A FLOW CALORIMETER FOR SPECIFIC HEATS OF GASES

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ABSTRACT

The calorimeter was designed for measuring the specific heats of gases accurately at pressures below 100 atmospheres and temperatures below 150° C. It is of the flow type with provision for adding heat electrically and for measuring the temperature rise by means of platinum resistance thermometers. Refinements have been adopted to keep the size within limits appropriate for moderately small samples of pure materials, to avoid thermal leakage, and to control conditions which affect steadiness. Thermal leakage by solid conduction was minimized by the use of appropriate lengths, sizes, and materials for all tubing and supports, leakage by gaseous conduction and convection was avoided by evacuating the space surrounding the calorimeter system, and leakage by radiation was opposed by exposing the calorimeter system only to surfaces maintained at the respective temperatures of the system within.

The calorimeter was made responsive by avoiding large or detached heat capacities, but, in addition, means were provided for keeping both power input and flow constant. Constancy of flow was accomplished through automatic control of the pressure in the calorimeter supply line and protection of the discharge line from the effect of fluctuations in condenser pressure. Provision was made for evaluating the small corrections for residual thermal leakage and for the effect of pressure drop through the calorimeter. Special accessory apparatus was provided for the control and measurement of temperatures and pressures.

The instrument has been tested in an extensive series of measurements of the specific heat of ammonia (published separately) at pressures between 0.5 and 20 atmospheres and temperatures between minus 15 and 150° C.

CONTENTS

I. INTRODUCTION

The calorimeter described here was developed for the accurate measurement of the specific heat of gases at pressures below 100 atmospheres and temperatures below 150° C. The immediate purpose of the instrument was for the determination of the specific heat of superheated ammonia vapor for use in preparing tables of the thermodynamic properties of ammonia. The measurements of ammonia have been completed and described elsewhere.[1] The purpose of this paper is to set forth the essential facts relating to the design, construction, and operation of the calorimeter.

Measurements of the specific heat of gases are, in general, more difficult than of solids and liquids because larger volumes of gas must usually be subjected to the experimental process in order to have heat quantities large enough for accurate measurement. The continuous-flow electric method, however, overcomes this difficulty to some extent.

This method does not necessitate the large apparatus required to exchange heat with the entire sample of gas all at once. By allowing only small portions to be subjected to the process at any instant the continuous-flow method allows heat to be exchanged with the gas at a rate which permits accurate control and measurement. Another advantage is that the thermal capacity of the instrument may be kept small and need not be known. These attributes of the flow method led to the choice of a flow calorimeter as the appropriate instrument for determining the specific heat of superheated ammonia vapor.

The principle of the continuous-flow electric method for determining the specific heat of a fluid is simple. The procedure is to observe the rise in temperature produced by a measured electric

[1] Specific Heat of Superheated Ammonia Vapor. B. S. Sci. Paper No. 501. Refrigerating Eng., 10, p. 145; 1923.

power added as heat to a stream of fluid flowing through the calorimeter at a steady measured rate. In the apparatus described here the rate of flow is measured by condensing and weighing the vapor discharged from the calorimeter in some definite time interval. The electric power input is obtained from measurements of the potential drop across and the current flowing through a resistor, by means of which the energy is transformed to heat and added to the vapor. The rise in temperature of the vapor is measured by two platinum resistance thermometers in the vapor stream, one before and one after the electric heater.

The accuracy of the specific heat determinations depends directly upon the accuracy with which these quantities are measured, and this in turn depends to a large extent upon the steadiness of the conditions while measurements are being made. One of the important advantages of this method is that effects which could lead to constant or systematic errors may be detected and eliminated by varying experimental conditions and noting the results. Another important advantage is that the steady condition required by the method favors accuracy of the observations because these may be made deliberately.

Other quantities which enter into the determination of the specific heat as small corrections are heat leakage and the effect of pressure drop. The pressure and temperature must be observed as independent variables which define the state of the vapor.

II. PREVIOUS DEVELOPMENT OF METHOD

The continuous-flow electric method of calorimetry was used for measurements of the specific heat of liquids by Callendar and Barnes.[2] Later it was adopted for measurements of the specific heat of gases by a number of experimenters, each of whom developed the method for a special purpose. Some of the chief features of their instruments will now be briefly mentioned without attempting to do justice to these experimenters by thoroughly reviewing their work, but merely illustrating how the nature of their experimental problem may affect the design of an instrument.

The calorimeter of Swann[3] was used for air and carbon dioxide at atmospheric pressure only and at the temperatures of 20 and 100° C. The flows employed varied from 0.3 to 1.0 g/sec. The thermal leakage correction was rather large, amounting to from 8 to 20 per cent of the heat added, but was determined with such remarkable nicety that in spite of this obstacle to accuracy Swann's results agree well with the most reliable determinations comparable with them.

[2] Report of Br. Assoc., pp. 552–553; 1897. Phil. Trans., 199 A., pp. 55–263; 1902.
[3] Phil. Trans., 210, pp. 199–238; 1910. Proc. R. S. A., 82, pp. 147–149; 1909.

The instrument of Scheel and Heuse [4] was likewise used for air and carbon dioxide, but inasmuch as it was smaller and hence suitable for smaller flows it was also well adapted for the measurements on 10 other gases which were less available in large quantities in the pure state than air and carbon dioxide. Flows from 0.02 to 0.1 g/sec. were used. The calorimeter was constructed chiefly of glass and was used for measurements at atmospheric pressure and at temperatures from 20 down to −182° C. Large thermal leakages were avoided by the use of vacuum insulation and radiation shields. The total correction for thermal leakage was only a few tenths of a per cent, and the results were probably accurate to one or two tenths per cent.

In contrast to both the foregoing instruments the calorimeter of Holborn and Jakob [5] was used for air up to 300 atmospheres pressure, but only one mean temperature of about 60° C. This calorimeter was large, and was built chiefly of steel to withstand these high pressures. Its heat capacity was so large that even with flows as great as from 2.5 to 11 g/sec. three to four hours were required to reach the steady state necessary for making observations. Extremely high accuracy could, of course, not be expected, but the results were probably accurate to within 1 per cent in spite of the difficulties incident to the control of such high pressures.

In further contrast the type of instrument used by Knoblauch [6] and his associates was designed to determine the dependence of the specific heat of steam on both temperature and pressure in the range of steam engineering practice. These added variations of conditions, of course, increased the experimental difficulties, and it is not surprising to find accounts in their records of thermal leakage corrections of from 5 to 40 per cent. Advantage was taken of the possibility of using large quantities of steam in the experiment. Flows of from 5 to 20 g/sec. were used, and the preference of this group of experimenters for apparatus of large proportions is evident. In such a comprehensive series of experiments an accuracy of 2 per cent commands respect.

The foregoing examples show how different characteristics have been developed in several calorimeters. The requirements of the ammonia investigation presented new problems in calorimeter design, for in order to determine specific heat accurately over a wide range of pressure and temperature an instrument was needed which combined the virtues and avoided the faults of former calorimeters.

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[4] Ann. d. Phys., 37, pp. 79–95; 1912; 40, pp. 473–492; 1913; 59, 86–94; 1919.

[5] Zs. Verein Deutsch Ing., 58, pp. 1429–1436; 1914; 61, 146–147; 1917.

[6] Phys. Zs., 6, pp. 801–802, 1905. Zs. Verein Deutsch Ing., 51, pp. 81–88, 1907; 55, pp. 665–673, 1911; 59, pp. 376–379, 1915; 66, pp. 410–423, 1922.

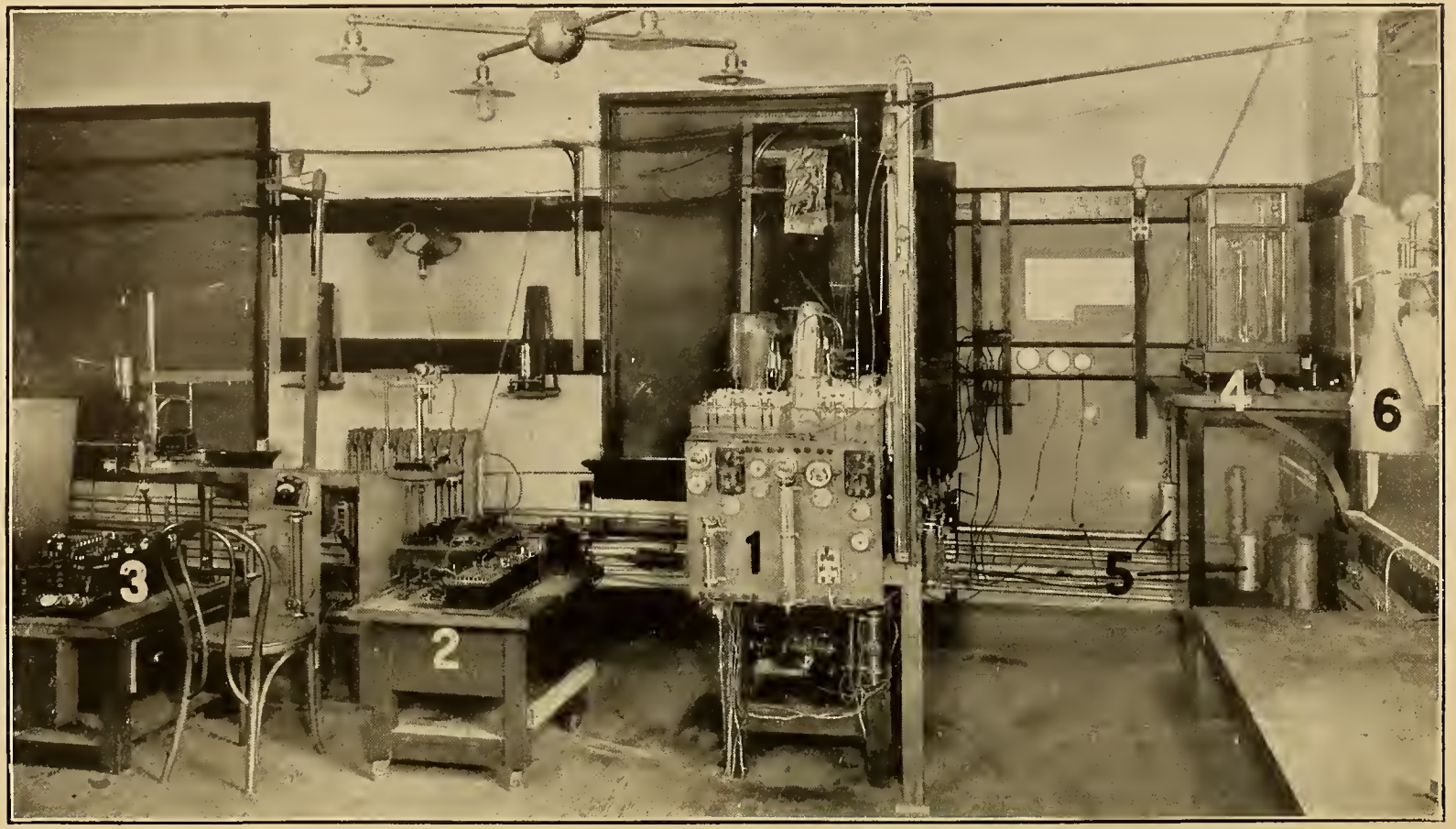

FIG. 1.—*General view of experimental set-up*

1, Assembled calorimeter with operating accessories; 2, potentiometer for observing thermocouples; 3, bridge for observing resistance thermometers; 4, balance and weighing chamber; 5, ammonia containers; 6, vacuum pump

III. GENERAL DESCRIPTION AND ARRANGEMENT OF APPARATUS

Before attempting to describe any of the details of design, construction, and operation of the somewhat complicated equipment, a general view of which is shown in Figure 1, we shall first indicate the general scheme of the calorimeter and its immediate accessories and trace the path of the vapor in the course of an experiment. For

