[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

THE SPECIFIC HEATS OF GASES AT HIGH PRESSURES. II. METHOD AND APPARATUS AT HIGH TEMPERATURES[1]

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Introduction

This paper is the second of a series from this Laboratory reporting methods and measurements of the specific heats of gases at high pressures and over a range of temperatures. The first paper[2] described the apparatus developed for use at ordinary temperature and over a range of pressures to 1000 atmospheres. The present one describes a new calorimeter suitable for measurements over the entire range of pressures and up to temperatures of 350° or more. The experimental method is essentially the same as previously described, the new features being concerned entirely with the calorimeter and thermostat. The arrangement of gas storage cylinders, compressor and recirculating system is unchanged. In order to carry the measurements to higher temperatures, an entirely new calorimeter and thermostat were designed and built.

The Thermostat and Calorimeter

Reference to Fig. 1 in the first paper in this series[2] shows the function of the thermostat. This piece of apparatus must be capable of delivering gas at the desired pressure and temperature to the calorimeter at a constant rate of flow. For temperatures used in this work a satisfactory thermostat was built by coiling up about 3.5 meters of 6.5-mm. by 1.5-mm. steel tubing and casting a cylindrical block of copper around the coiled portion. An electric heater was wound on the casting and a Beckmann thermometer placed in a hole drilled in the casting. The temperature was manually controlled by external resistances and could be held to about 0.01°. The gas leaving the thermostat entered the calorimeter through a short, well-insulated tube.

The calorimeter is shown in Fig. 1. The gas, preheated to a temperature usually 5 or 6° below the calorimeter temperature, enters through the horizontal tube shown sectionally at the left.

It passes down through the vertical tube, also shown in section, through the coiled portion, then up through the right-hand tube and out through the horizontal tube shown in full. The coiled portion of the calorimeter tubing is embedded in a copper casting 7.5 cm. long and 6.4 cm. in diameter. This casting also contains an electric heater and a thermometer. By means of the heater the temperature of the calorimeter block is maintained constantly about 5 or 6° above the temperature of the thermostat. During its passage, therefore, the gas takes heat from the calorimeter and its temperature rises. The heat taken up by the gas is continuously supplied by the electric heater, so that the temperature of the calorimeter remains constant. To reduce as much as possible the heat losses by conduction, radiation, etc., the calorimeter is enclosed in a pyrex Dewar flask having an internal diameter of 7 cm. and an internal length of 29 cm. Surrounding

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[1] Presented at the Atlanta meeting of the American Chemical Society, April 9, 1930, before the Division of Physical and Inorganic Chemistry.

[2] Krase and Mackey, THIS JOURNAL, **52**, 108 (1930).

the Dewar flask is a heavy, cylindrical copper casting 46 cm. long, 10 cm. inside diameter, and having a wall 15.5 mm. thick. Copper disks close both ends of the cylinder; openings in the upper disk are provided for the necessary electrical leads, the thermometer, and the two steel tubes carrying thermocouple wires shown in the drawing. The other wires and the thermometer and heater are not shown. In order to operate the calorimeter adiabatically, the copper jacket is kept at the same temperature as the calorimeter by means of an electric resistance heater wound around the casting. A thermometer inserted in a hole drilled through the top disk and into the wall of the cylinder indicates the jacket temperature. A thick layer of insulation covers the jacket.

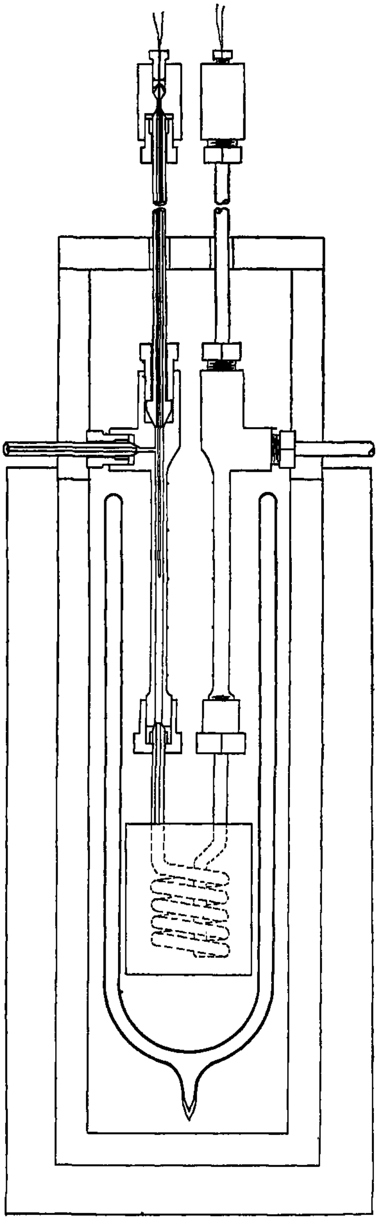
Fig. 1.

