The excited molecule must collide with another nitrosyl chloride molecule to yield the decomposition products.

The presence of structure in the visible absorption bands of nitrosyl chloride of course does not preclude that at shorter wave lengths the phenomenon of predissociation may not show itself. The observations recorded here rather support this supposition, although indicating that the "predissociation" state of a molecule is not necessary for its chemical activation.

Summary

1. Quantum yield measurements in the nitrosyl chloride decomposition show that the quantum yield is constant and is equal to two with wave lengths from 6300 to 3650 Å.

2. Study of the absorption spectrum of nitrosyl chloride indicates that it has banded structure throughout the visible part of the spectrum.

3. It is concluded that the mechanism of nitrosyl chloride decomposition consists in formation of an excited molecule and in a subsequent decomposition on collision.

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THE SPECIFIC HEATS OF GASES AT HIGH PRESSURES. I. METHOD AND APPARATUS AT ROOM TEMPERATURE[1]

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Introduction

An obvious need for data regarding the properties of gases at high pressures has made it desirable to develop a method for measuring specific heats. This is the first of a series of papers from this Laboratory reporting methods and measurements. It is confined to a description of a continuous flow, adiabatic gas calorimeter suitable for measuring specific heats up to 1000 atmospheres at ordinary temperature.

The literature contains practically no data on this important property of gases above 200 atmospheres. Holborn and Jacob[3] have published results on air but their apparatus could not be used over the entire range of pressures. An excellent review of the existing data and methods has recently been published.[4]

[1] Submitted in partial fulfilment of the requirements for the degree of Ph.D. in Chemistry in the Graduate School of the University of Illinois.

[2] Research Assistant in Gas Engineering. University of Illinois, Engineering Experiment Station. Work of B. H. M. published by permission of the Director.

[3] Holborn and Jacob, *Berl. Ber.*, 1, 213 (1914).

[4] Partington and Shilling, "The Specific Heat of Gases," E. Benn, London, **1924**.

Experimental Method and Apparatus.—The principle of the adiabatic constant temperature flow calorimeter is well known. The present apparatus differs from previous ones particularly in the methods of measuring the several heat loss corrections.

Figure 1 is a simplified flow diagram of the method as used for nitrogen. High pressure gas storage cylinders, I, II and III are connected through a copper deoxidizer and soda lime scrubber to a thermostat. A long coil of steel tubing immersed in the liquid of the thermostat brings the temperature of the flowing gas to a constant value. Passing through a short, well-insulated tube to the calorimeter, the gas flows through the coil immersed in the calorimeter liquid. Since the temperature of the calorimeter is maintained about 6° higher than that of the thermostat, the flowing gas is heated during passage. To compensate for this continuous removal of heat by the flowing gas and for the heat losses by conduction along the steel tubing and the usual calorimeter losses, a carefully measured quantity of electrical energy is introduced into the calorimeter liquid to maintain its temperature constant. The rise in temperature of the flowing gas due to its heat absorption is measured by thermojunctions placed in the gas stream. After leaving the calorimeter the gas is expanded to about atmospheric pressure, the rate of flow being indicated by a sensitive capillary flowmeter. After humidifying the gas, the rate of flow is measured in a calibrated wet meter and the gas then is collected in a water-sealed gas holder. As needed the gas is recompressed by means of a three stage gas compressor into cylinder I and, for work at 300 atmospheres or more, is further compressed above a water piston formed by the hydraulic pump. The usual method of maintaining a constant pressure on the calorimeter was to pump cylinder III to the desired calorimeter pressure and cylinder II to a higher pressure. By adjustment of the pressure regulating valve between the two, the calorimeter pressure was held constant.