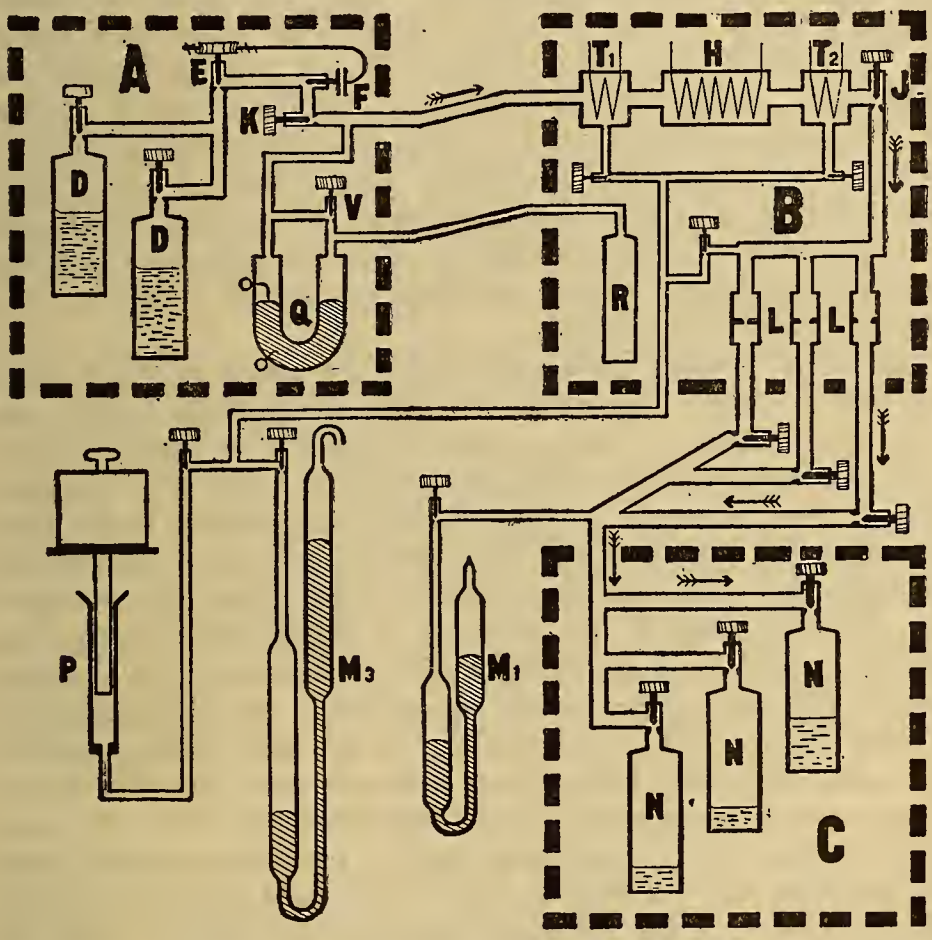

FIG. 2.—*Diagram of general arrangement*

A, boiler bath. *B*, calorimeter bath. *C*, condenser bath. *D*, reservoirs used as evaporators. *E*, *F*, and *K*, valves for regulating rate of flow. *H*, heater cell. T_1 and T_2, thermometer cells. *J*, reducing valve. *L*, flow control orifices. *N*, reservoirs used as condensers. M_1, one-atmosphere mercury manometer. M_3, three-atmosphere mercury manometer. *P*, piston gauge. *Q*, manometer for actuating pressure regulator. *V*, by-pass valve. *R*, reservoir for reference pressure.

illustrative purposes we shall describe the apparatus as used with ammonia.

A diagram of the arrangement of the important parts is shown in Figure 2. The three large heavily dotted squares, *A*, *B*, and *C*, represent stirred, thermally controlled liquid baths, and the parts within any one of these squares are supposed to be at or near that particular bath temperature. The first, or "boiler bath," indicated by the square *A*, furnishes heat to evaporate the ammonia in the

reservoirs D, which are immersed in the bath. The evaporation takes place at a pressure from 3 to 8 atmospheres higher than the working pressure in the calorimeter. From these reservoirs the vapor passes through three needle valves in series, where the pressure is reduced and regulated. Thus far the path of the vapor has been in a region controlled to a uniform temperature. From here the path of the vapor next leads into the second or calorimeter bath B, which is another region of uniform temperature. Here the vapor first passes through a length of tube to bring it to the bath temperature and is then led into the calorimeter itself. Within the calorimeter the vapor continues successively through thermometer cell T_1, heater cell H, and thermometer cell T_2. From the calorimeter the path of the vapor leads through the reducing valve J, through one or more control orifices in parallel, and there leaves the calorimeter bath and enters the third or condenser bath C. Here the ammonia is led into one of the reservoirs N, which are cooled by the bath in order to condense and collect the ammonia.

The cell H contains the electric heater, by means of which measured heat is added to the stream of vapor. Each of the cells T_1 and T_2 contains a resistance thermometer to measure the temperature of the vapor, one before and the other after the addition of the heat. Each of these thermometer cells also has a connection to the pressure-measuring apparatus which permits observation of the pressure simultaneously with the temperature. Two gauges are provided, one a mercury gauge M_3 for pressures up to three atmospheres, and the other a piston gauge P for higher pressures up to 100 atmospheres. The pressure just before the orifices L may also be observed by these gauges. The condenser line is provided with a mercury manometer M_1, which will indicate pressures under one atmosphere.

The mercury manometer Q, with electric contact wires, the reservoir R, located in the calorimeter bath to provide a constant reference pressure, and the by-pass valve V are used, together with the valves E and F, in the automatic regulation of pressure before the calorimeter. This pressure regulation combined with the controlling effect of the orifices L accomplishes the regulation of the flow and keeps it constant. This constancy of flow is necessary to maintain that steady state which is a vital requirement of the continuous-flow method of calorimetry.

IV. DESCRIPTION OF CALORIMETER

Although the term "calorimeter" might be applied to the entire group of apparatus used to measure the heat in an experimental process, this term will, for convenience, be used here to denote that portion of the apparatus in which the experimental process occurs; that is, the place where this process is isolated from external influ-

ences so that it may be accurately controlled and observed. We shall next take up the description of this calorimeter as the nucleus of the experimental equipment and the part to which a large share of the study and labor has been devoted in developing the complete apparatus.

The calorimeter was designed and constructed primarily for measuring the specific heat of ammonia vapor at temperatures up to 150° C. and at pressures up to 20 atmospheres. It was found convenient to make the instrument suitable for pressures as high as 100 atmospheres, and this opportunity was taken to increase its utility for measurements on other vapors and gases. To meet the requirements of the ammonia research, it was desirable to combine into one instrument a number of features which are advantageous but which are not usually all associated in a single-flow calorimeter. Among these features are: Utility over a wide range of temperature and pressure, small size and heat capacity, small thermal leakage, and means for accurately observing temperature and heat added. The advantages of some of these features are obvious, and those of others will appear as we proceed.

Simplification of the particular thermal process which we wish to observe in a vapor has been provided for in this case by the development of an instrument of somewhat complicated construction. In order not to pass too abruptly from the general conception of how the whole apparatus works to the details of why and how each particular part was made as it is, we will first outline the basic principles of some of the more complicated and vital features of the calorimeter, then describe the actual construction and later elaborate the details.

1. CONTROL OF THERMAL LEAKAGE

The keynote of this description is the manner of effecting conservation of the heat added to the system within which it is proposed to account for the amount of vapor passing through, its state, and the amount of energy added. It is a fundamental fact that the extent of our ability to avoid unmeasured thermal leakage limits the accuracy of determining the net heat added, which is a direct factor of the result. Added to this fact the inherent limitation on the thermal insulating properties of materials gives this feature the predominating influence in the design.

In this "calorimeter system," which is that part of the calorimeter in good thermal contact with the vapor stream between and including the two thermometer cells, loss or gain of heat other than through the electric heater may occur by (1) conduction, either along the tubes in which the ammonia flows, the supports of the system, or the

electric lead wires; (2) gaseous conduction and convection; and (3) radiation. In designing the features to combat the tendency for thermal leakage two obvious courses were followed: First, to interpose resistance in the path of the leakage, and, second, to avoid temperature differences which would induce leakage, by controlling the temperatures of the calorimeter system and of the bodies which surround it. As a result of these measures it has been found possible to keep the corrections for thermal leakage small and accurately determinable.

In principle, gaseous conduction and convection is the simplest to control of these three kinds of heat transfer, for the exhaustion of the space surrounding the calorimeter system to a sufficiently low pressure will reduce the heat transfer by these means to a negligible amount, regardless of shape. Pressures below 0.001 mm of mercury were low enough, and this degree of exhaustion in a metal envelope is not difficult to maintain after the plumbing has been put in order.

Thermal leakage by radiation is controlled by surrounding the system with metal guards maintained at temperatures nearly identi-

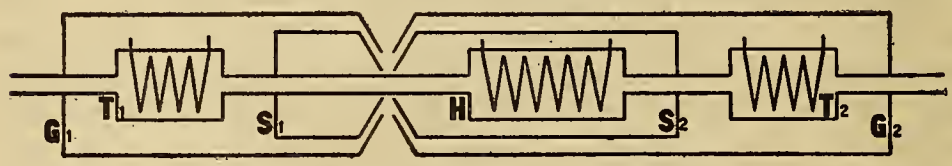

FIG. 3.—*Diagram of thermal shielding*

cal with the temperatures of the exposed parts of the system within. To make this possible, a configuration of the system was devised which would keep practically all the exposed surface at either the initial or the final temperature of the vapor. Only two protecting guards were then necessary, one at each temperature. One of these was kept at the initial temperature by the incoming gas stream, and the other was controlled by an auxiliary electric heater and regulated by the observer to maintain that guard surface close to the temperature of the exposed surface of the system within.

It is evident from the nature of the flow method that there must be a temperature rise along the system between the two thermometers. This rise will be most abrupt in the region where the gas first encounters the heater. To permit the best thermal guarding, it is desirable that the exposed surface of the system be differentiated sharply into two parts at the initial and final temperatures. The general scheme of doing this is shown in Figure 3, which is a diagram illustrating the principle of the method of shielding from radiation losses.

2. CONTROL OF RADIATION LOSSES

In this diagram T_1, H, and T_2 represent, respectively, the first thermometer cell, heater cell, and second thermometer cell with the same simple arrangement of connections between them as shown in Figure 2. S_1 represents a metal shield attached to the vapor tube in the region where the temperature of the tube is that of the entering vapor indicated by thermometer at T_1, unaltered as yet by approach to the heater. This shield surrounds and extends forward over a portion of the gas tube toward the heater. A similar shield S_2 is attached where the gas tube has attained the final higher temperature to be indicated by the thermometer at T_2. This shield surrounds and extends back over the gas tube and heater cell to a point near the end of shield S_1. These two shields envelop the entire region where the gas is heated, except a short length between the shields. Each of the shields is made of a good thermal conductor and well coupled thermally with the gas stream where attached. The shields form part of the calorimeter system and accomplish the sharp differentiation of exposed surface which is desired. Heat radiated from parts of the system having an excess of temperature is either reflected or led by conduction back to other parts of the system having a deficiency of temperature. The conducting power of these paths may be chosen so that the temperatures of the shields depart but little from uniformity.

It is now a simple matter to add the two copper guards G_1 and G_2, each coupled to the gas stream and each surrounding that part of the system which is at the corresponding temperature. Of course, provision must be made to compensate these guards for loss or gain of heat so that they may be kept at the temperatures of the parts which they envelop. The manner of applying these principles of guarding against radiation losses is to some extent dependent upon the means for controlling conduction along the vapor-flow tube, and as a result of these combined influences the actual construction is not nearly so simple as that of the diagram.

Consideration has been given to choice of materials for the flow tubes and the disposition of these materials as to size, thickness, and course of the tubes in order to obtain thermal separation and thermal coupling, each in the place where it will favor the control of the heat. A better appreciation of how these various factors affect the design may be gained from the description of the actual construction than from an abstract discussion of the principles involved. Analysis of the heat transfer between a stream of vapor and the tube in which it flows was found useful in perfecting the design, and after the design has taken concrete form most of the vital features which have been introduced to control thermal leakage appear ob-

vious. After all, the experimental test of actual performance of the apparatus is more to be trusted than preliminary calculations as to what the apparatus ought to do, and we may regard the substantiation of the expected performance in this case as a confirmation of the principles which were followed.

3. CONSTRUCTION

An idea of the actual figure of the calorimeter may be obtained from Figures 4 and 5. In the sectional drawing German silver is represented by light lines and copper by heavy lines. We may recognize again the first thermometer cell T_1, heater cell H, and second thermometer cell T_2, which were indicated diagrammatically in Figures 2 and 3.

The figure of the flow channel and the manner in which the vapor is led along to the various regions where its state is altered and observed are important. We will again trace the path of the vapor through this very important part of the instrument in order to complete the explanation of the way the chief parts are intended to work and to get a clear idea of thermal shielding.

Before entering the calorimeter the vapor passes through a tempering coil (shown in fig. 6) for the purpose of bringing the vapor to the temperature of the calorimeter bath. This coil contains 75 cm of tubing wound into a helical form and bathed externally by the bath liquid. It is important that on entering the calorimeter the vapor and the parts of the calorimeter in contact with it should be near equilibrium with the temperature of the bath. To this end the vapor next passes through the coil B, which is soldered to the calorimeter casing or envelope, and is bathed by the liquid. The vapor tube passes through the envelope and across the vacuum space to the copper guard G_1. There are 27 cm of tube soldered to this guard, winding spirally upward and then back to the lower end, where it passes inside the guard G_1 to the entrance of thermometer cell T_1. It is intended that the guard G_1 should thus be kept automatically as nearly as possible at the temperature of the vapor as it enters the thermometer cell in order that the initial temperature of the vapor may be correctly indicated.

