series of eight ignitions and extinctions of the flame car-
ried out calorimetrically and under the same conditions as in
the main calorimetric combustion experiments, but with the
extinction immediately following the ignition. From the
evolved reaction energy, obtained from the temperature rise

Table 3. Experiments determining the amount of cyanogen remaining unburned in each ignition and extinction of the flame

Experiment	Electrical energy equivalent	$\Delta H_{corr.}$	Calorimeter energy	Spark energy	Reaction energy	Calculated mass of CO_2 formed	Observed increase in mass of absorption tube	Calculated mass of C_2N_2 unburned	Deviation from mean
	int j/abs. ohm	abs. ohm	j	j	j	g	g	g	g
1	152,540	0.001210	184.6	31.1	153.5	0.01233	0.02961	0.01728	-0.00002
2	152,540	.001824	278.2	31.1	247.1	0.01985	.03721	.01736	+ .00006
3	152,580	.001737	265.0	31.1	233.9	.01879	.03564	.01685	- .00045
4	152,580	.001590	242.6	31.1	211.5	.01699	.03513	.01814	+ .00084
5	152,650	.000936	142.9	24.9	118.0	.00948	.02658	.01710	- .00020
6	152,650	.000810	123.6	31.1	92.5	.00743	.02457	.01714	- .00016
7	152,410	.000756	115.2	24.9	90.3	.00725	.02444	.01719	- .00011
8	152,410	.001142	174.1	31.1	143.0	.01149	.02885	.01736	+ .00006

Average 0.01730

Standard deviation of the mean . . . . ± .00013

of the calorimeter and its energy equivalent (and correcting
for the spark energy), there was computed the mass of carbon
dioxide corresponding to this quantity of energy, which would
have been formed in the pure combustion of cyanogen. In this
calculation there was used for the heat of combustion of
cyanogen the value 1096 kilojoules per mole. The difference
between the calculated increase in mass of the carbon-dioxide
absorption tube and that actually observed was assumed to be
unburned cyanogen. The data of these experiments are given
in table 3, and the average value was taken as the mass of
unburned cyanogen in calculating the amount of reaction in
the main calorimetric combustion experiments. The uncertainty
is taken as twice the standard deviation [9].

3. Combustion Experiments

The data of ten calorimetric combustion experiments are
given in table 4. The various quantities have the same sig-
nificance as above (section III).

In order to alter the amounts of nitrogen oxides formed
in the combustion of cyanogen, a second set of calorimetric
combustion experiments was performed in which the oxygen used
for the combustion was saturated with water vapor at $0°$ C.
Since this water would have to be accounted for stoichiometrial-
ly, ten experiments were performed to determine the reproduci-
bility of the mass of water which would be added to the
products of combustion in this way. The experiments were
carried out by flushing the oxygen line (connected with the

Experiment	ΔR^1	k	K	U	Electrical energy equivalent of calorimeter system	Gas energy	Spark energy	Net reaction energy	Increase in mass of CO_2 absorber	Mass N_2O_3 determined	Mass N_2O_5 determined	Mass CO_2 from CO oxidation	Mass of $CO_2{}^2$
	ohms	min^{-1}	ohms	ohms	int.j/ohs. ohms	j	j	j	g	g	g	g	g
1	0.399517	0.001919	0.015576	0.000374	152,727.4	+75.0	31.1	58,488.7	4.8125₆	0.1062₇	0.0162₅	0.1028₀	4.77555
2	.397917	.001920	.014564	.000787	152,742.1	+70.0	24.9	58,410.7	4.7978₈	.1012₂	.0250₇	.1220₈	4.77224₇
3	.397188	.001925	.016081	.000812	152,457.0	+41.4	31.1	57,997.8	4.7573₄	.0997₃	.0309₄	.1319₅	4.74073₀
4	.397277	.001931	.015343	.000163	152,651.3	+ 4.2	31.1	58,258.0	4.7710₅	.1071₄	.0008₆	.1548₄	4.77725₈
5	.398778	.001929	.015493	.000189	152,515.4	+ 4.2	31.1	58,385.6	4.7618₃	.1047₂	.0183₈	.1777₂	4.79786₆
6	.397527	.001936	.014975	.000202	152,625.6	+ 6.8	31.1	58,718.3	4.7551₁	.1055₁	.0170₈	.1824₄	4.79767₇
7	.397478	.001931	.018540	.000000	152,626.9	- 0.2	43.5	57,792.8	4.6947₀	.1111₁	.0242₉	.2302₀	4.77315
8	.399497	.001921	.014628	.000210	152,686.1	+23.1	35.2	58,673.8	4.7887₅	.1022₆	.0207₄	.1692₁	4.81777₆
9	.398411	.001910	.014541	.000124	152,495.1	+36.6	37.3	58,445.5	4.7675₆	.1028₃	.0212₆	.1941₃	4.82802₄
10	.397811	.001930	.014097	.000288	152,405.2	+ 2.8	31.1	58,402.2	4.7505₇	.1012₅	.0140₁	.1951₂	4.81314₄

