[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Low Temperature Precision Adiabatic Calorimeter Adapted to Condensed Gases from 10°K. to Room Temperature

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The accuracy with which the height of potential barriers hindering the rotation about single bonds in organic compounds can be calculated from a comparison of entropies from molecular data and from thermal data down to low temperatures is limited by: (1) uncertainties in the shape of the potential energy curve, (2) incomplete knowledge of the vibration frequencies, and (3) the accuracy of the thermal data in the neighborhood of room temperature.

In the hope that further light on (1) and (2) will soon be forthcoming, it was decided to devote some attention to the improvement of the accuracy of the thermal data. Accordingly an adiabatic calorimeter has been designed for condensed gases which has an accuracy of at least 0.05% from 40°K. to room temperature in all the thermal data. This corresponds to about 0.03 e. u. per mole for the simple organic compounds, as compared to an accuracy of 0.2–0.3 e. u. by the best methods heretofore when the compounds boil near to room temperature.

The apparatus in use by Giauque and his collaborators[1-3] makes use of a constant temperature environment, consisting of a heavy radiation shield. Accurate correction is made for the heat leak—both for its effect on the temperature and in producing thermal gradients in the calorimeter. Accurate knowledge of the correction depends on the use of a resistance thermometer heater, wrapped on the outside of the calorimeter in intimate contact with the wall, to measure the temperature rise (and there seems no other simple alternative).

Such a resistance thermometer has to be calibrated continuously against a thermocouple (or strain-free resistance thermometer), under conditions of no heat leak, *during* each series of measurements in order to eliminate possible strain.

In an adiabatic calorimeter[4] there are no temperature gradients after equilibrium has been reached and a strain-free resistance thermometer heater can be used to measure the temperature rise, thus requiring only occasional checks on its original calibration.

This in itself is sufficient reason for making a calorimeter adiabatic. However, the remarkable accuracy of the low temperature adiabatic calorimeter of Southard and Brickwedde for measurements on solids and high boiling liquids[4] also makes it desirable to adapt this system to condensed gases.

The chief obstacle to the use of an adiabatic method is that the calorimeter filling tube must make intimate contact with the top of the adiabatic shield. This gives rise to reflux condensation for high vapor pressures when the shield temperature oscillates about that of the calorimeter. The difficulty can be eliminated by keeping the mean temperature of the top of the shield a small definite amount above the calorimeter such that oscillation never brings it below (0.1–0.2° will suffice). The very small, but constant, heat leak resulting is easily corrected for.

Nevertheless there are other complications. To keep the shield temperature uniform Southard and Brickwedde found that heat leak down the wires, which lead to it, must be reduced by preliminary contact with a metal ring (or block). At low temperatures this must be below (rather than above) the temperature of the adiabatic shield so that the heat leak from the shield can be compensated for by heating. The filling tube, however, *cannot* make contact with this ring because it must always be warmer everywhere, to avoid condensation. Therefore heat leak down this tube must be taken up by contact with a second block whose temperature is slightly higher than the shield. If all the heat leaking down the filling tube is taken up by the shield, the "hot spot" produced is serious. To this block it is convenient to attach the radiation shields, encasing the filling tube, which are necessary to ensure that no section of the latter is colder than the calorimeter.

The Calorimeter.—Fig. 1 shows a diagram to scale, with explanatory legend, of the apparatus finally used.

The calorimeter itself is similar to that of Southard and Brickwedde.[4] It is made of copper, gold plated inside and out, with walls 0.06 cm. thick. This calorimeter will hereafter be designated calorimeter B. Twelve radial

(1) Giauque and Wiebe, THIS JOURNAL, **50**, 101 (1928).
(2) Giauque and Johnston, *ibid.*, **51**, 2300 (1929).
(3) Giauque and Egan, *J. Chem. Phys.*, **5**, 45 (1937).
(4) Southard and Brickwedde, THIS JOURNAL, **55**, 4378 (1933).