The thermometer cell T_1 and its counterpart T_2 are cylindrical shells of German silver. The initial velocity of the vapor at the entrance is dissipated by admitting the stream through four radial ports, which can not well be shown. The construction of these cells and of the bare platinum wire coils, which serve as thermometers, and also the heater cell and heating coil will be described later.

The vapor is led across from the guard G_1 through a German-silver tube. This is a place where a good thermal connection would

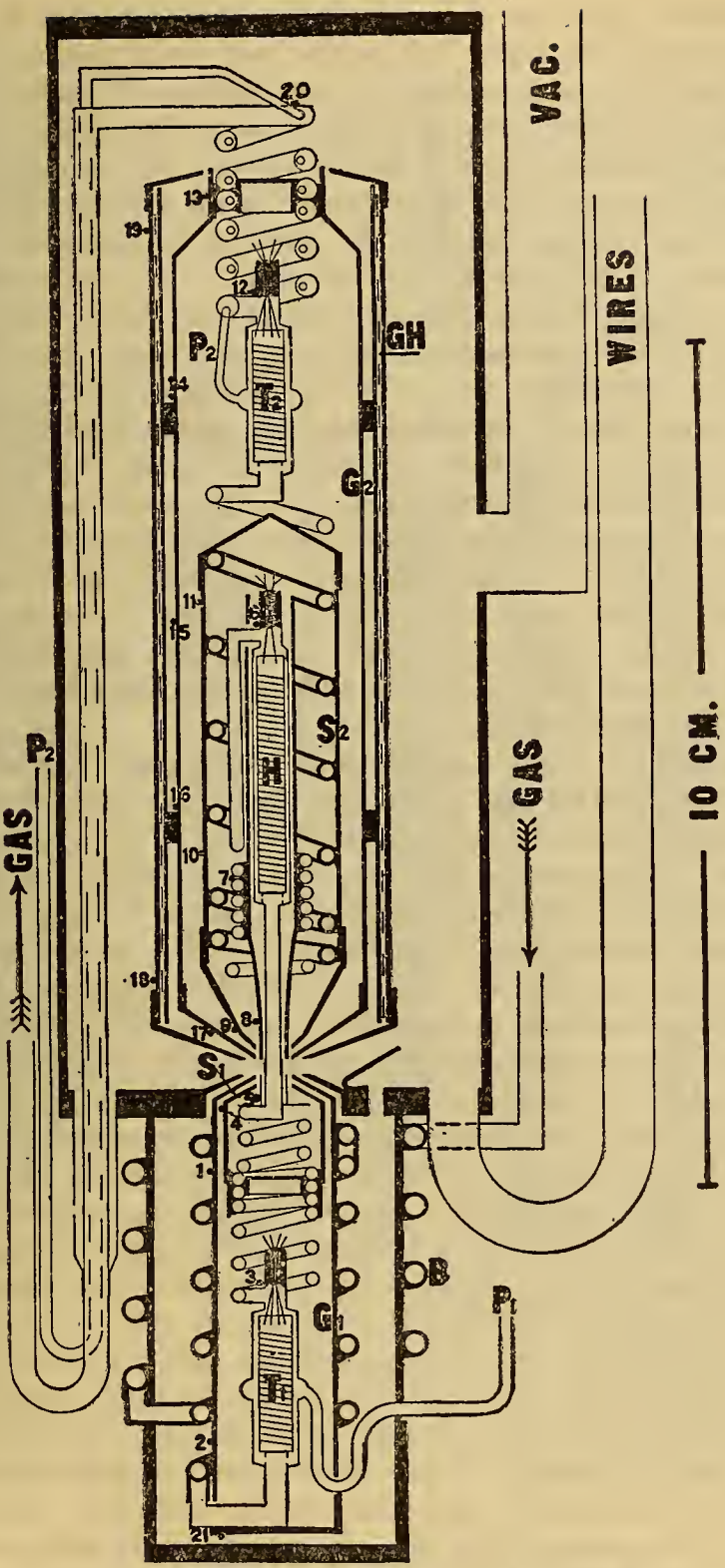

FIG. 4.—*Sectional drawing of calorimeter system (full scale)*

Copper in heavy lines; german silver in light lines; location of thermojunctions indicated by numbered dots. *B*, helix soldered to envelope. *H*, heater cell. T_1 and T_2, thermometers. S_1 and S_2, isothermal shields for conserving heat in calorimeter system. G_1 and G_2, isothermal guards for protecting calorimeter system from thermal leakage. P_1 and P_2, pressure connections to thermometer cells. *GH*, heater for guard G_2. *VAC*, connection to vacuum pump

be undesirable, for here the vapor leaves indeterminate sources of heat and enters the region where the heat exchanged is to be accounted for. The connection P_1 to the thermometer cell is for determining the initial pressure of the vapor. In passing from the thermometer cell to the heater cell the vapor is led through a coil of German-silver tube. This tube contain in all a length of about 21 cm before reaching the straight tube entering the heater cell. About three turns of this tube containing about 9 cm are soldered together in a copper bushing to furnish attachment for the copper shield S_1. This shield is soldered to the bushing, and is thus closely coupled thermally to the stream of vapor. The shield provides an isothermal surface for this part of the system near the temperature of the guard G_1, to which it is opposed. It screens the parts within, so that radiation is intercepted and saved to the system according to the principles previously explained. A copper disk attached in the axis intercepts radiation which might otherwise reach the thermometer cell. Just at the upper extremity of this coil of tubing there is attached another radiation shield made up of a flat circular disk normal to the straight axial tube and bearing a short length of tube coaxial with the flow tube.

At this point in the system where the flow passes from the region of initial temperature into the region where the vapor is heated the construction is somewhat complicated and fine. The system is narrowed or necked down to the bare essentials required to transmit the vapor, and the shields are brought as close to the vapor tube and to each other as mechanical technique will permit, so that there may be left exposed to radiation only the least possible amount of surface at an indeterminate and uncontrolled temperature. The function of the "neck" is to confine definitely the flow not only of the ammonia vapor but also the quantities of heat with which we are dealing.

The vapor enters the heater cell H and receives the energy which is added through the electric heater. It is impossible in so restricted a space as this to distribute the heat supplied so perfectly as to avoid temperature differences. It is the purpose of the parts through which the vapor next flows to equalize the differences in temperature between the vapor and its flow channel and to provide temperature control of shielding surfaces to protect the inclosed parts from loss or gain of heat. At the upper end of the heater cell the channel turns abruptly to the side and again downward for a few centimeters and then winds spirally for five turns about the cylindrical copper shell which incloses the heater cell itself. The flow tube here is soldered to this copper shell, which thus serves to intercept radiation and at the same time constitutes a first approximation to an isothermal surface. After thermal contact with this sheath the vapor is next led through the coiled tube soldered to the cylindrical copper

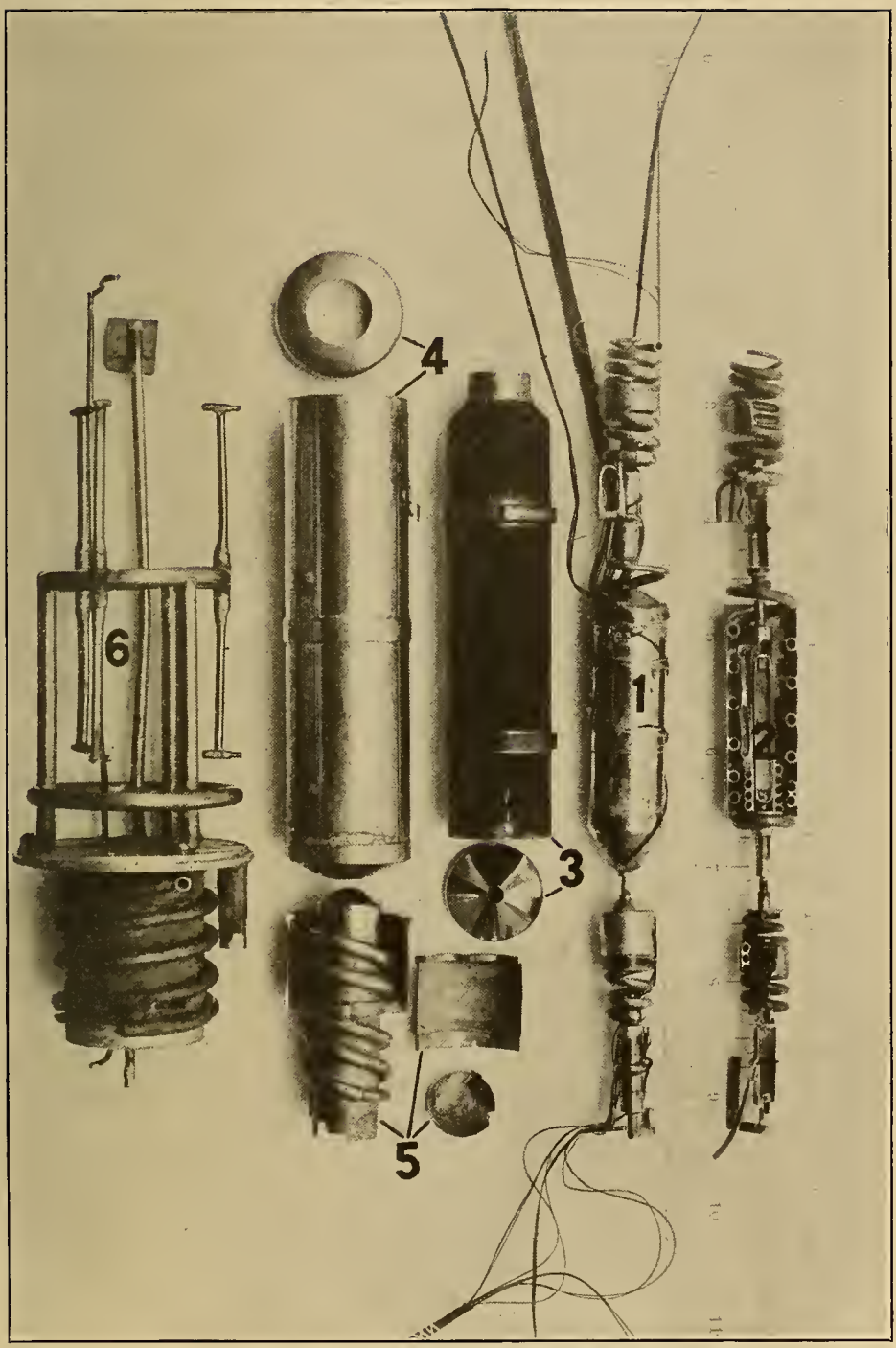

FIG. 5.—*Parts of calorimeter, 3/5 size*

1. Calorimeter system. 2. Sectioned duplicate. 3. Guard, G_2. 4. Guard heater, GH. 5. Guard, G_1. 6. Supporting frame and part of envelope