[1] The average temperature of the calorimeter was 25.00° C for experiments 9 and 10; 25.01° C for experiments 2, 3, 4, 5, 6, and 7; and 25.02° C for experiments 1 and 8.

[2] Includes a correction of -0.0173₀ g as the average amount of unburned cyanogen absorbed in each experiment.

Table 5.   Experiments on the reproducibility of the mass of
           water collected from water-saturated oxygen used
           in the combustion of cyanogen under these conditions

Experiment	Mass of water collected	Deviation from mean
	g	g
1	0.0504_6	-0.0018_8
2	$.0542_0$	$+ .0018_6$
3	$.0589_5$	$+ .0066_1$
4	$.0507_7$	$- .0015_7$
5	$.0568_5$	$+ .0045_2$
6	$.0580_5$	$+ .0057_2$
7	$.0493_7$	$- .0029_7$
8	$.0495_0$	$- .0028_4$
9	$.0484_7$	$- .0038_7$
10	$.0467_5$	$- .0055_9$

Mean 0.0523_4

Standard deviation of the mean $\pm 0.0013_7$

Table 6. Calorimetric results of the reaction experiments for cyanogen, using in the combustion oxygen saturated with water at 0° C.

Experiment	ΔR[1]	k	K	U	Electrical energy equivalent of calorimeter system	Gas energy	Spark energy	Net reaction energy	Increase in mass of CO_2 absorber	Mass N_2O_3 determined	Mass N_2O_5 determined	Mass CO_2 from CO oxidation	Mass of CO_2[2]
	ohms	min^{-1}	ohms	ohms	int.j/abs. ohms	j	j	j	g	g	g	g	g
1	0.398436	0.001929	0.015599	0.000170	152,698.4	− 0.1	31.1	58,409.2	4.8660$_8$	0.0950$_2$	0.0188$_4$	0.0155$_8$	4.7039$_9$
2	.397995	.001937	.014992	.000158	152,665.8	+ 3.1	32.2	58,782.1	4.8474$_7$	.0757$_5$	.0198$_6$	.0175$_6$	4.7078$_7$
3	.398508	.001938	.014792	.000160	152,634.8	+ 7.5	31.1	58,238.6	4.8237$_4$	.0766$_6$	.0114$_1$	.0239$_4$	4.7011$_5$
4	.398307	.001921	.015214	.000154	152,317.8	+15.8	31.1	58,281.5	4.8588$_4$	.0956$_0$	.0218$_8$	.0170$_6$	4.6967$_4$
5	.396970	.001931	.017534	.000155	152,481.0	+12.2	35.2	57,785.7	4.8310$_8$	.1039$_0$	.0181$_2$	.01374	4.6544$_0$
6	.399237	.001930	.015243	.000092	152,761.9	+ 0.9	31.1	58,618.4	4.8944$_2$	.0992$_8$	.0253$_6$	.0153$_1$	4.7236$_1$
7	.398415	.001935	.017928	.000195	152,712.6	+ 2.8	31.1	58,041.5	4.8528$_6$	.1020$_4$	.0183$_5$	.0136$_8$	4.6705$_0$

[1] The average temperature of the calorimeter was 25.00° C for experiment 6 and 25.01° C for experiments 1, 2, 3, 4, 5, and 7.