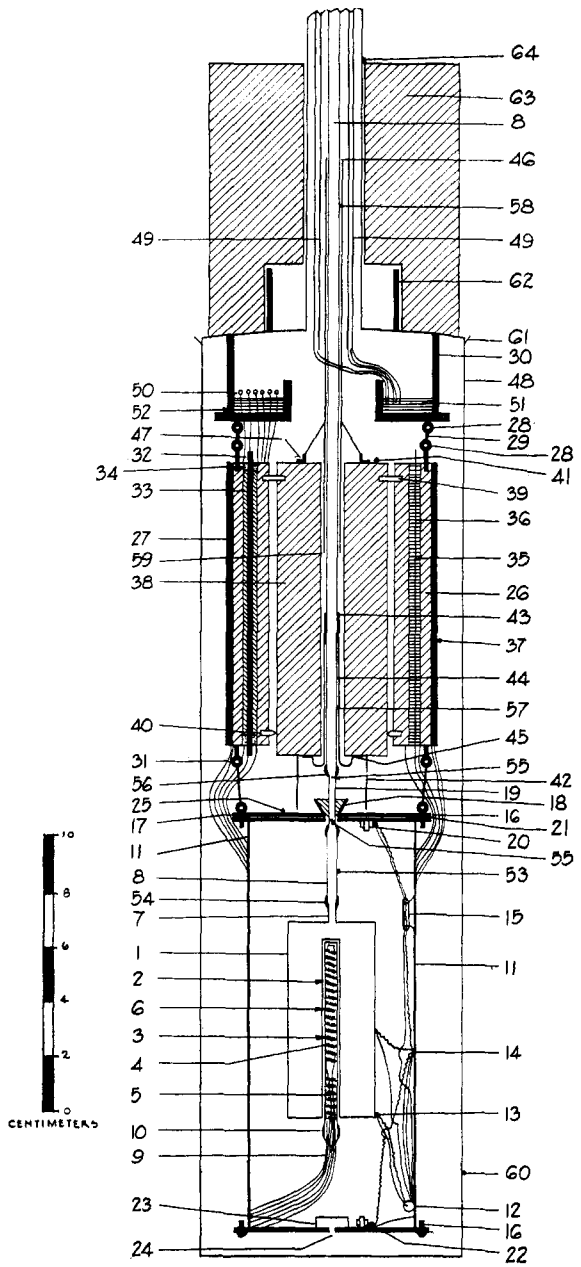

Fig. 1.—Description of low temperature adiabatic calorimeter for condensed gases: 1, calorimeter (volume 48 cc.); 2, thermometer well; 3, thermometer case (of platinum); 4, Pt–Rh (10%) thermometer; 5, constantan thermometer; 6, Rose metal filling; 7, platinum tube 2 mm. o. d., 0.2 mm. wall; 8, soft glass tube; 9, platinum thermometer supply wires; 10, platinum–cobalt glass seal; 11, radiation shield cylinder; 12, thermocouple guide tube (filled with paraffin); 13, standard thermocouple junction; 14, difference thermocouples; 15, couple support (glass tube); 16, brass screws; 17, radiation shield top; 18, Wood's metal thermal contact; 19, platinum tube; 20, difference thermocouple well (detachable paraffin filled lug); 21, partial thermal insulation (silk gasket); 22, radiation shield bottom; 23, radiation trap; 24, 2-mm. hole for evacuation; 25, thermocouple junction; 26, 650 g. lead filling for 27; 27, copper case of massive ring, 750 g. of copper; 28, eye-bolts; 29, cord; 30, copper ring; 31, eye-bolt; 32, enameled copper wires; 33, Wood's metal contact; 34, bakelite; 35, holes filled with paraffin; 36, thermocouple wires and insulated platinum potential leads; 37, thermocouple junction; 38, inner lead block, 1150 g. lead; 39, hardwood pegs (wedge shaped section); 40, pointed hardwood pegs; 41, thermocouple junction; 42, copper radiation shield; 43, Wood's metal contact of 44 with 8; 44, copper tube radiation shield; 45, copper lugs; 46, copper tube radiation shield; 47, copper lugs; 48, monel cryostat container; 49, glass tube guides for supply wires; 50, coiled wires and thermocouple; 51, paraffin-filled trough; 52, thermocouple junction; 53, first filling tube thermocouple; 54, platinum–cobalt glass seal; 55, platinum radiation shields; 56, platinum–cobalt glass seal; 57, second filling tube thermocouple; 58, third filling tube thermocouple; 59, end of copper tube radiation shield; 60, thermocouple junction; 61, soft-soldered joint; 62, copper tube; 63, lead block (8500 g. lead); 64, thermocouple junction.