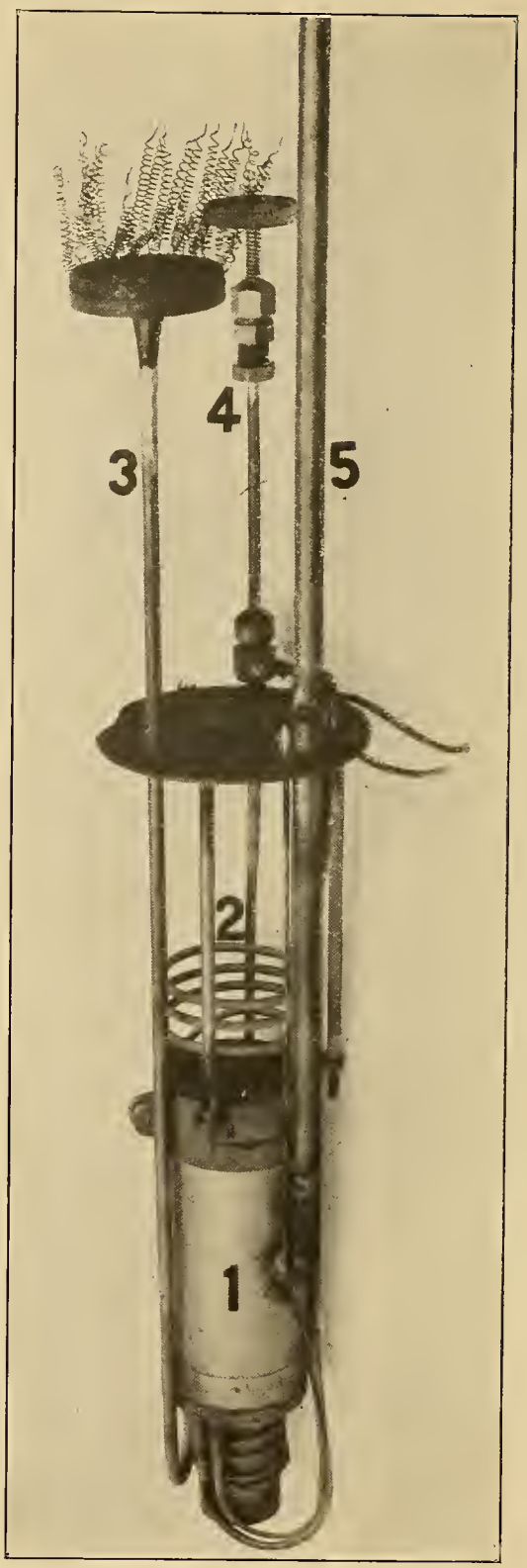

FIG. 6.—*Assembled calorimeter, 1/3 size*

1. Calorimeter casing or envelope. 2. Tempering coil. 3. Electric leads. 4. Reducing valve. 5. Connection to vacuum pump

shield S_2, so that the shield and vapor tend to approach the same temperature; that is, the final temperature of the vapor. A single spiral turn of German-silver tube carries this isothermal stream of vapor to the second thermometer cell T_2. From here the vapor passes on through the six turns of spiral German-silver tube to the straight channel, which, bending abruptly, then leads down and out through the wall of the casing into the bath again. Two turns of this spiral coil are attached to a bushing which bears the cylindrical guard G_2, with conical extremities and also a disk in the axis, very similar to the manner of attaching shield S_1. The pressure tube P_2 is led out inside the flow tube to prevent conduction along this pressure tube between the thermometer cell and the casing which is at a much lower temperature. The guard G_2 incloses virtually all the exposed portion of the calorimeter system which is at the higher or final temperature of the ammonia vapor. This guard is maintained at this same temperature by an electric heater. This heater is located in the annular cylindrical space between two concentric copper shells and is called the guard heater *GH*. Of course, most of the heat supplied to this heater escapes by radiation to the casing about it, the small part supplied as required to the guard G_2 being transmitted either through the two close-fitting bushing rings between guard and heater or else getting across by radiation. At this place thermal coupling is needed, but it should not cause any inequality in temperature of the guard. Thermocouples on the guard, on the shield, and on the thermometer cell permit the relative temperatures of these parts to be observed, and this means is used for gauging the regulation of temperature of the guard so as to annul the thermal leakage to or from the calorimeter system.

Having described the essentials of the calorimetric scheme, we may now devote a little attention to some of the finer details which individually seem somewhat trivial, yet each of which has been the subject of close analytical study, of careful development of handicraft in fashioning or assembling, and of thorough test as to mechanical integrity.

4. DETAILS OF SPECIAL PARTS, ASSEMBLING, AND TESTS

There are several details of construction of the calorimeter which, although of themselves not vitally essential, yet taken together have affected the development of the design considerably. A few of these will be mentioned briefly, not as models of craftsmanship to be recommended for others to follow, but as a group of problems in applied mechanical technique which may be of interest either to the close student of experimental arts or to the critic.

The size or scale upon which the apparatus has been built has affected not only its utility but also its construction. In order to avoid useless bulk and thermal capacity which would require either preparation of unnecessarily large amounts of purified ammonia, or else sacrifice either time or accuracy in operation, some effort was made to keep the proportions small. In this respect the flow channel within the calorimeter and the electric elements installed in it were, perhaps, the most severe test of resources, for this portion really forms the nucleus around which the rest developed, and therefore here more than elsewhere the reduction of size would be limited either by what would be appropriate or by what could be constructed. The actual size may be judged by reference to the scale of the illustrations.

The thermometer cells and heater cell were made of cylindrical tubes, each having two end caps fitted as plugs which could be soldered in place. The caps carried suitable fittings for attaching to the flow tubes. The lower caps were attached by hard solder, the upper ones were soldered in place with pure tin after installing the respective resistance coils. The construction of these coils was similar in thermometer and heater except for size and materials. Each thermometer coil contained about 54 cm of platinum wire 0.05 mm in diameter wound about 7 turns to the millimeter on a notched strip of mica cut to fit snugly into the cell. The potential terminal arrangement of leads was chosen, and the four platinum leads from each thermometer were brought out of the upper end of thermometer cell through a glass seal. This seal was made in a small steel tube which fitted the tube extending up from the cap and was soldered in with tin. The mica strip was borne by a clip inside this upper cap. This semirigid attachment served to hold the coil while connecting the leads and installing in the cell. Soldering the end cap in place in the cell completed it as a unit to be assembled with the other parts of the flow channel after test. In the fashioning of the whole central element of the calorimeter with its helical coils and radiation shields there was considerable nice metal forming and hard soldering which required perseverance to bring to satisfactory completion. The helical coils of thin-walled tube were made by bending about forms while filled with ice. The ice was formed by filling the tube with water, closing the ends with corks and immersing the tube in a bath of crushed ice and salt. The advantages of ice as a filler for bending thin tubing are its effectiveness, cleanliness, and the facility with which it may be introduced and removed. This method makes it very easy to reanneal the metal when the curvature is such that several stages in the bending are necessary to avoid fracture or buckling of the thin metal. The heater coil H contained about 100 ohms of

bare calido wire wound on a mica strip very much like the thermometer. Current leads of platinum wire pass through a glass seal, and potential leads were attached just outside this seal.

The thermometers had fundamental intervals of 10.8 and 10.7 ohms, so that a sensitivity of the temperature measuring apparatus to 0.001° C. was not at all difficult to secure. As to the type of lead connections to the thermometers and the manner of their use it might seem that the use of a pair of differentially connected Callendar type thermometers was appropriate here, as such an arrangement would have required only a single reading of resistance to evaluate the temperature rise instead of the four readings necessary with the two potential terminal thermometers. Nevertheless, the choice of the two potential terminal type of thermometer was made deliberately for the purpose of obtaining increased accuracy. One advantage was that small leads could be used, which facilitated installation and limited conduction of heat to or from the thermometer cells. The principal advantage, however, of this type of connection is that it requires the resistance of the leads to remain constant only during the two readings necessary for each determination of a temperature in order that the resulting thermometer resistance shall be dependent only on the coil within the thermometer cell. This is a particular advantage in this case where the leads had to be brought out through a pressure seal. It is not true of the compensated lead type, and consequently the use of that type entails special vigilance to insure against changes in lead resistance.

The principal advantage which differential thermometers might possess would be the possibility of obtaining measurements of temperature difference when the experimental conditions are unsteady. Under such conditions, however, the accuracy attainable with a flow calorimeter is necessarily limited. If steady conditions for observation can be attained, the matter of convenience in observation would not justify the inherently less satisfactory compensated lead type of thermometer. The choice of compensated lead thermometers, whether dictated by unsteady experimental conditions or by considerations of convenience, would in either case have meant a sacrifice of accuracy.

The calorimeter system naturally divides into two parts at the " neck," one part of the "cold end " and the other the " warm end." The casing, or envelop, is made appropriately for assembling these two parts as separate units with a joint to be completed at the neck. This casing is in two parts, which unite at a soldered joint around the horizontal deck to which the lower casing and the supporting frame are rigidly attached, as shown in Figure 5. The upper part

consists of a plain cylindrical cap meeting this deck. A stage in the assembling of the calorimeter just before closing the casing is shown in Figure 7. The joint in the neck and the two envelop joints were made with special electrically heated soldering tools.

Leakage of heat from the calorimeter system by conduction through the supports was opposed by using the German-silver tubes which convey the ammonia as the two chief supports of the system. For staying the middle of the system three fine wires of low thermal conductivity were tightly stretched between shield S_2 and guard G_2.

A system of thermocouples was installed in the calorimeter for two purposes, one for the survey of temperature distribution as reassurance regarding the effectiveness of the means of shielding against radiation losses and the other for an indication which would serve as a basis for the regulation of the temperature of the heated guard and evaluation of the thermal leakage correction. There are, in all, 21 thermocouples, of which a group of 5 with their reference junctions are located in the lower part, or cold end; a group of 16 are located in the upper part, or heated end, except for one junction of couple No. 21, which is located at the cold-end group of reference junctions. Each of the 21 working junctions is soldered to the point the temperature of which it is to indicate relative to a particular group of reference junctions. The location of these working junctions is shown by the numbered dots from 1 to 21 in Figure 4. These locations were chosen as being characteristic points for exhibiting the temperature distribution. The reference junctions for each group, except for No. 21, were located in the same end of the system as the working junctions, so that the emfs to be observed would be as small as possible, corresponding only to the small differences of temperature within that portion of the system. Each group of reference junctions was assembled with the object of keeping the individuals separate electrically, but as nearly as possible at the same temperature. This is easier said than done, and while the arrangement actually used did prove good enough for what it was required to do, yet it fell somewhat short of expectations. All the reference junctions were embedded in bakelite cement inside of copper sheaths. The sheath containing reference junctions of couples 1 to 5, together with their copper leads, is soldered to the lower end of guard G_1 directly below thermometer T_1. The other sheath containing reference junctions of couples 6 to 21, together with their copper leads, is located at the upper end of guard G_2 in an element of the cylinder. This sheath is thermally connected to the guard through soldered metal connections.

The working junction of couple No. 21 was attached to the lower reference junction sheath, and this couple indicates the difference in temperature between the two groups of junctions, and thus permits