[2] Includes a correction of −0.0173$_0$ g as the average amount of unburned cyanogen absorbed in each experiment, as well as a correction for the mass of water vapor introduced with the combustion oxygen (see p. 27).

reaction vessel and a water absorption tube) with dry oxygen, flowing at the rate normally used in the combustion; by-passing it for 46 minutes (the usual time of flow in the combustions) through a gas-washing bottle having a fritted-glass bubbler, and immersed in an ice bath; and again flushing with dry oxygen. The data of these experiments are given in table 5. The average amount of water absorbed in this way was $0.0523_4 \pm 0.0027_4$ g. The estimated uncertainty of the determination of the amount of reaction due to this amount of water was ± 0.057 percent.

The data of seven calorimetric combustion experiments carried out under these conditions are given in table 6. In those experiments for which the time of flow of water-carrying oxygen differed from 46 minutes, when computing the stoichiometric correction for this, the amount of water absorbed was assumed to vary linearly with the time of passage of the oxygen. The effect of carrying out the combustion of cyanogen in this manner was to reduce the amount of carbon monoxide to about one-tenth of its former value, and the fixed nitrogen to about 80 percent of its previous amount.

VI. RESULTS OF THIS INVESTIGATION

For the final calculation of the heat of combustion of cyanogen, it is necessary to identify the particular oxides of nitrogen formed in the reaction vessel during the combustion, in order that appropriate corrections for their respective heats of formation may be made to the calorimetric observations. For this purpose there must be considered nitric oxide, nitrogen dioxide (in equilibrium with its dimer, nitrogen tetroxide), nitrogen trioxide, and nitrogen pentoxide (as well as nitric acid vapor in the case of those experiments in which water vapor was present in the reaction chamber). All these substances, except nitric oxide, are absorbed by solid sodium hydroxide. Under the conditions of the present experiments, no oxides of nitrogen were detected in the exit gas from the carbon dioxide absorption tube. Hence it follows that at least half the nitric oxide issuing from the calorimeter was oxidized to nitrogen dioxide.

Nitrogen pentoxide is known to decompose completely at 25° C (p. 552 of reference [19]). According to Mellor (p. 449 of reference [19]), in the gaseous state, the dissociation of nitrogen trioxide to nitric oxide and nitrogen dioxide is virtually complete. This is corroborated by a calculation based on the equilibrium data of Verhoek and Daniels [26], and according to the conditions of a typical combustion experiment of this investigation.

It thus appears that, during the combustion of the
cyanogen, the fixed nitrogen present in the effluent gas
from the reaction vessel was a mixture of nitric oxide and
nitrogen dioxide (in equilibrium with nitrogen tetroxide).
Concerning the absorption by solid alkali of these substances,
Mellor reports the following: (1) nitric oxide reacts with
solid potassium hydroxide in the presence of excess oxygen,
to form mainly potassium nitrite, but that some nitrate is
formed as well (p. 432 of reference [19]); (2) nitrogen
dioxide or tetroxide should react with solid alkali to give
equimolal amounts of nitrate and nitrite, but that larger
amounts of nitrate may be formed (pp. 539-40 of reference
[19]); and (3) nitric oxide and nitrogen dioxide in equimolal
amounts are absorbed by alkali as pure nitrite. Burdick and
Freed [27] state that assuming these absorptions of nitrogen
oxides as pure reactions is subject to some qualification.

A reasonable interpretation of the processes occurring,
with respect to the fixation of nitrogen during the combustion
of the cyanogen, is the following. The primary fixation was
the formation of nitric oxide, which then oxidized to the ex-
tent indicated by the analyses to nitrogen dioxide. Letting
a and b be, respectively, the amounts of nitrite and nitrate
determined analytically, the fixation reaction in the
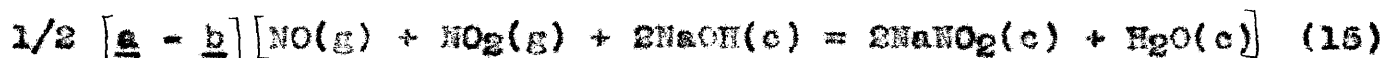calorimeter was

$$[\underline{a} + \underline{b}] \left[1/2\ N_2(g) + 1/2\ O_2(g) = NO(g) \right] \tag{13}$$