This calorimeter differs from the one previously described particularly because of certain improvements in the method of measuring the temperature rise of the flowing gas and the heat losses by conduction along the steel tubing.

As will be noted in Fig. 1, the wires comprising the couples for reading the rise in temperature of the flowing gas enter at the top ends of steel tubes extending about 13 cm. above the calorimeter cover. This arrangement not only removes the bakelite compression seals from the heated zone but also reduces the temperature gradient along the portion of the tubes through which the gas flows. This latter fact is extremely important in reducing heat conduction losses along the steel tubing. A secondary advantage, also, is the reduction in heat flow along the thermocouple wires as a result of this arrangement. The ends of the coiled calorimeter tubing are connected by "gradient" tubes having a uniform steel cross section for a length of 10 cm. to the gas inlet and outlet tubes. Five copper–constantan thermocouples equally spaced along each of these gradient tubes provide readings of the temperature drop along the tubes and thus data for calculating the heat flow away from the calorimeter block. The thermojunctions for measuring gas temperature rise are located at the midpoint of the uniform section of the gradient tubes. The thermocouples can be removed from position and calibrated without disturbing the bakelite seals or other connections.

For calorimeter temperatures to 150° Beckmann thermometers are most satisfactory. Since these thermometers are used only to indicate constancy of temperature, the absolute temperature need be known only to about one-tenth of a degree. The settings were checked using liquids of known boiling points as calibration standards.

Experimental Methods

Reference to the first paper is suggested for experimental details. In addition to the measurements described previously it was thought desirable to know the absolute temperature of the gas leaving the calorimeter. The usual experimental routine involved measuring only the gas temperature rise—not its absolute temperature. Since the question of average gas temperature for a given measurement is important for accurate work, a number of experiments were performed designed to measure the exit temperature of the gas. A copper–constantan couple similar to those used in the calorimeter was inserted together with the Beckmann thermometer in the jacket well and the constantan wire connected with that of the couple in the exit tube of the calorimeter. If the exit gas temperature and jacket temperature were the same, the reading of the couples would be zero. The results of a number of such trials showed that the exit gas reached practically the same temperature as the calorimeter within an experimental error of about 0.06°. Practically perfect heat transfer was, therefore, accomplished between gas and calorimeter and the temperature of the calorimeter may be taken as the gas temperature for all purposes.

In this work, the rates of gas flow used ranged from 0.7 to 1.5 moles per minute and the results were entirely independent of rate of flow, indicating the absence of systematic errors in measurements. Further refinements in measuring the rate of gas flow involved enclosing the indicating capillary meter and the wet meter as well as the gas humidifier in a compartment whose temperature was thermostatically controlled. Small changes in temperature were sufficient to alter the calibration of the wet meter considerably.

The use of an adiabatic calorimeter at elevated temperatures involves heating the jacket to practically the same temperature as the calorimeter. In the present case this was accomplished by winding a nichrome electrical resistance coil on the copper casting and passing a 110-volt alternating current through it, controlled by an external resistance. It was found that this arrangement generated heat by induction in the copper casting inside the Dewar flask. The effect was very considerably reduced by using a non-inductive winding on the jacket but was not entirely eliminated. Separate measurement of this induced heat was, therefore, necessary at each calorimeter temperature used. The use of direct current for jacket heating was the obvious remedy but this, unfortunately, was not available. The correction was measured by using the same gas flow as during a regular experiment but raising the thermostat temperature so that the gas entered the calorimeter at practically the calorimeter temperature. No heat was supplied to the calorimeter proper except that received by induction from the jacket current. The rise in gas temperature was measured and this subtracted from the observed rise in the regular experiment. The correction measured in this way not only included the induced heat but also any heat change due to a Joule–Thomson effect within the calorimeter.

Table I shows typical results for nitrogen from 30 to 150° at 500 atmospheres pressure. A subsequent paper will give complete data for nitrogen over a range of pressures to 700 atmospheres and temperatures to 150°.

TABLE I

TYPICAL RESULTS FOR NITROGEN

Experiment no.	30	80	108	122
Absolute pressure, atm.	500	500	500	500
Av. calorimeter temp., °C.	30	50	100	150
Gas temp. rise, °C.	6.85	6.84	7.63	6.78
Gas flow, moles/min.	1.412	1.496	1.335	1.383
Heat loss by conduction	0.1	0.15	0.2	0.3
Heat gain by induction	...	0.5	1.4	4.7
Corrected power input	88.2	90.6	85.4	76.5
Molal heat capacity	9.12	8.85	8.39	8.13

Summary

A constant-temperature, adiabatic, flow calorimeter for the measurement of specific heats of gases at high pressures and temperatures has been developed. Typical results for nitrogen together with the methods of measurement and calculation are given.

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