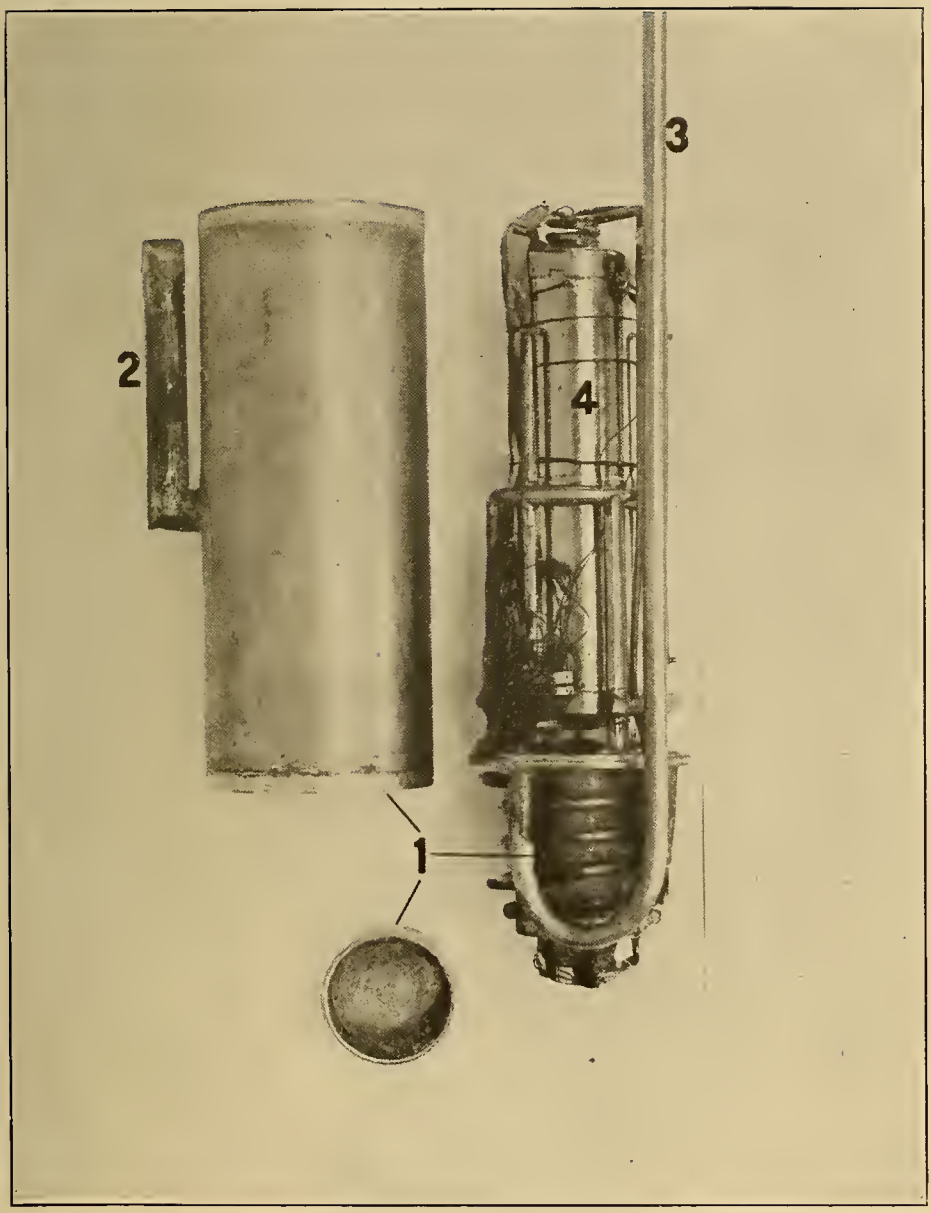

FIG. 7.—*Calorimeter just before closing casing, 1/2 size*

1. Casing. 2. Vacuum connection. 3. Electric lead duct. 4. Guard heater, *GH*

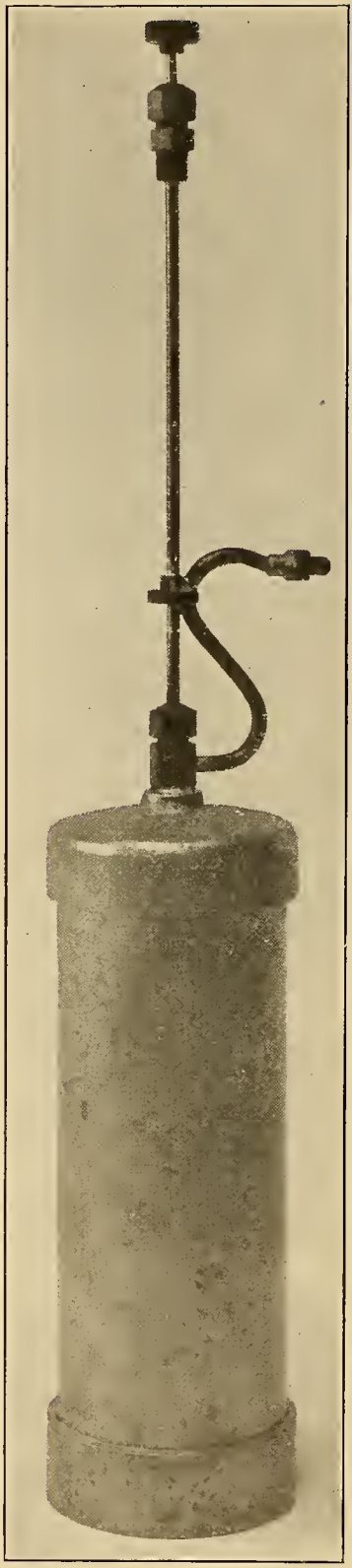

FIG. 8.—*Ammonia reservoir, 3/8 size*

reference of one group to the other. This gives an optional way of observing the temperature rise of the vapor by means of couples 3, 12, and 21, which could be used instead of the resistance thermometer, but which was not so used in actual experiments because inferior in accuracy. This arrangement of couples could be used in lieu of resistance thermometers in any set-up where simplicity outweighs the possible sacrifice in accuracy. A comparison of thermocouple with thermometer measurements in 16 experiments when both measurements were made at the same time showed an average discrepancy of about 0.2 per cent.

The electric wires leading from the resistance thermometers, electric heaters, and thermocouples within the calorimeter were connected to extensions which were brought out through a tube marked "*wires*" in Figure 4 through a vacuum seal at the top to the outside where they could be connected with the instruments for operating and observing. For convenience in installing these extension wires were assembled in four groups, each consisting of a layer of parallel wires cemented together with bakelite between two flat strips of mica, thus producing a ribbon of some flexibility. These four strips of wires were introduced into the bent tubular conduit so as to leave the wires at both ends of sufficient length to make the connections. The connections to the wires from the calorimeter were made by soldering with tin in the region of the envelope space conveniently near the exit point. These joints were then insulated with silk or tissue paper and bakelite cement and arranged securely in place. The appearance of this group of connections is shown in Figure 7. At the outer or upper end of the conduit the wires were first spaced by rigid bakelite spacers. Then, after removing the silk insulation the assemblage of wires was cemented rigidly to the circular flat metal extremity of the conduit with de Khotinsky cement. This sealed the passage from the vacuum space to the outside where the wires emerged. This seal was sufficiently remote from the control bath to be unaffected by its temperature.

At various stages in the construction of the electric parts of the calorimeter, the extension wires and their installation, the insulation resistance was tested, using a "megger" putting on 500 volts potential difference. These tests usually showed insulation resistance of many megohms.

V. DESCRIPTION OF ACCESSORY APPARATUS

1. STORAGE AND TRANSMISSION OF THE AMMONIA

Six steel containers or reservoirs served to hold the ammonia experimented upon, being used interchangeably for storage or as

evaporators, condensers, and weighing vessels. These reservoirs, together with the calorimeter, pressure gauges, auxiliary reservoirs, tubular transmission lines, and the valves used for regulating or shutting off flow constituted a closed system, within which the purified sample of ammonia was confined during the experiments.

The form of the storage reservoirs is shown in Figure 8. They were made of seamless drawn steel tubing 2¾ inches diameter and three thirty-seconds inch wall thickness. The end caps were machined of solid steel and threaded to screw on. The parts were very carefully tinned inside and out, and the end caps finally screwed in place with the threads filled with melted tin. The capacity of each of the reservoirs was about 550 cm.³ The S-shaped side tube is for connecting to the ammonia line, and the straight part extending up from the valve body is the sleeve inclosing the extended valve stem. The stuffing box for the stem is at the top, sufficiently distant from the level of immersion to avoid melting the paraffine in the packing by heat conducted up the stem and sleeve. The bushing on the sleeve to which the side tube is soldered is used to support the reservoir from the cover of the tank.

We shall not attempt to describe in detail the configuration of the ammonia line to and from the calorimeter, but merely point out some of the things which did not appear in Figure 2 or in previous descriptions. At each of the unions where reservoirs could be attached the ammonia lines had valves to close off the line when the union was open. The transmission tube was made of copper. Joints were hard soldered where possible, and in other places—such, for example, as in connecting to a valve—pure tin was used as solder. Some parts of the line between the supply reservoir and the calorimeter were thermally attached to the boiler bath by soldering them directly along the outer wall of the tank. The object of this thermal coupling was to admit the heat required to compensate for the cooling of the vapor which would result from reduction of pressure. It would operate to reheat the ammonia vapor to approximately the temperature of the boiler bath before it passed across to the calorimeter bath. Where the temperature of the valves was of consequence, which was usually the case, the valve bodies were attached to copper brackets soldered to the tanks at the top as shown in Figure 9.

All parts of the ammonia lines were tested for strength and tightness in a manner similar to that used for the calorimeter. These tests included reservoirs, valves, and manometers, and the detection and repair of leaks in the completed apparatus was no small item on account of the complexity of the structure and the time element involved in making the vacuum tests, which were the only ones found trustworthy for finding leaks.

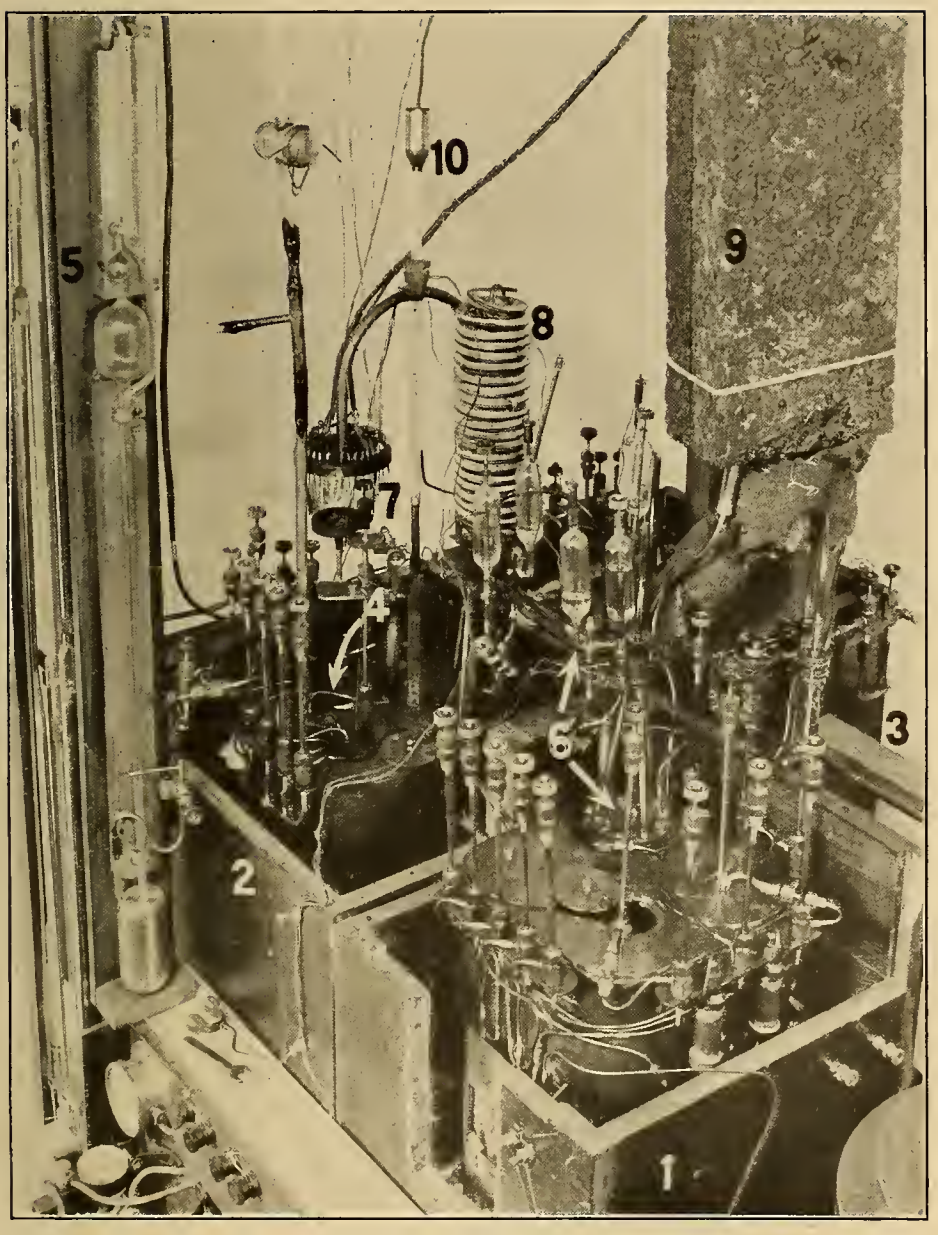

FIG. 9.—*Three baths showing arrangement and accessories, 1/8 size*

1. Boiler bath. 2. Calorimeter bath. 3. Condenser bath. 4. Calorimeter. 5. Pressure and vacuum gauges. 6. Temperature control unit of bath 1. 7. Electric leads. 8. Heat exchanger of CO_2 cooling system for bath 2. 9. CO_2 lines and heat exchangers. 10. Standard platinum resistance thermometer

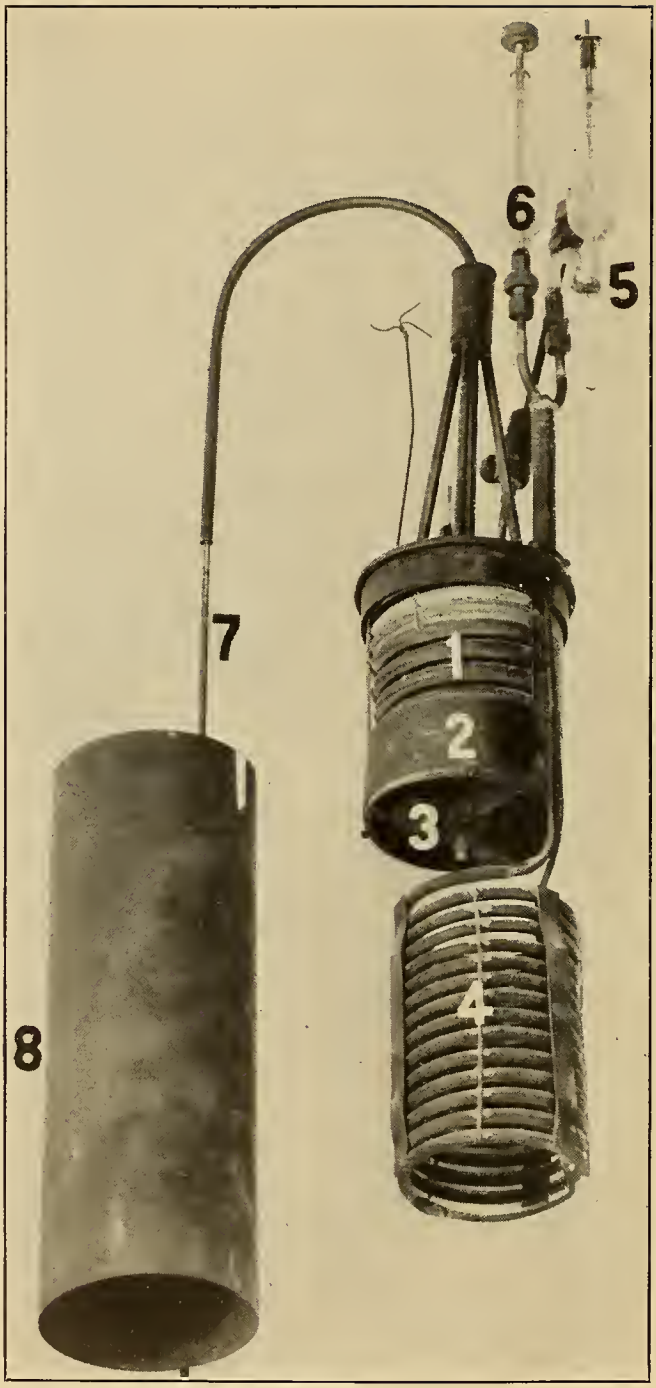

FIG. 10.—*Control unit of thermoregulated bath, 2/5 size*

1. Refrigerating coil. 2. Ring-bearing electric heater coils. 3. Propeller. 4. Thermoregulator bulb. 5. Contact maker for actuating thermoregulator. 6. Setting valve and liquid reservoir. 7. Flexible shaft. 8. Casing removed

2. THERMOREGULATED BATHS

Considerable attention was devoted to the design and construction of the temperature-control baths to simplify construction, economize space, and promote reliability of operation. The three baths are similar in general construction, each having modifications to adapt it to the performance of a particular service. Each bath included about 13 liters of liquid held in a copper tank about 36 cm deep and about 19.5 cm square, with rounded corners. For thermal insulation each tank was installed in a wooden box about 30 cm square and the intervening space of about 3 cm filled with cork, except near and over the top, where wool was used for covering. The shape of these insulated tanks favored the assembling of the entire calorimetric equipment upon a table in a compact group, the important elements of which were easily accessible, either for manipulation or observation (see figs. 1, 2, and 9).