Also, the nitrogen dioxide was formed according to the

equation

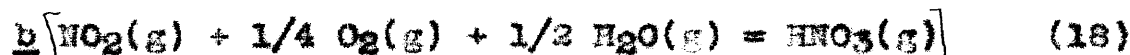$$1/2 [\underline{a} + 3\underline{b}] [NO(g) + 1/2\, O_2(g) = NO_2(g)] \tag{14}$$

The absorption of the oxides of nitrogen took place according to the reactions

$$1/2 [\underline{a} - \underline{b}][NO(g) + NO_2(g) + 2NaOH(c) = 2NaNO_2(c) + H_2O(c)] \tag{15}$$

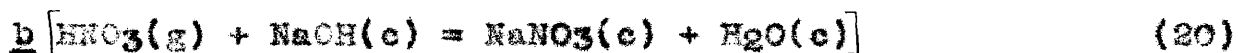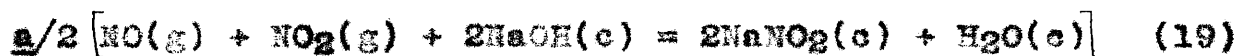$$2\underline{b}[NO_2(g) + NaOH(c) = 1/2\, NaNO_2(c) + 1/2\, NaNO_3(c) + 1/2\, H_2O] \tag{16}$$

A similar interpretation holds for those experiments in which water vapor was present in the combustion chamber. In addition, however, some of the nitrogen dioxide formed reacted with the water vapor, to form nitric acid vapor. The reactions which occurred were

$$[\underline{a} + \underline{b}][1/2\, N_2(g) + 1/2\, O_2(g) = NO(g)] \tag{13}$$

$$1/2[\underline{a} + 2\underline{b}][NO(g) + 1/2\, O_2(g) = NO_2(g)] \tag{17}$$

$$\underline{b}[NO_2(g) + 1/4\, O_2(g) + 1/2\, H_2O(g) = HNO_3(g)] \tag{18}$$
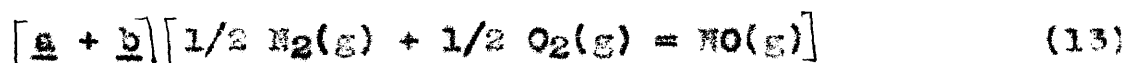
The absorption by Ascarite of these substances took place according to the reactions

$$\underline{a}/2 [NO(g) + NO_2(g) + 2NaOH(c) = 2NaNO_2(c) + H_2O(c)] \tag{19}$$

$$\underline{b}[HNO_3(g) + NaOH(c) = NaNO_3(c) + H_2O(c)] \tag{20}$$

The calorimetric data obtained (section V) were calculated on the bases of these assumptions, and the data are presented in tables 7 and 8. The fraction of nitrogen dioxide present as nitrogen tetroxide was computed by an equilibrium calculation based on the data of Giauque and Kemp [28], and it was found to be negligible in the present experiments. For the heats of formation of the nitric oxides and of nitric acid, values were taken from the compilation of Bichowsky and Rossini [29], and the value of the heat of combustion of carbon monoxide was taken as 282.94 int kj/mole [30].

Table 7. Calculation of the heat of combustion of cyanogen from the data of table 4.