vanes 0.01 cm. thick are fastened to the thermometer well, 2 (the numbers refer to parts of Fig. 1). The 0.2-cm. o. d. platinum tube at the top is for filling and joined by fusing (cobalt seal) to the short glass tube, 8. The section of platinum tube, 19, which joins this section to the main glass tube, 8, is connected similarly. Its purpose is to improve the thermal contact at the top of the radiation shield. By closing off opposite halves with semi-circular plates at either end, this tube was also made to act as a radiation trap. The platinum tube, 19, is brought into good contact with the top of the radiation shield by Wood's metal at 18.

The main glass tube, 8, makes intimate contact with the block, 38, by means of a set of flexible copper radial strips, 45, which are soldered to the block and connected to a sleeve, 44, which makes good thermal contact with the main tube at 43 through a ring filled with Wood's metal. The sleeve, 46, is connected similarly to the same block; as this acts only as a radiation shield, it makes only a spring contact with the main tube. The ring, 42 (also soldered to the block, 38), the block, 38, itself, and the sleeves, 44 and 46, constitute a system of radiation shields which entirely covers the main tube where it might otherwise radiate to colder surroundings.

The entire radiation shield is gold plated and polished inside. Its cylindrical portion, 11, has a wall 0.15 cm. thick; the detachable top, 17, and bottom, 22, are 0.1 cm. thick. The difference couples between the calorimeter and the top, bottom, and side of the shield are similar to those of Southard and Brickwedde.[4] The connecting wires to these and to the terminals of the thermometer were wound in separate grooves on the outside of the side of the shield—each was 80 cm. long. All are of copper except the potential leads to the resistance thermometer, which are of platinum to eliminate thermal e. m. fs. The heaters for the different parts of the radiation shield are of no. 30 B. and S. D. S. C. constantan, wrapped bifilarly with close winding; that on the side of the shield covers the connecting wires just mentioned. All make a tight contact with bakelite

varnish and are covered with a sheet of thin copper. The bottom of the radiation shield, 22, makes a good thermal contact with the cylinder by means of a V-V joint and the brass screws, 16. The top of the radiation shield is separated by a gasket of silk, 21, designed to give a relatively poor thermal contact so that its temperature is easily maintained above the rest.

The lead block, 38, is suspended in the massive ring of copper and lead, 26, by means of hard wooden pegs with knife edges, 39, and wooden spacers, 40. The ring, 26, carries enamel covered wires, 32, fastened in with Wood's metal. These serve as terminals for the thermometer current and shield heater supply wires. The double silk insulated difference thermocouple leads, the auxiliary thermocouple on the shield, 25, and the standard thermocouple, 13, to be discussed presently, together with the platinum thermometer potential leads pass through holes, 35, in this ring. All are fastened in with paraffin for good thermal contact. Both the block, 38, and the lead ring, 26, are equipped with electrical heaters and auxiliary thermocouples.

All sections of the filling tube are closely wound with electrical heaters of no. 30 B. and S. D. S. C. constantan wires baked on with Bakelite lacquer, with "tap-outs" of no. 36 B. and S. copper wire which also serve as thermocouples.