Each bath was provided with a control unit (fig. 10), the function of which was (1) to circulate the liquid medium for distributing or exchanging heat, and (2) to control the temperature of this medium. Each bath had a close-fitting brass cover from which parts of the apparatus were suspended in the bath. Parts of the apparatus requiring less perfect temperature control were mounted upon the outside of the tanks. The control unit included a screw propeller, a refrigerating coil using carbon dioxide, an electric heating coil, and a thermoregulator actuated by expansion of a confined liquid. These parts were assembled in a tubular housing or penstock about 7.5 cm in diameter. The assembled control unit stood vertically in one corner of the tank. The rest of the space in the tank was available for installing such parts of the apparatus as required temperature control. The refrigerating coil, heating coil, and propeller were located in the upper end of the penstock where the liquid was taken in. The three operations of cooling, heating, and mixing took place in a small space near the intake at the top of the bath. Consequently, local disturbances of temperature, whether coming from the more exposed top surface of the bath or proceeding from the region of tempering itself, were taken in by the converging stream and carried into the control unit, where they were obliterated instead of being allowed to affect the main part of the bath where uniform temperature was wanted. The method of control was to overcool somewhat by a proper setting of the carbon dioxide throttle valve and compensate the overcooling by electric heating, so controlled by the automatic regulating device as to keep the fluctuations of temperature within the desired limits.

The liquid used to actuate the thermoregulator was the same as that of the bath; that is, toluol at temperatures not over 70° C. and

a mineral oil of higher flash point at the higher temperatures. The thermoregulator liquid was confined in a "bulb" composed of about 290 cm of copper tubing 5 mm in diameter, wound into a helical coil 6.8 cm in diameter, which was placed in the penstock below the propeller. This bulb was bathed in the stream of liquid immediately after the tempering and mixing at the place where it would promptly respond to changes in temperature.

Selective setting of the thermoregulator to operate at any desired temperature was provided, using a principle long in service at this bureau, but only briefly mentioned heretofore.[7] Metal capillary tubes led from each end of the bulb, one connecting to the setting valve and the other to the electric contact maker. When the setting valve was open, expansion could take place freely into the reservoir beyond. When the valve was closed, expansion of the liquid was communicated to the short column of mercury in the U tube, causing it to make or break electric contact with an adjustable needle point. When the temperature of the bath had been brought to the desired value, the automatic control could be brought into operation by closing the setting valve, after which fine adjustment of the temperature could be effected by the slow motion of the needle point.

The needle point used was that of an ordinary fine steel sewing needle, which was soldered to the threaded brass stem for adjusting. Experience has shown that these contact points operate satisfactorily when submerged beneath a hydrocarbon fluid, provided they are used only for the low voltage relay circuit and, if necessary, protected by a condenser to suppress the spark.

Extremely fine regulation was necessary only in the calorimeter bath, and it was found possible to control this bath so that no fluctuations or drift of more than 0.001° C. could be observed over a period of 30 minutes or longer. The reliability of operation of this thermal control and the relief of the operator from this care was a factor contributing to the character of the final results.

The contact maker and setting valve with their glass overflow reservoirs were located far enough above the top of the tank to be unobscured by the lagging. The support for these parts and also the tripod which supported the propeller shaft bearing were made of thin German-silver tubing in order to make them rigid and at the same time avoid unnecessary heat conduction to or from the bath. Such heat conduction is objectionable, not only because it imposes a greater duty on the control unit in maintaining a steady and uniform temperature within, but also because when operating the bath at low temperatures the condensation of water from the atmosphere on exposed cold parts may become a nuisance.

[7] An Aneroid Calorimeter, B. S. Bulletin, 12, p. 22; 1915. Sci. Paper, No. 247.

The propeller shaft carries a chuck at the top for coupling to the flexible drive shaft. The upper bearing and coupling is covered with a housing which extends over the flexible shaft to exclude dust, lint, etc., and steady the shaft.

The three control units were placed in the adjacent corners of the baths. This made it convenient to accommodate the driving mechanism for the propellers in a small space where it was not in the way. A single motor beneath the table distributed power to three vertical shafts, passing up through tubular casings in the adjacent corners of the lagging boxes. These shafts were each joined at the top to an extension of flexible shafting which extended through the curved tubular housing to the propeller shaft. This driving mechanism was simple, quiet, unobstructive, convenient, dependable, and safe.

When in operation the baths are often subjected to large changes of temperature. In order to avoid the change in level which would result from the expansion of the liquid, each bath was provided with an auxiliary reservoir which automatically admitted or let out liquid to compensate the volume change.

The condenser bath was provided with an arrangement which automatically prevented sudden changes in level due to the removal and replacement of the ammonia reservoirs during the course of experiments.

3. VALVES

About 40 valves were used on the closed ammonia system, which must needs be tight for trustworthy experimental work. Considerable study was devoted to the improvement of a type of small needle valve which had already been developed at this bureau for nice experimental work with fluids at moderate pressures. Improvement in workmanship was found to be the most important element in attaining reliability. The two principal points where changes were found desirable were at the bearing of the threads in the valve body in the seat and in the stuffing box. The construction of one of the types of valves with extension stem, which exhibits the essential features of the whole series, is shown in the sectional drawing, Figure 11. The brass valve bodies were accurately machined, the seats reamed, the burr and chips removed with care, the threads on the stems lapped smooth, and stainless steel tips attached, ground, and polished to a taper about 4° less than that of the seat. The part of the stem working in the packing was lapped and polished to reduce friction and prevent wear of the packing. The packing rings were of fine-grained leather impregnated with paraffin and held between two brass retaining rings, each fitted to the stem and box so closely as to prevent serious exuding of the packing. A steady pressure

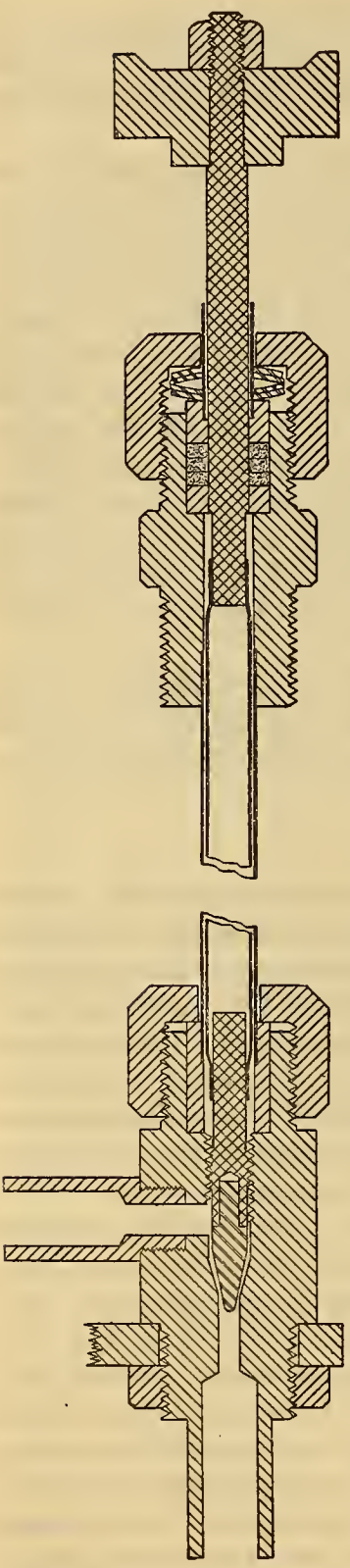

FIG. 11.—*Sectional drawing of valves, 5/3 size*

was kept on the packing by a set of cupped spring washers of tempered steel between the bonnet and the top retaining ring.

Many of the valves operated at temperatures considerably higher or lower than that of the room. It was important to locate the valves within the space where temperature was controlled but at the same time leave the stuffing box outside the lagging where the paraffine seal would not fail on account of temperature. This was accomplished by mounting the stuffing boxes on thin-walled German-silver tubes extending out from the valve bodies and also extending the stems by similar tubes within the sleeve.

These various measures were found sufficient for the purpose of these experiments. The stuffing boxes were found to be reliably tight both for vacuum and for pressures up to 1,500 lbs./in.^{2}, and the performance of the seats was satisfactory. The reduction in valve friction contributed to the reliability of the automatic pressure-control device, and the dependability of the entire group of valves both for vacuum and pressure contributed much to reliability of the experimental results.

4. REGULATION OF RATE OF FLOW

The rate of flow of the vapor is regulated by controlling the pressure in the line before and after the calorimeter. Use is made of the principle that gaseous flow through an orifice is practically independent of the low side or back pressure, provided this pressure is less than a certain fraction of the high side or fore pressure. The vapor lines are so arranged that after leaving the calorimeter the vapor is discharged through one or more of three orifices in parallel into the condenser line. The sizes of these orifices

were chosen to give the desired range in rate of flow with fore pressures ranging from 1 to 3 atmospheres. To adjust the flow when the calorimeter pressure was greater than three atmospheres there was a throttle valve which could be used to reduce the pressure from the working pressure in the calorimeter to an appropriate fore pressure to use on the orifices. In the experiments with ammonia it was found that when the back pressure in the condenser line was kept less than 0.35 of the fore pressure on the orifices the flow through the orifices and, therefore, through the calorimeter was sensibly dependent only upon the pressure in the calorimeter. In operation a rather rough control on the condenser line pressure as a prerequisite reduces the fine regulation of flow to a problem of control of the pressure in the calorimeter. Since a constant flow is the condition desired for promoting accuracy in the calorimetric measurements, the device for regulating this pressure to constancy is a vital part of the apparatus.

The operation of the pressure regulator proceeds from the manometer Q (fig. 2) in a manner somewhat analogous to the operation of a thermoregulator. One arm of this manometer connects with the flow line ahead of the calorimeter and the other to a reservoir R, which is immersed in the calorimeter bath for constancy of temperature. The pressure in this reservoir may be adjusted to any chosen reference value by transmitting ammonia through the by-pass valve V, which is then closed for operation of the regulating device. The pressure in the calorimeter line is balanced against this reference pressure by the automatic operation of the regulating valves, actuated by the fluctuations of the line pressure through manometer, relay, and motor. Departure of the line pressure from the reference value causes the mercury in the manometer to make or break electric contact with the platinum wires sealed through the glass. Making or breaking this contact controls, through a relay, the direction of rotation of an electric motor, which, in turn, through a mechanism, controls the settings of the valves E and F. When electric contact is made in the manometer by the line pressure falling too low, the motor opens valve F by an adjustable, small amount, and also starts a very slow opening of valve E by means of worm gearing. This continues until the increase in flow causes an increase in pressure, which breaks contact, reverses this process, and completes the cycle. By properly adjusting the initial openings of valves E, F, and K the amplitude of opening of valve F and the speed of the motor the line pressure may be kept constant except for a small periodic variation.

The manometer and connections are shown in Figure 12. The exposed parts of the two regulating valves and the mechanism by which they are operated are shown in Figure 13. The shafts, coupled by a flexible section working in the curved tubular sleeve, are rotated in either direction by an electric motor beneath the table. Shaft S, by means of the automatic double action friction clutch C, engages the valve stem F, and after rotating it through a definite chosen arc releases it. Upon reversal of the motion of S the clutch returns F to its former position. Thus, the valve F is alternately opened and closed by a definite amount which may be adjusted. The immediate result is to change the flow and reverse the direction of pressure change toward the reference value. When the operation has become steady, there is a periodic oscillation of the mechanism and a corresponding periodic fluctuation of the line pressure, the two actions being mutually dependent. The period and amplitude of the pressure fluctuations are subject to the control of the operator through the various selective adjustments, such as the settings of valves E, F, and K (fig. 2), the amplitude of rotation of valve F, and the speed of the motor. The action of the slow motion of valve E is to provide compensation for gradual or progressive changes in the line pressure which may proceed from the source of vapor supply, while the action of the oscillating valve F is to compensate for the small abrupt changes by absorbing them in the periodic fluctuations. It was usually found possible to adjust the apparatus so that the period was from 5 to 10 seconds and the extreme fluctuation of pressure not more than 1 mm of mercury.