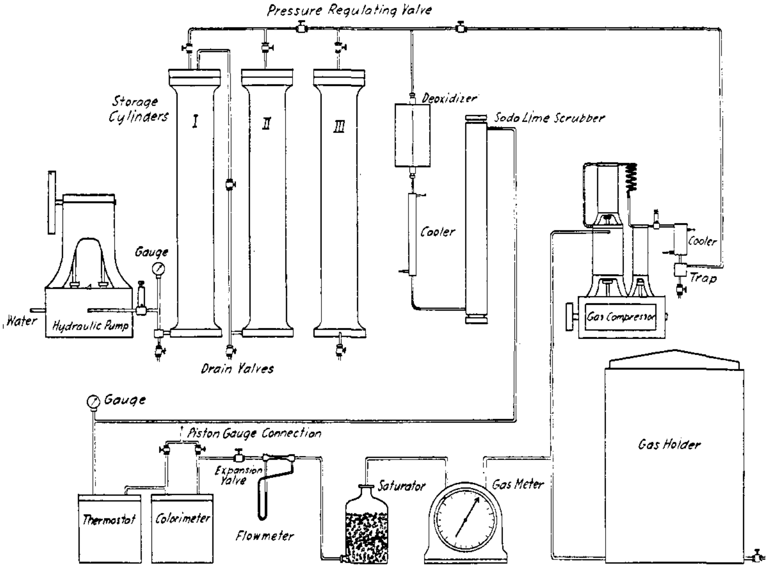

Fig. 1.

The actual manipulation during an experiment, in addition to that just described, consisted in adjusting the electrical energy input to the calorimeter so that its temperature remained constant. With a constant rate of gas flow at a constant pressure, a steady calorimeter temperature indicated that the energy input exactly equaled the energy absorbed by the gas and the energy lost by conduction, radiation, etc. Measurements of the several losses and subtraction from the total gave the energy absorbed by the gas in its passage through the calorimeter. Measurement of the gas temperature rise corresponding to this heat gives directly the heat capacity at the pressure used.

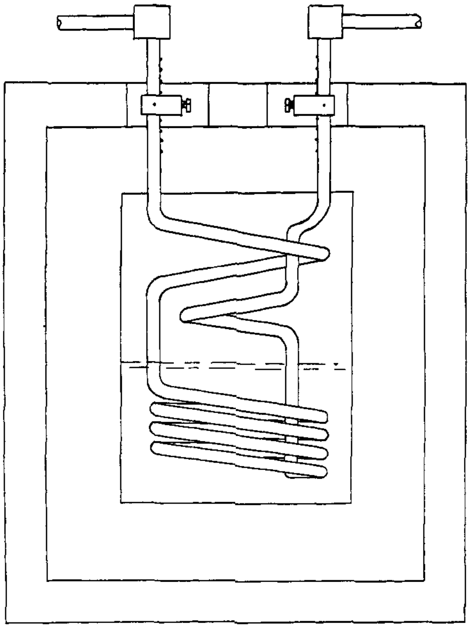

Fig. 2.—High pressure calorimeter.

The Calorimeter.—Because the requirements to be met in this problem were radically different from any recorded in the literature, the final calorimeter as used was the result of experience and trial. An exact evaluation of the conduction losses and the measurement of the gas temperature rise offered the principal difficulties. The essential features of the calorimeter are shown in Fig. 2. A Parr adiabatic calorimeter was modified in several ways. The water jacket and cover together with the circulating pump were retained. A small resistance heater was placed in the jacket and the heat input controlled by an external resistance. The inside compartment consisted of a small copper can containing 1000 cc. of kerosene. Four feet of steel tubing, one-quarter inch in outside diameter and one-sixteenth inch bore, was coiled inside the can. By leaving a turn of tubing above the liquid the temperature gradient along the tubes leading out was reduced. The kerosene was stirred in the usual way and a resistance coil immersed in it and controlled by a sensitive external resistance furnished temperature regulation. A twelve-volt storage battery supplied a steady source of current. The jacket and calorimeter temperatures were measured by means of Beckmann thermometers.

The connections between the ends of the calorimeter tubing and the external tubing carrying gas into and out of the calorimeter were made by means of specially designed "gradient" tubes. These are shown in Fig. 3. The purpose of these tubes is two-fold. Since they connect the inside of the calorimeter with the outside, it is necessary to measure their temperature gradient in order to evaluate the heat conduction loss along them. They also contain the thermocouples that indicate the incoming and outgoing gas temperatures. Since the tubes are well insulated so that no heat is lost to or gained from the surroundings, any difference in the amount of heat carried by conduction along different sections may be accounted for as having gone into the gas. Consequently the amount of heat passing the section where the gas temperature is read is the true conduction loss. In order to introduce the "gas" couples into the stream, it was necessary to enlarge the gradient tubes at this point. The thermocouples were made from No. 40 copper and No. 36 constantan wire, double silk insulated and coated with paraffin. These wires were threaded through a small Bakelite compression cone, a steel conical disk and a nut as shown. On assembling and tightening the nut, the Bakelite was crushed around the wires, keeping them electrically insulated and sealing the opening. By connecting the constantan wires of the two gas couples together, the difference between the temperatures of the incoming and outgoing gas was read directly. This is the "rise" desired.