All the wires make good thermal contact with the vacuum tight container, 48, by spiraling in the annular trough, 51, which is filled with paraffin.

The standard thermocouple alone *does not* pass through this trough.

The platinum case, 3, carries two four-lead resistance thermometer heaters; one of no. 38 90% platinum–10% rhodium alloy (R_0 = 80 ohms), 4; the other of no. 40 constantan (R_0 = 120 ohms), 5. Both of these consist of helices wound bifilarly on the same mica cross.[5a,b] A current and a potential lead are common to both. Thus only six leads are used. These are of no. 36 B. and S. platinum wire sealed through vacuum tight glass cap, 10. The thermometers were annealed on the cross (but not in the case) at between 500 and 600° in a hydrogen atmosphere to a constant resistance at 25°. The thermometer case was finally filled with helium at 0.3 atm. These thermometers will be designated, respectively, as R-200 and R-102. The constantan thermometer is used below 25°K. in specific heat measurements as a thermometer heater and in the heat of vaporization measurements simply as a heater—hence its position nearer the cap. Thus it lies near the bottom of the calorimeter and is less likely to produce superheating of the vapor during measurements of heats of vaporization.

For comparison of temperatures one of the laboratory standard couples, S-9,[6] is soldered to a lug on the bottom of the calorimeter at its junction and then passes directly to and through a semi-circular copper tube soldered to the inside of the shield which is filled with paraffin for good thermal contact. Thus twelve centimeters of the couple are taken up.

The standard couples had been calibrated with 72 cm. at constant temperature,[6] therefore 45 cm. are wrapped around the adiabatic shield and fastened there with paraffin and adhesive tape to make a good thermal contact. The rest of the 72 cm. are used up in passing through the paraffin filled hole, 35, to the top of the ring, 26.

The entire apparatus is suspended by the central tube inside a large dewar tube, $4^{5}/_{16}$" i. d. × $35^{5}/_{16}$" inside length (11 × 89 cm.), which fits inside a monel case with a cover. The apparatus is cooled by liquid air or liquid hydrogen which is blown into the dewar through a German silver vacuum jacketed transfer tube which passes through a hole in the cover. In the cover of the monel case are also tubes for evacuation, for leading hydrogen to the gas holder, and for connection to safety valves. There is also a tube leading to the bottom of the dewar for blowing out liquid air used in cooling. The heavy lead block, 63, gives a sufficient heat capacity to the monel container, 48, to allow its temperature to change only slowly after the refrigerant has been removed.

The Electrical Apparatus.—Most of the electrical connections, the method of supplying and measuring energy, and measuring resistance were as already described.[6,7a,7b] The calibration of the electrical apparatus has been described before.[7b] The stop watch was checked regularly.[7b]

A thermometer current of about 8×10^{-4} amp. was used. This gave a precision of 0.001 in measuring the temperature rise.

The side and bottom of the adiabatic shield are heated in series. To keep the temperature of both rising at the same rate, a variable shunt is placed in parallel with the shield bottom heater. The top of the shield is heated separately.

One galvanometer reads the e. m. f. of the difference couples between the side of the shield and the calorimeter or the bottom of the shield, the other reads the difference between the side of the shield and the top. Both galvanometer systems have a sensitivity of 2 cm. per microvolt.

The Temperature Scale.—Because the temperature scale of this laboratory is in terms of the copper–constantan thermocouple,[6] it seemed simplest for the present to compare the resistance thermometers against the laboratory standard couple during the first calorimetric measurements.

During comparisons the shield side and bottom were kept within 0.02° of the temperature of the calorimeter, and the top between 0.1 and 0.2° above it. However, a difference of 0.5° between the shield and the calorimeter did not produce enough heat leak (or change in temperature gradient) to the thermocouple junction to affect its reading. The ring, 26, was usually one or two degrees colder than the calorimeter but it was found that several degrees offset did not produce appreciable effects on the reading of the standard couple which made contact with it.