The degree of dependability attained in the operation of the thermoregulators was not to be expected in the automatic pressure regulator. There were adjustments which made the manipulation of this device a matter of skill and judgment. The range of automatic compensation was not very large, and so the operation was sensitive to fortuitous influences and could not be left unattended for long without danger of spoiling an experiment. With due vigilance it could be kept performing faithfully for hours at a time. The constancy of flow which was the result of these measures permitted an accuracy in the measurements which would otherwise have been impossible and also expedited completion of the experimental program.

5. SAFEGUARDS

In an elaborate experimental set-up it is advantageous to consider safeguards in advance where the hazards can be anticipated. It is by no means always sufficient to guard against the more usual hazards of violent accidents, such as fire or explosions, for other kinds of accidents may be equally disastrous to an experimental

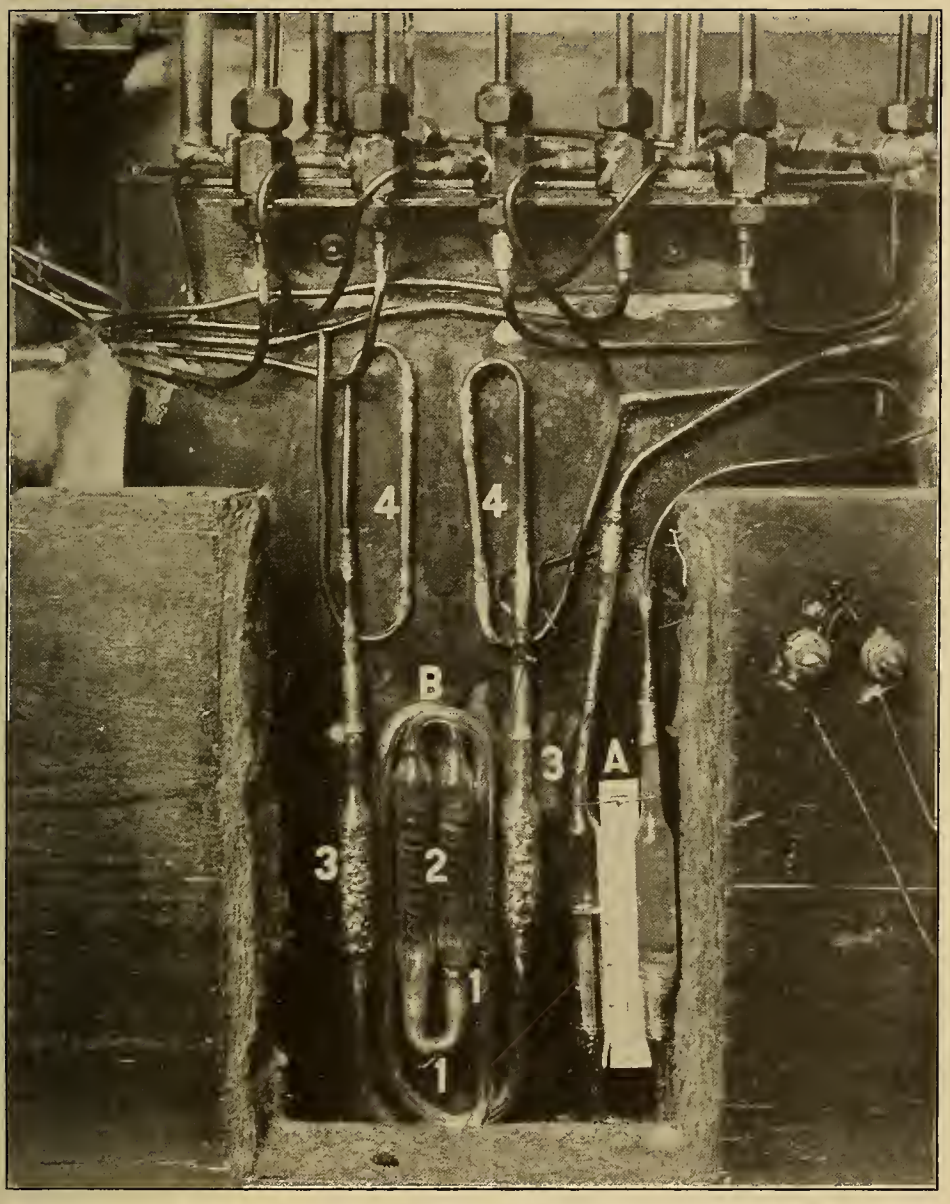

FIG. 12.—*Manometers for regulating and measuring pressures, 1/2 size*

A. Manometer connecting to piston gauge
B. Manometer for actuating pressure regulator
1. Electric contact wires. 2. Iron wire baffles to intercept drops of mercury. 3. Alloy to absorb mercury vapor. 4. Check valves

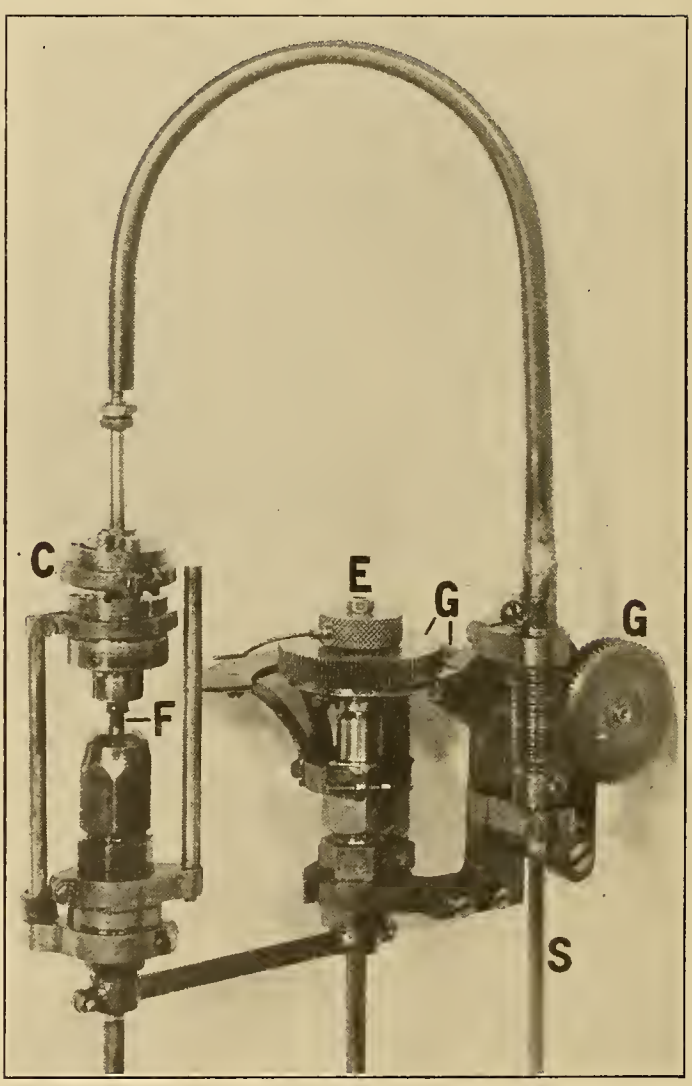

FIG. 13.—*Valve mechanism for automatic pressure control, 5/8 size*

S. Shaft. C. Clutch F. Valve stem to on and off valve. E. Valve stem to slow-motion valve. G. Worm gear train

project. We shall mention only briefly the safeguards of the ordinary sort adopted in the present equipment. The danger of explosion is provided for in the tests of the ammonia storage and transmission lines and the allowance of a factor of safety. Danger of fire is chiefly from the possible occurrence of an electric spark above the baths where the vapor might be explosive. By avoiding electric motors above the bath and by keeping a constant level of the bath liquid, so that the heating coil would be always submerged, the most likely sources of fire were removed. A danger which was quite as serious to the metal flow lines or the calorimeter itself was the possibility of invasion by mercury from the numerous gauges which were attached. These gauges are fragile, being made for the most part of glass. The fracture of one while the ammonia system was evacuated might admit mercury into the most remote parts and ruin them. Consequently, every one of the mercury gauges or manometers required a trap for mercury between it and the calorimeter.

Of these mercury hazards the most precarious in its action was the manometer used to actuate the pressure regulation, and a number of measures were adopted here not only to protect the apparatus from damage but also to prevent interruption of service. A small amount of mercury was used and the tube shaped so that the vapor could pass by the mercury, and thus relieve a pressure difference somewhat greater than the operating range. An enlarged section above the mercury, with baffles of iron wire in spiral form, intercepted and returned mercury projected upward as drops. Another section filled with thin strips of tin-cadmium alloy was intended to intercept mercury vapor. Check valves on each side were to hold back sudden pressure increase and prevent violent blowing through. Beyond the check valves one line led to the reference pressure reservoir and the other to the ammonia flow line through a trap large enough to hold all the mercury in the manometer. A similar trap was placed between the flow line and the piston gauge. These precautions may have been unnecessarily thorough, but the fact that all the safeguards were not called into play need not cause any more regret than would the possession of insurance on property escaping accident.

6. OTHER ACCESSORIES

Other accessories, such as vacuum pumps, McLeod gauges, pressure gauges, potentiometers, thermometer bridge, and balance, although essential parts of the experimental set-up, are so familiar and well described elsewhere that they need only be mentioned briefly here. Two vacuum pumps and McLeod gauges were used. One pump was used to evacuate the calorimeter envelope and the other to evacuate the flow line or the connections to the condensers,

as desired. The vacuum pumps are of the mercury-vapor type as designed and described by one of the authors.[8]

Two pressure guages were installed for measuring the pressure of the ammonia vapor during determination. For pressures up to three atmospheres an ordinary open-end mercury-in-glass manometer was used, supplemented by a barometer. For higher pressures an oil sealed, dead weight, rotating piston gauge was used.

A Leeds & Northrup type K slide wire potentiometer with volt box and standard resistance was used for the power measurements and a Wolff-Disselhorst potentiometer for the thermocouple readings. For the resistance thermometer readings a Mueller type Wheatstone bridge,[9] with shunt decades was used.

The steel containers with ammonia were weighed on a Rueprecht balance rated at 2 kg capacity. The balance was mounted on a shelf and was provided with suspensions which extended from the scale pans down into an inclosed weighing chamber (see fig. 1).

The time signals used to measure the duration of flow in the determinations of the rate of flow were controlled by a Riefler clock with electric contacts.

7. MEANS FOR INSURING DRYNESS OF VAPOR

Besides the provision made for observing the quantities from which the specific heat may be derived, there is another factor, no less vital to accurate results than any of the refinements in equipment or operation. This factor is the quality of the vapor. Of course, if the vapor is truly superheated and the state is truly indicated by the observed temperatures and pressures no question of quality would be encountered except at the saturation limit. But if, on the contrary, a liquid spray or fog were to be formed at any place in the stream before it entered the calorimeter, and if these mechanically entrained droplets should be swept on into the calorimeter, the resulting value of the specific heat would evidently be in error on account of the heat required to evaporate this spray in the calorimeter.

The measures taken to avoid this occurrence are for the most part automatic in operation. The stream of vapor coming from the reservoirs in the boiler bath A (fig. 2) passed to the needle valve E in the regulating train. It was then throttled successively in each of the three valves E, F, and K. Each of these three valve bodies was in very good thermal connection with the boiler bath through a copper bracket soldered to the copper wall of the tank. This connection would tend to supply heat to the stream of ammonia at each valve to compensate for any cooling caused by the throttling. Besides this first approximation to isothermal throttling, further

[8] Jour. Wash. Acad. of Sci., 7, p. 477; 1917.
[9] B. S. Bulletin 13, p. 547; 1916. Sci. Paper, No. 288.

opportunity was given the ammonia stream to reheat between valves F and K, and again after valve K by soldering a length of the flow tube directly to the wall of the tank. In operation the total reduction in pressure in this regulating train of valves was usually from 3 to 8 atmospheres. This process of isothermal throttling in three stages would tend to eliminate any traces of liquid which might otherwise have been swept through.

Besides these precautionary measures to guard against wetness or nonuniformity in the ammonia stream entering the calorimeter there was an effective means of test which would disclose any sensible effect produced on the results by wetness. This test was the repetition of experiments with different rates of flow. The principle of this test was that if spray or fog were entrained in the process of evaporation the degree of wetness would depend upon the rapidity of the evaporation, and the elimination of entrained liquid would be the more perfect the slower the flow. Agreement of the resulting values of specific heat for different rates of flow assures us of the proper dryness of the vapor.