The temperature gradient on each side of the enlarged section was measured by similar junctions placed at the dots shown on Fig. 2. A constantan wire was placed along the outside of the tube with copper wires soldered on at known intervals. These junctions were electrically insulated from the steel by lacquer. By plotting the temperatures of the thermocouple points against their distance from one end, a smooth curve is obtained. The slope at any point gives the amount of heat passing that point; the heat quantity desired, however, is that passing the enlarged section containing the gas couple. The slope at one side gives the heat entering this section and the slope at the other gives that leaving; their average is taken as very close to the true value for the section.

All thermocouple readings were made using a low resistance Type HS Leeds and Northrup galvanometer and a White ten thousand microvolt single potentiometer. It was possible to estimate tenths of a microvolt from the galvanometer deflection. All switches and connections were copper and all junctions soldered. The galvanometer was mounted on a concrete pier set through the floor to eliminate vibration. The scale distance was one and one-half meters.

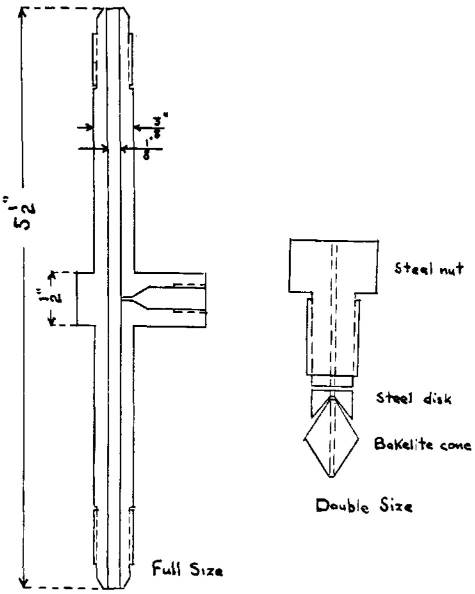

Fig. 3.—Gradient tube.

Auxiliary Measurements.—Other quantities measured during an experiment were (a) the pressure of the gas in the calorimeter tubing, (b) the pressure drop across the calorimeter, (c) the rate of flow of gas, (d) the heat of stirring and miscellaneous calorimetric loss. These measurements will be described in order.

A dead weight piston gage[5] was used as a standard and all Bourdon gages were frequently calibrated against it. Such calibrated gages were then used during experiments. The connections in the tubing at the upper end of each gradient tube permitted direct measurement of the gas pressure in the calorimeter. The piston gage is too sensitive for measurement of the flowing gas pressure and indicating gages are perfectly satisfactory. The change of C_p with pressure is greatest at low pressure and is of the order of 0.1% per atmosphere. Regulation to this accuracy is easily accomplished.

In order to measure the pressure drop of the flowing gas, a glass U-tube was connected to the two tee outlets. The use of glass is safe up to about 200 atmospheres. According to the laws of fluid flow the pressure drop for a given rate of flow of expanded

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[5] Publications from the Massachusetts Institute of Technology, 63, No. 28, July, 1929.

gas should decrease with pressure; the measured drop at low pressures therefore permits a calculation of the Joule–Thomson effect due to expansion in the calorimeter. The measured pressure difference at 100 atmospheres is less than one-fourth of an atmosphere. The error due to this is discussed later.

The rate of flow of gas is determined by measurements after expansion. In order to increase the sensitivity of control of the rate, a special valve was used having an extended handle. This valve was heated to counteract the cooling due to expansion since this seemed to improve the regulation. The gas then passed through a capillary flowmeter having an inclined tube to magnify small changes in head of the indicating liquid. This meter served merely to indicate constancy of rate. After humidification the gas passed through a wet meter. The rate was read with anaccurate stop watch. The wet meter was calibrated immediately after each experiment under exactly the same temperature and rate conditions as obtained during the experiment. The calibration consisted in weighing a small steel cylinder containing compressed gas, expanding this gas at the same rate used during the experiment, reading the indicated volume and time interval, and re-weighing the cylinder. The weight of gas was usually about 500 grams and readily could be weighed to one gram.