A comparison of S-9 was made with fixed points to check its original calibration by the methods already described[6] and at the same time the resistance thermometers R-200 and R-102 were calibrated against the fixed points.

These comparisons showed that the thermocouple had or was undergoing a change. At the boiling point of oxy-

(5) For details of this type of construction see (a) Southard and Milner, THIS JOURNAL, **55**, 4384 (1933); (b) Meyers, *Bur. Standards J. Research*, **9**, 807 (1932).

(6) Aston, Willihnganz and Messerly, THIS JOURNAL, **57**, 1642 (1935).

(7) (a) Gibson and Giauque, *ibid.*, **45**, 93 (1923); (b) Aston and Messerly, *ibid.*, **58**, 2354 (1936).

gen (90.04°K.)[6,8] and points on the oxygen vapor pressure curve the couple had changed its calibration by −0.05°. Similar comparisons at the melting point (54.40°K.)[2] and upper transition point of oxygen (43.77°K.),[2] the boiling point (20.45°K.)[6] and triple point (13.95°K.)[9] of hydrogen showed changes of −0.05, −0.02, −0.27, and −0.37°, respectively.

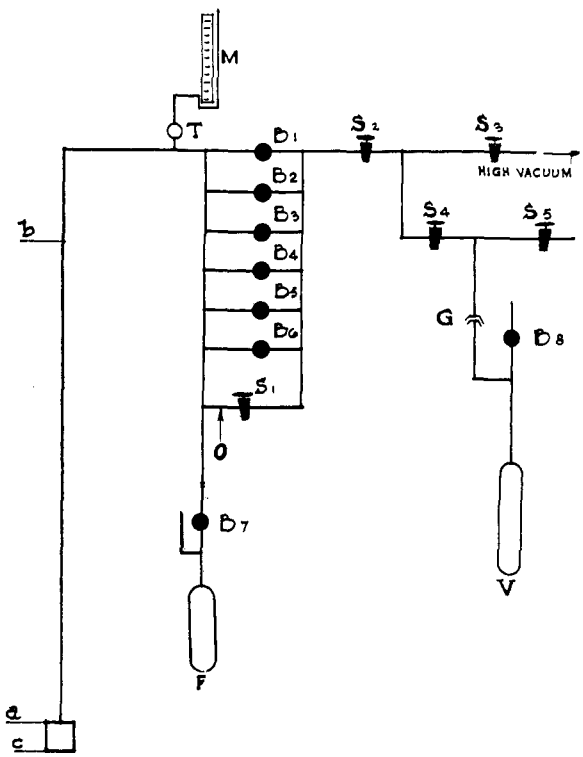

Fig. 2.—Filling and vaporization line (line volumes: calorimeter ac, 48.1 cc.; line in temperature gradient, a to b, 6.9 cc.; b to B_1 and reference mark on manometer, 34.5 cc.; B_1 to S_2, 84.9 cc.; S_2 to S_3 and S_4, 8.7 cc.).

The changes in the thermocouple down to 40°K. are within the accuracy of our original scale (0.05°). Below that the uncertainty (0.05–0.1°) produced, after correcting for the changes, is within the accuracy of the heat capacity measurements as limited by the resistance thermometer derivatives.

The deviation plot for the thermocouple was corrected for these changes. Temperature–resistance tables were made for the resistance thermometers on the basis of the readings at the above fixed points, comparison against oxygen and hydrogen vapor pressures and with the standard thermocouple S-9. The last was used to interpolate between the fixed points and extend the table from 90°K. to room temperature. Arrangements are being made to compare these and other strain-free resistance thermometers with a very accurate gas thermometer over the entire range.

(8) Where the fixed points were determined on our original scale[6] our own values are used. Other fixed points are corrected to our pressure coefficient $\alpha_A = 1/273.16$.

(9) Comparisons were also made against hydrogen vapor pressures.

Filling the Calorimeter.—Figure 2 shows a schematic diagram of the filling line. As much of the line as possible is made from 2 mm. i. d. capillary tubing. The volume and temperature of its various sections are accurately known.