Experiment	Amount of nitrite determined	Amount of nitrate determined	Amount of NO formed	Amount of NO_2 formed	Amount of CO formed	Heat of formation of NO	Heat of formation of NO_2	Heat of combustion of CO	Corrected reaction energy	Amount of C_2N_2 burned	Heat of combustion at 25°C	Deviation from mean
	moles	moles	moles	moles	moles	int. j	int. j	int. j	int. j	moles	int.j/mole	kj/mole
1	0.002792_0	0.000300_8	0.001247_6	0.001849_2	0.002336_3	-112.7	-62.1	661.0	59324.6	0.054255_3	1093.43	-1.33
2	$.002663_2$	$.000463_0$	$.001100_1$	$.002026_1$	$.002773_9$	-99.4	-68.1	784.1	59352.2	$.054219_8$	1094.84	+ .08
3	$.002624_0$	$.000572_8$	$.001025_6$	$.002171_2$	$.002998_1$	-92.7	-72.9	848.3	59011.7	$.053855_0$	1095.75	+ .99
4	$.002713_6$	$.000483_2$	$.001145_2$	$.001991_6$	$.003517_9$	-103.5	-66.9	995.4	59423.7	$.054221_5$	1095.94	+1.18
5	$.002755_2$	$.000340_4$	$.001207_4$	$.001888_2$	$.004026_9$	-109.1	-63.4	1139.4	59698.5	$.054517_8$	1095.03	+ .27
6	$.002776_0$	$.000316_2$	$.001229_9$	$.001862_3$	$.004155_5$	-111.1	-62.3	1144.?	59?3?.?	$.054506_6$	1094.12	- .64
7	$.002923_2$	$.000431_2$	$.001246_0$	$.002108_4$	$.005229_2$	-112.6	-70.8	1472.?	59455.8	$.054328_0$	1096.40	+1.64
8	$.002690_4$	$.000384_0$	$.001153_2$	$.001991_2$	$.003849_4$	-104.2	-64.5	1089.2	59921.7	$.054734_8$	1094.95	+ .19
9	$.002705_6$	$.000393_6$	$.001156_0$	$.001943_2$	$.004411_1$	-104.5	-65.3	1248.1	59863.3	$.054763_0$	1093.13	-1.63
10	$.002664_4$	$.000259_4$	$.001202_3$	$.001721_1$	$.004433_5$	-108.6	-57.8	1254.4	59823.1	$.054682_3$	1094.01	- .75

Average   1094.76

Standard deviation of the mean   ±0.34

Table 8. Calculation of the heat of combustion of cyanogen from the data of table 6.

Experiment	Amount of nitrite determined	Amount of nitrate determined (= amount of HNO_3 formed)	Amount of NO formed (= amount of NO_2 formed)	Amount of CO formed	Heat of formation of NO	Heat of formation of NO_2	Heat of formation of HNO_3	Heat of combustion of CO	Corrected reaction energy	Amount of C_2N_2 burned	Heat of combustion at 25°C	Deviation from mean
	moles	moles	moles	moles	int. j	int. j	int. j	int. j	int. j	moles	int. kj/mole	kj/mole
1	0.002526_4	0.000348_8	0.001263_2	0.000354_0	-114.1	-42.4	8.0	100.2	58657.9	0.053442_3	1097.59	+0.82
2	$.002019_2$	$.000367_8$	$.001009_6$	$.000399_0$	-91.2	-33.9	8.5	112.9	58611.7	$.053486_4$	1095.82	-.95
3	$.002016_8$	$.000215_0$	$.001008_4$	$.000543_9$	-91.1	-33.9	5.0	153.9	58512.5	$.053410_0$	1095.53	-1.24
4	$.002515_2$	$.000405_2$	$.001257_6$	$.000387_6$	-113.6	-42.3	9.3	109.7	58537.7	$.053359_9$	1097.04	+.27
5	$.002733_6$	$.000333_6$	$.001366_8$	$.000312_2$	-123.5	-45.9	7.7	88.3	58035.8	$.052878_9$	1097.52	+.75
6	$.002612_0$	$.000469_6$	$.001306_0$	$.000347_8$	-118.0	-43.9	10.8	98.4	58862.9	$.053665_2$	1096.85	+.08
7	$.002684_8$	$.000339_8$	$.001342_4$	$.000310_8$	-121.3	-45.1	7.8	87.9	58288.0	$.053130_0$	1097.08	+.31

Average   1096.77

Standard deviation of the mean   ±0.30

VII. CONCLUSION

The data of the present experiments indicate that the value of the heat of combustion of cyanogen, at 25° C and a constant pressure of 1 atm., lies between the limits 1094.5 and 1097.0 int kj/mole, or 261.6 and 262.2 kcal/mole. These limits have the following relation to the existing data, listed in ascending order of value:

Investigation	Year reported	Value (kcal/mole)
McMorris and Badger [6]	1933	251.4
Thomsen [4]	1886	259.4
Von Wartenberg and Schütza [5]	1933	261.3
Present	1941	$261.6 < x < 262.2$
Berthelot [3]	1879	264
Dulong [2]	1838	275

While the present investigation has fixed the value with an uncertainty of ±0.12 percent, it is hoped that additional experimentation with regard to the nature and amount of the products formed in the oxidation of the nitrogen will reduce the uncertainty.

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