The heat of stirring and the losses due to radiation, convection, evaporation, etc., are determined by making measurements with no gas flowing but with all other conditions exactly as during a regular experiment. The heat put into the calorimeter as electrical energy plus the heat put in by the stirrer exactly equal the losses due to conduction along the steel tubing and all other losses. Since the electrical energy input and the conduction loss are accurately measured, their difference is equal to the difference between the heat of stirring and the other losses. This last difference varies only slightly with room temperature and may be used as a constant of the calorimeter under normal conditions.

Typical Results

Data taken from duplicate experiments at 200 atmospheres are shown in Table I.

TABLE I

RESULTS OF TYPICAL EXPERIMENTS

			Expt. 11	Expt. 12
Absolute pressure, atm.			200	200
Room temperature, °C.			24	20
Calorimeter temperature, °C.			29.8	29.6
Thermostat temperature, °C.			22.4	21.8
Gas temperature, rise, °C.			6.80	7.60
Voltmeter reading			11.2	11.0
Ammeter reading			0.569	0.562
Wet meter reading, cu. ft. per minute			1.418	1.183
Wt. of gas passed in calibration, g.			590	674
Vol. of gas passed in calibration, cu. ft.			18	20.0
Gas flow, moles per minute, corrected			1.66	1.422
Gradient tube temp. differences, °C. (enlarged section)	Inlet	Above	0.37	0.83
		Below	0.32	0.72
	Outlet	Above	0.44	0.99
		Below	0.38	0.85
Conductivity loss, calories per minute			0.4	0.9
Power input, corrected			93.2	89.9
Value of MC_p			8.25	8.31

A typical set of data for the evaluation of the heat of stirring and other corrections is given in Table II. The result, 2.20 calories per minute, is used to correct the power input in Table I.

TABLE II

TYPICAL SET OF DATA

Room temp., °C.	23.00
Calorimeter temp., °C.	29.80
Voltmeter reading	0.40
Ammeter reading	0.02
Power input, calories per minute	0.115
Temp. difference along inlet tube, °C.	0.86
Temp. difference along outlet tube, °C.	0.99
Cross sectional area of tubing, sq. cm.	0.633
Conductivity of tubing metal	0.110
Conduction loss inlet tube = (0.86 × 0.633 × 0.11 × 60)/3.33 =	1.08
Conduction loss outlet tube = (0.99 × 0.633 × 0.11 × 60)/3.33 =	1.24
Conduction loss (total), calories per minute	2.32
Net correction, calories per minute = 2.32 − 0.115 = 2.20	

Discussion of Errors

The reduction of the size of the errors in a problem such as this is of prime importance because approximate results have comparatively little value. A constant error would not change the relative value of the results but relative values as determined by this method would probably be inferior to those obtained from compressibility data.

The nitrogen used in these experiments was purchased from the Linde Air Products Company and was their regular grade of atmospheric nitrogen guaranteed to be better than 99% pure. The deoxidation by heated copper and drying should leave only a trace of argon present as an impurity. No analysis was made to determine the purity.

The pressure regulation was accurate to about an atmosphere during an experiment. This is about the order of the sensitivity of the gages used. These gages were calibrated frequently against the piston gage so no large error due to change in calibration was possible. The change of C_p with pressure is somewhat less than 0.1% per atmosphere change between one and two hundred atmospheres. The change is greater here than in any other interval so this error may be taken as less than 0.1%.

The voltmeter and ammeter used to measure the power input were calibrated against a Leeds and Northrup Type K potentiometer using Leeds and Northrup resistance boxes. The calibrations should be reliable to 0.1% of the full scale reading. The ammeter readings were taken at about half the scale value so an error of 0.2% might be introduced here. The voltmeter readings were usually close to the maximum scale value, so the error here would be of the order of 0.1%.