The inner sealed capillaries, B_1–B_8, can be broken open by hammers of iron, sealed in glass, which move in a short tee-piece at right angles under the influence of a magnet. The section of the line containing B_1–B_6 has the greatest volume and is protected from draughts by an asbestos shield. The sample bulb, F, is equipped with one of these capillaries, B_7, and is attached to the line by a glass seal. The system is pumped out to 10^{-6} mm. of mercury through the stopcock, S_1, which is then sealed off at O. The sample bulb, F, is cooled to liquid air temperatures before breaking open B_7. The weighed sample then can be distilled slowly into the calorimeter without coming into contact with stopcock grease.

The stopcocks, S_2 and S_3, are for evacuation of the calorimeter filling line; S_4 and S_5 are used in the measurement of heats of vaporization.

While the calorimeter is being cooled the filling tube, 8, is kept warmer than the calorimeter by means of the electrical heaters and by blowing a stream of warm air over the tube leading to the cryostat.

Vapor pressure measurements are taken after completion of specific heat measurements, using the manometer, M, connected to the line by capillary tubing through the small trap, T, filled with gold leaf to protect the calorimeter from mercury.

For measurements of the heat of vaporization one of the inner sealed capillaries, B_1–B_6, is broken open. The procedure for vaporizing a weighed amount of sample is, then, as described for our old type calorimeter.[7b] The only difference is that the heater is turned on about 0.5°K. below the temperature when condensation starts to occur in the bulb, V.

Heat Capacity Measurements as a Test of Accuracy.—To test the accuracy of the apparatus heat capacity measurements were made on a sample of methylamine, from the batch used in previous heat capacity measurements (0.025 mole % impurity), over the entire liquid range to the boiling point.[10]

This substance was chosen because it boiled sufficiently high (266.84°K.) to allow heat capacities to be taken where the accuracy is low by previous methods; also because it had a high vapor pressure in this region, thus allowing a test of the efficacy of the precautions to prevent condensation in the filling tube. To magnify errors the calorimeter was only one-third filled with sample.

At high temperatures correction was made for the material in the filling line, for the proportion of the material in the calorimeter that was vapor and for the heat required to vaporize material as the temperature was raised.

In correcting for the difference in heat capacity between the vapor and liquid in the calorimeter the heat capacity data of Felsing and Jesson were used.[11] For this and the other corrections the density of methylamine was taken as 0.699 g. per cc.[12]

(10) Aston, Siller and Messerly, THIS JOURNAL, **59**, 1743 (1937).

(11) Felsing and Jesson, *ibid.*, **55**, 4418 (1933).

(12) "International Critical Tables," McGraw-Hill Book Company, Inc., New York, Vol. I, 1926.

In the regions of appreciable vapor pressure the top of the shield was kept 0.1 to 0.2° above the calorimeter and the rest of the shield within 0.02° of the calorimeter. This produced a heat leak correction at the highest temperatures of about 0.15% which was known to about 10% of its value. The ring, 26, which took up the main heat leak down the wires was set at a temperature slightly below that of the calorimeter at the beginning of a measurement. The block, 38, was set at such a temperature as to be slightly above the temperature of the calorimeter at all times during the heat capacity measurement.

With the shield balanced as above, raising the temperature of the inner block, 38, by 4° produces an extra heat leak past the shield of 1×10^{-3} cal. per minute at 180°K. due to conduction down the filling tube. If this were not corrected for from the observed drifts the error produced would be about 0.02% at the most.

A correction was also necessary for the heat generated in the current leads to the thermometer heaters both inside and outside the glass cap. Inside the glass cap there is 1.9 cm. of no. 36 B. and S. platinum wire and outside 1.2 cm. of no. 36 B. and S. platinum wire to each end of each thermometer; 2.7 cm. of no. 36 B. and S. copper wire connect each of these to the main supply wires which are wrapped around the shield. All the heat generated in the wire inside the glass cap was assumed to go to the calorimeter. Only half of that generated outside was assumed to go to the calorimeter. The total correction amounted to a maximum of 0.1% at room temperature.