VI. OPERATION

Use of the calorimeter to determine specific heat involved not only the direct measurements of the heat capacity of ammonia vapor but also preliminary observations for calibrating resistance thermometers and other auxiliary measuring apparatus and supplementary experiments to determine the corrections for pressure drop and thermal leakage. A detailed description of these various operations will be found in an account of the series of experiments on superheated ammonia [10] and need be only briefly outlined here.

1. CALIBRATION OF THERMOMETERS

The two platinum-resistance thermometers, designated as thermometers 1 and 2, which were used in measuring the initial and final temperatures of the ammonia vapor, were especially designed and constructed for use in the flow calorimeter. These thermometers were located directly in the vapor stream in order to obtain the best possible indication of the temperature of the vapor. This, of course, required that they be permanently installed in the calorimeter and a way devised for their calibration in place. They were calibrated after the calorimeter was assembled by comparison with a third standard resistance thermometer. This reference standard thermometer was immersed throughout the comparisons and experiments in the stirred liquid bath used to control the temperature of the

[10] Specific heat of superheated ammonia vapor, Refrigerating Eng., 10, p. 145; 1923. B. S. Sci. Paper No. 501.

calorimeter. This thermometer was used not only to calibrate thermometers 1 and 2 but also to observe the temperature of the calorimeter bath in actual experiments for the purpose of checking the nicety of the temperature regulation.

In order to bring thermometers 1 and 2 to the temperature of the reference standard for the purpose of intercomparisons, a stream of hydrogen at about atmospheric pressure was passed through the calorimeter. Hydrogen was used as a medium for promoting thermal equilibrium on account of its remarkably high specific heat, high thermal conductivity, and low Joule-Thomson coefficient. During the comparisons, hydrogen was also admitted into the envelope space, ordinarily evacuated, to favor still further the attainment of thermal equilibrium throughout the system. For the rates of flow used the drop in pressure of the hydrogen was not enough to cause any appreciable rise in temperature due to the Joule-Thomson effect.

All of the auxiliary measuring apparatus, including the mercury manometer scale, the piston gauge, Wheatstone bridge, potentiometer, electrical standards of resistance, and electromotive force, and standard weights, was subject to independent verification and calibration.

2. PROCEDURE IN DETERMINING SPECIFIC HEAT

At the beginning of an experiment the envelope of the calorimeter was evacuated to a pressure of 0.001 mm of mercury or less, and the evacuation was continued throughout the course of an experiment. The value of this envelope pressure was found to affect the rate of thermal leakage, and it was therefore frequently observed as one control on the thermal leakage. No extreme difficulty was found in keeping the pressure as low as 0.001 mm even at 150° C. after once getting it pumped down, but the initial exhaustion was possible only after the most thorough eradication of leaks.

Each of the three baths was brought to the desired temperature, which was thenceforth controlled. Close adjustment of the temperatures of the boiler and condenser baths was not required. The only requirement of the condenser bath temperature was that it be kept low enough to prevent the back pressure of the vapor from affecting the rate of discharge through the orifices. The calorimeter bath temperature required extremely close regulation. This temperature was maintained constant to about 0.001° C. by means of the thermoregulator.

When all was ready the flow of ammonia vapor was started. The final pressure in the calorimeter was adjusted to the desired value and thereafter maintained constant by means of the pressure regulator. The calorimeter heating current from a storage battery was

then turned on and adjusted to produce the desired rise in temperature of the vapor. Heating current was also supplied to the guard heater in order to maintain the surface of the guard at the same temperature as the surface of the calorimeter system which it surrounds, and thus help control thermal leakage.

After the rate of flow and the calorimeter heating current had been maintained constant for a period of about one-half hour, periodic observations of the initial and final temperature of the vapor were begun. When these observations became constant it indicated that the calorimeter had reached a steady state. The initial and final pressures were then observed alternately, using the same pressure gauge, and a determination of the rate of flow was started by diverting the flow into a weighed reservoir.

During the flow determination several potentiometer readings were made of the current and potential drop in the calorimeter heating coil, the initial and final temperatures of the vapor were observed frequently, and the current in the guard heater was manually controlled to maintain a constant indication of the regulating thermocouples. After a chosen interval of time, usually 20 minutes, the flow was again diverted to another reservoir. This procedure provided the data for a single determination of the specific heat and could be repeated as often as desired. Before weighing the reservoirs they were warmed, washed with water, dried, and brought to room temperature.

In carrying out the experiments it was found desirable and convenient to employ four persons in making the numerous manipulations, adjustments, and readings. The duties were apportioned somewhat as follows: First, regulation of boiler bath and rate of flow, manipulation and adjustment of pressure-regulating mechanism, orifices, and appropriate valves; second, operation of vacuum pumps and condenser bath, observations of the initial and final pressures in the calorimeter, observations of jacket pressure, weighings, and manipulations in the determinations of the rate of flow; third, regulation of calorimeter bath and electric heating, adjustment of current in guard heater, observations of the power, thermometers, and thermocouples; fourth, recording of all observations and computation of results.

3. CORRECTION FOR PRESSURE DROP

The procedure in the determinations of the Joule-Thomson coefficient μ, which was needed in the evaluation of the correction for pressure drop, was similar to that followed in the specific heat experiments except that no electric heating was employed and the rate of flow was not measured during the course of those determinations.

These experiments were not made previous to each specific heat experiment because of the length of time required to bring the calorimeter to a new steady state after a portion of it had been heated several degrees in a preceding experiment and also because the correction for the effect of pressure drop in any experiment could be determined better from the data obtained with large flows.

4. CORRECTION FOR THERMAL LEAKAGE

As already has been emphasized, the conservation of the measured heat added to the vapor and the avoidance of unmeasured heat leakage to or from the vapor are vital to the accuracy of the experimental results, since the specific heat can be determined no more accurately than can the net amount of heat which the vapor gains in passing from the initial to the final state. The means adopted to meet these ideal conditions are: (1) Construction and operation of the calorimeter so as to make the thermal leakage small, and (2) determination of the small amount of thermal leakage as a correction to the directly measured heat added. The details of construction and operation have already been described and they were found effective to the extent that only rarely did the correction for thermal leakage exceed 0.2 per cent of the heat supplied in any experiment. We shall next proceed to describe how this correction was evaluated.

The configuration of the apparatus is too complex to permit a quantitative analysis of the thermal leakage by the numerous possible paths, and the alternative course was followed of evaluating the entire correction empirically. The fact that only a small quantity of heat remains to be evaluated after the means for reducing the thermal leakage had been effected makes the choice of an empirical relation for this use a less critical matter than would otherwise be the case.

The empirical relation adopted in the ammonia experiments to correct for thermal leakage is

$$X=(N-0.2\Delta\theta)x$$

in which N is the number of microvolts indicated by the regulating thermocouples on the guard and heater shield, $\Delta\theta$ is the observed temperature rise of the vapor expressed in degress centigrade, and x is the coefficient of thermal leakage; that is, the ratio between the thermal leakage X and the mean effective temperature difference between the calorimeter system and its immediate surroundings. Experiments showed that this mean effective temperature difference could be obtained by applying a correction of 0.2 $\Delta\theta$ to the indicated temperature difference between the guard and the heater shield. The fact that the regulating thermocouples did not always indicate this exact mean effective temperature difference may have been the result either of imperfections of the individual couples or of the in-

herent difficulty of determining the average temperature of a complicated surface by means of a limited number of couples.

N and $\Delta\theta$ were observed in each determination of the specific heat, but the coefficient x required supplementary experiments to determine its value for various temperatures of the calorimeter and various degrees of evacuation of the envelope space. The coefficient of thermal leakage x was determined for any single combination of experimental conditions by making two successive but separate experiments in which the only conditions varied sensibly were the indicated temperature difference N between the calorimeter shield and guard and the resulting change in the temperature rise of the vapor $\Delta\theta$.

The method of testing the correctness of this evaluation is based upon the assumption that the thermal leakage is independent of the power input and rate of flow as long as the temperature rise is sensibly constant. In other words, it is assumed that the temperature distribution within the calorimeter is independent of the power input and rate of flow under these conditions. There is experimental evidence in support of this assumption, for the indications of the thermocouples were found to be but slightly changed by doubling the rate of flow and keeping the temperature rise constant. The principle of the method was to perform two or more specific heat experiments at the same temperature and pressure with approximately the same temperature rise but different power inputs and different rates of flow. The test of the proper correction for thermal leakage is that the values of C_p obtained from these experiments shall be independent of the rate of flow. Any appreciable outstanding leakage which is not accounted for will produce a different percentage error in the values computed for the heat added, and consequently the resulting values of C_p will vary with the rate of flow. With very large flows the leakage will become negligible in comparison with the power input. For example, by plotting the values of C_p against the reciprocal of the rate of flow and extrapolating to infinite flow the correct value of C_p may be obtained. This method of procedure is often called the method of extrapolation to infinite flow. This method was used in the selection of the empirical relation used in calculating the correction for thermal leakage, but the ultimate test of validity of the correction was the reproducibility of the final result, C_p, using various rates of flow. It may be remarked incidentally that this examination of the values of C_p obtained from experiments with different rates of flow is a crucial test not only of the correction for thermal leakage but at the same time of the correction for pressure drop and as previously noted, of the dryness of the vapor.

5. PERFORMANCE

A brief account of the performance of the calorimeter in actual service may be of some interest. The series of measurements which were made on ammonia vapor furnished an excellent opportunity for learning the characteristics of the instrument in respect to convenience of operation, dependability, reproducibility of observations, and reliability of results.

When the completed calorimeter had been assembled, the first try out was made, using air. This preliminary work included a tentative calibration of the thermometers, tests of the thermocouples, study of the manipulation of the apparatus, and an examination of some of the characteristics of the instrument by using it to measure the specific heat of air. The values found agreed well with the most authentic values of previous observers, showing that the instrument had no glaring faults.

Next a trial series of observations on ammonia was made for the purpose of perfecting the manipulation of the apparatus, discovering defects, and making a preliminary survey of the behavior of ammonia in the superheat field. Thirty-five complete determinations of specific heat were made, for the most part with smaller rates of flow than were afterwards found appropriate. This first series yielded valuable experience. The results obtained at this time were inferior in accuracy to those obtained later when certain faults had been remedied. Nevertheless, this try out demonstrated the successful operation of the most vital parts of the set-up. One important thing learned was that close control on the exhaustion of the envelope space was needed in order to evaluate the thermal leakage correction.

As a result of this knowledge a second vacuum pump was installed for the sole purpose of continuously exhausting the envelope space, in lieu of the intermittent exhaustion which had previously been provided for. After this the pressure in the envelope space was kept well controlled. The first vacuum pump was then left free for exhausting ammonia lines and connections when needed.

A final series of 108 complete determinations of specific heat were made which established the value of the specific heat at 35 different states in the temperature range from −15 to 150° C. and the pressure range 0.5 to 20 atmospheres. Several determinations of the Joule-Thomson effect were made incidentally for the evaluation of the correction for pressure drop.

There are several ways of appraising the accuracy or precision of experimental results, depending on what aspect of accuracy we are interested in. If we wish to know to what extent accidental errors, either of observation or manipulation, affect the results we examine

the degree of reproducibility of a single result. We may enlarge the scope of such a test by comparing directly observed results with values given by a suitable empirical equation, and thus judge throughout a range of experimental conditions the precision or nicety of coordination of instruments and observers.

If we wish to know just how the precision of each element of the measurement affects the resulting value of the quantity determined, we may estimate these elements separately. We may combine them properly and then compare the estimated reproducibility with that actually found. Such a test, if satisfactory, fortifies the incomplete evidence of reliability resulting from the examination mentioned previously. It furthermore indicates whether refinements in experimentation and observing have been ill or well planned.

Both of the above-mentioned tests were applied to the experimental results on specific heat of ammonia vapor. In the final series of 108 experiments the individual results agreed with the representative equation over the entire range of temperature and pressure on the average to within 0.1 per cent, and the greatest deviation was within 0.3 per cent. The largest correction for thermal leakage was 0.37 per cent, the average being 0.10 per cent. Comparison of the observed accidental errors with itemized estimates was satisfactory.

However, the most forcible and convincing test of the absolute accuracy of the results is found in the correlation of the results of these calorimetric measurements on the superheated vapor with the entire group of other properties of ammonia made in this same laboratory on the same quality of ammonia but in several independent investigations. These data have been brought together into a complete formulation of thermal properties, consistent with the laws of thermodynamics. The experimental data resulting from calorimetric measurements agree with this formulation within 0.2 per cent and in 95 per cent of the cases within 0.1 per cent.

This check agrees well with the other tests of consistency and indicates an accuracy more than adequate for most engineering purposes.

Apart from the consideration of bare accuracy of results, the reliability of operation of the apparatus deserves mention. This characteristic of the apparatus resulted from deliberate refinement of design and construction of accessory parts, and though requiring time to perfect these refinements, the outlay was well repaid in economy of time and effort during the period of experimenting.

WASHINGTON, July 21, 1924.