The error in the gas flow measurement can be reduced to the order of the power input error. The flowmeter reading can be held constant to 0.05% as checked against the wet meter with a stop watch. It is unlikely that any appreciable error is ever introduced due to the change in calibration of the wet meter during the experiment or between the experiments and the subsequent calibration. The flowmeter reading always has checked the wet meter reading when timed during the run and during the calibration. The weight of gas passed during calibration is usually about 500 g., accurate to one gram, so this error may be 0.2%.

The thermocouples have already been described in connection with the temperature measurements in the calorimeter. The calibration of the difference couples after being sealed into the tubes presented some difficulty. This was done by calibrating similar couples made at the same time as the difference couples. This calibration held to a tenth of a per cent. for several sets of couples, so all calculations have been made using the value found in this manner. The accuracy of the couples reading the temperature gradient along the tubes is not so important, as the quantities involved are small.

The errors introduced by the potentiometer circuit are probably small. All connecting wires are of insulated copper and the thermocouple switches are also of copper, so large parasitic thermal e.m.f.'s are improbable. The White potentiometer has an arrangement to correct for the e.m.f.'s in the potentiometer and galvanometer circuits. All difference readings can be read to a tenth of a microvolt, which is usually about 0.04% of the reading.

Conduction losses have been discussed also in connection with the calorimeter. They should introduce no larger error than 0.1 to 0.2% in the final result. The conduction losses during a run are rarely greater than 0.5 calorie per minute and it is not likely that the correction should be in error by more than 20% of this. The correction, called heat of stirring, depends for the most part on the conduction loss during a static calibration. The actual heat of stirring should be very constant, as the stirrer speed and liquid level are always the same. This correction has always been found to be 2.2 calories per minute with a variation of not more than ±0.1 calorie. If the largest variation is considered, the total result is affected by slightly over 0.1%.

A discussion of the errors in a flow gas calorimeter would be incomplete without some mention of the size of the Joule–Thomson effect due to the pressure drop in the calorimeter. At 100 atmospheres the pressure difference was less than one-fourth atmosphere for the largest flow used in regular experiments, *i. e.*, 1.45 cubic feet per minute. The pressure difference decreased with an increase in total pressure when the flow remained constant and increased when the total pressure was decreased. Using Bartlett's[6] value for $-(\mathrm{d}T)/(\mathrm{d}p)H$ of 0.14 calculated from his com-

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[6] Private communication.

pressibility data at 100 atmospheres, the temperature drop in expanding through the calorimeter would be slightly less than 0.04°. When the total temperature rise is 6°, this factor causes the final result to be too high by about 0.6%. This correction is less as the pressure is increased because $-(\mathrm{d}T/\mathrm{d}p)H$ approaches zero and finally changes sign.

Faulty technic in operating the apparatus is probably the main cause for errors in the final result. An average experiment takes about four hours and all conditions should be very constant for at least half an hour before the readings are taken. This is rather difficult to do since quite frequent gas compression is necessary with the high rates used.

During a satisfactory experiment the temperature of the calorimeter does not change more than 0.01° in half an hour. A correction can be applied for a slight temperature change by taking into account the water equivalent of the calorimeter and the rate of temperature change. The water equivalent is roughly one kilogram. A 0.01° rise indicates that 10 calories have been absorbed and if the rise takes place in 30 minutes, 0.3 calorie is being absorbed per minute. This correction is usually less than 0.5%. The results are reproducible to something better than 0.5% under good conditions.

Summary

A constant temperature continuous flow adiabatic calorimeter has been described. The apparatus for measurement of the specific heats of gases at ordinary temperatures and up to 1000 atmospheres pressure is described. Typical results for nitrogen at 200 atmospheres are given together with the method of calculation.

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[CONTRIBUTION FROM THE PICATINNY ARSENAL]

THE HEATS OF COMBUSTION AND FORMATION OF AROMATIC NITRO COMPOUNDS

BY WM. H. RINKENBACH[1]

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Although numerous investigators have studied the relationship existing between the constitution and thermochemical constants of organic compounds and particular attention has been paid to this relationship as regards nitro explosives, stereoisomers, homologs, etc., there still exist gaps in the values available for series of compounds and their derivatives. As the availability of such physico-chemical constants is of increasing importance and certain data of this nature were desired for use in connection with other work, it was considered desirable to make accurate determinations of the heats of combustion of a number of aromatic nitro com-

[1] Chief Chemist, Picatinny Arsenal, U. S. War Department.