The calorimeter came to equilibrium in about three minutes at liquid hydrogen temperatures and in ten minutes close to room temperature.

The results are shown graphically in Fig. 3 along with the results previously obtained.[10] As can be seen the agreement is within the accuracy claimed for the previous measurements. The new data lie on a smooth curve within 0.1 to 0.2%. The previous data[10] already had shown evidence of the maximum at 245°K. Remembering that the calorimeter is only one-third full these results are an indication of a precision of 0.05%.

The heat capacity measurements of the calorimeter itself from 11°K. to room temperature were also a test of its accuracy. The results showed a precision the same as that of Southard and Brickwedde,[4] namely, slightly better than 0.1% except below 40°K.

The results in the following paper on dimethylamine[13] are a further test of the precision of the apparatus. A graph of the results on the liquid only (in order to enlarge the scale) is given in Fig. 4. Evidently the precision is about 0.05% even close to room temperature. Because a stop watch was used, part of this is due to the error in the time (0.03%).

The comparison with the methylamine data obtained by the other method only rules out the possibility of constant errors greater than a few tenths of a per cent. However, it is hard to see just how a constant error greater than 0.2% could arise from all sources including the uncertainty in the resistance thermometer derivatives. The error in an entropy calculated from the data would be much less because the integration largely eliminates the oscillating error in derivatives.

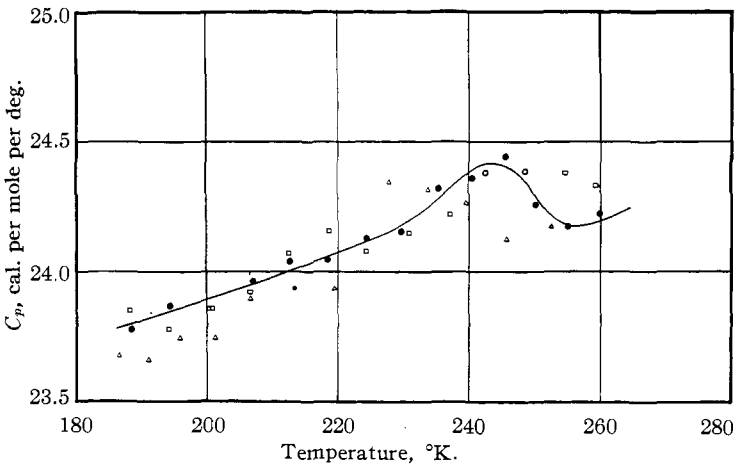

Fig. 3.—Molal heat capacity of liquid methylamine: ●, this research, adiabatic calorimeter, one-third full; □, Aston, Siller and Messerly (0.79 mole % impurity); △, Aston, Siller and Messerly (0.025 mole % impurity).

Heats of Vaporization.—In the next paper the heats of vaporization determined on dimethylamine at about 279°K. indicate an accuracy of about 0.1% but most of this error is due to the uncertainty in estimating the amount of material in the line and to effects of absorption of material in the grease of the unavoidable stopcocks.

Discussion

From the standpoint of accuracy the calorimeter is superior to any others designed for condensed gases. It should be particularly useful in studying slow thermal changes such as occurred in solid methylamine in the region below the melting point.[10]

A big disadvantage is that an extra operator is required to control the shield. This is partly offset by the elimination of the large amount of labor required in making the intricate calculation of the corrections required in the old type of apparatus.

The apparatus herein described requires about 10 liters of liquid hydrogen to cool it from liquid air temperatures to 11°K. However, as our hydrogen liquefier can make about twenty liters of liquid hydrogen per hour this has proved no obstacle.

(13) Aston, Eidinoff and Forster, THIS JOURNAL, **61**, 1539 (1939).

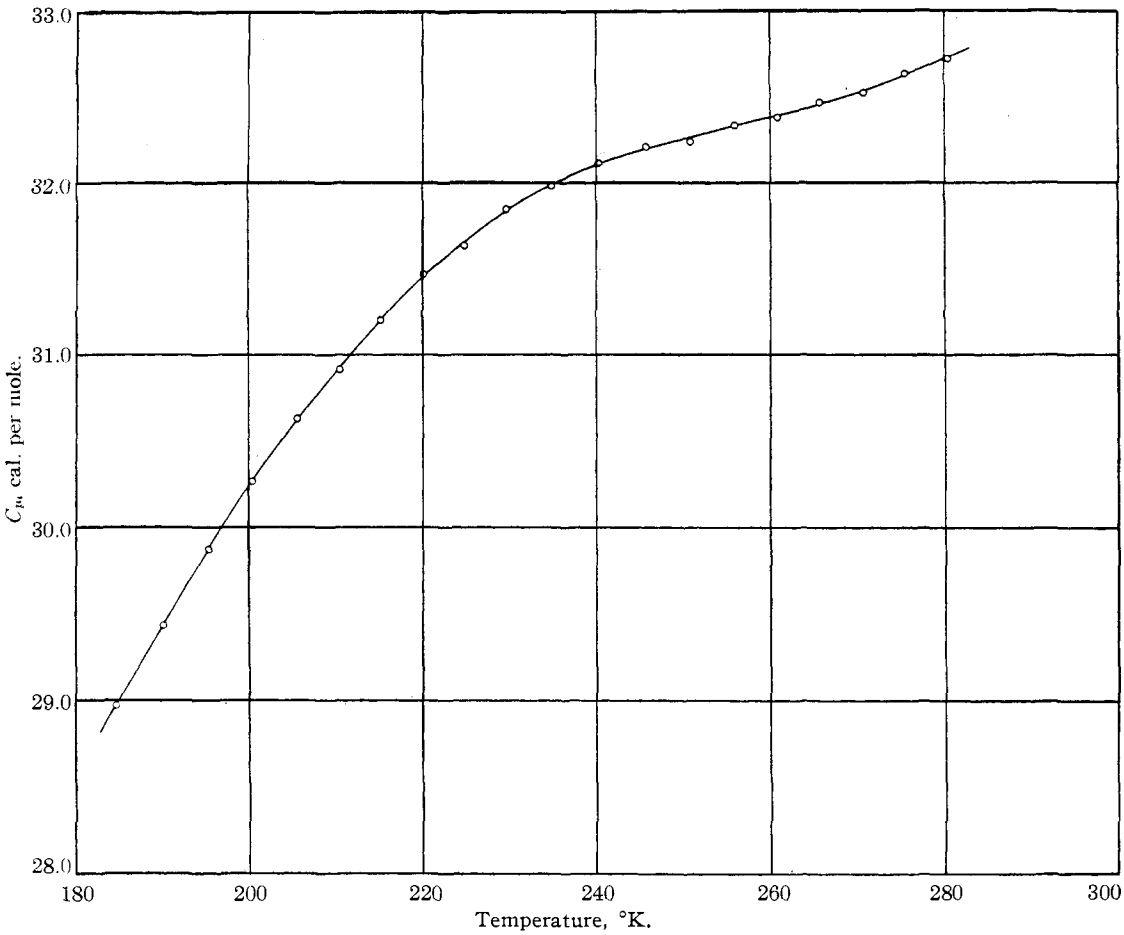

Fig. 4.—Molal heat capacity of liquid dimethylamine.

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Summary

1. A low temperature adiabatic calorimeter for condensed gases has been described.

2. The precision of this apparatus is about 0.05% in specific heat measurements up to room temperature and about 0.1% for heat of vaporization measurements close to room temperature.

3. The heat capacity of liquid methylamine has been determined over the entire range below room temperature and agrees with previous measurements.

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