[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND PURDUE RESEARCH FOUNDATION, PURDUE UNIVERSITY]

The Heat Capacity of Organic Vapors. V. Acetaldehyde

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The work reported in this paper is a continuation of a program for measuring the heat capacity of organic vapors. The heat capacity of acetaldehyde has been measured at 1 atm. pressure and temperatures from near its boiling point to 150°, using a constant-flow method first devised by Callendar and later adapted by Swann.[2] No calorimetric data on acetaldehyde have been published. The accuracy of the calorimeter was checked by measuring the heat capacity or heat of vaporization of benzene for comparison with the data of Scott, *et al.*[3] The heat of vaporization of acetaldehyde at 1 atm. pressure has also been measured.

Experimental

Materials.—"Niacet" acetaldehyde was rectified to ±0.1° in a four-foot Fenske-type column, sealed into Pyrex ampules and stored in the dark. The density of the purified acetaldehyde was determined at several temperatures since the values found in the literature[4] varied by about 0.5%. A pycnometer was made with a 50-ml. bulb and a stem 20 cm. long of 8-mm. tubing. A sample of acetaldehyde was distilled into the pycnometer after the air had been swept out of the system. A small excess was collected and distilled out again. The stem was then sealed off. The position of the meniscus was measured at three different temperatures. The measurements are estimated to be accurate to within 0.1%; the apparent precision of numerous measurements was better than 0.03%. At 0.0° the density was found to be 0.8054 and at 25.0°, 0.7720. These results coincide with the lowest of the values recorded in the literature.

Thiophene-free benzene from the Barrett Company was dried over sodium and rectified.

Apparatus.—In the Swann type of calorimeter, the vapor flows through a straight, thermally insulated tube at a known rate, and the temperature rise due to a known heat input is measured. In such a calorimeter heat is lost to the surroundings at a rate closely proportional to ΔT such that the heat input, Q, equals $C_pF\Delta T + k\Delta T$, or $C'_p = Ct + p'/F$. The apparent value of the heat capacity, C'_p, is plotted against the reciprocal of the flow rate, F, and the true value, C_p, is obtained by extrapolation to infinite rate of flow.

The calorimeter used in this investigation was designed to decrease the direct heat transfer from the heater to the thermometers, either by radiation across the intervening space as might occur in the Pitzer[5] modification of the Swann calorimeter, or by internal reflection around the U-bend. Platinum resistance thermometers were used in place of thermels to decrease the heat leak along the lead-out wires. The U-tube inside the main jacket of the calorimeter (see Fig. 1) was 20 cm. long and made of very thin-walled tubing, 8 mm. inside diameter, drawn from larger tubing. The bottom was flattened to diminish the reflection of radiation from one side to the other. Both jackets were silvered; the main jacket was evacuated continuously during the runs. The temperature of the incoming vapor was measured at T_1, the heater was at H, and the temperature rise was measured at T_2.

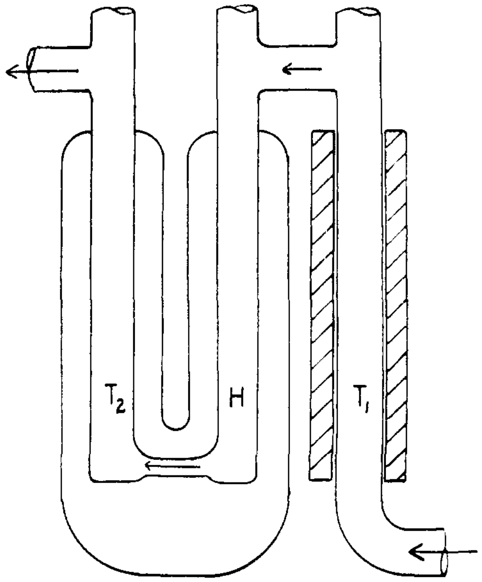

Fig. 1.—Schematic diagram of calorimeter.

The thermometer elements were made according to the instructions of Meyers,[6] except that the mica crosses were 3.5 cm. long with about 0.8 mm. between turns of the platinum helix. The lower parts of the gold leads were supported with mica insulators. The upper parts of the leads were insulated with glass capillaries. The gold leads were sealed into the Nonex-tipped Pyrex heads with Housekeeper-type seals. After proper annealing, the thermometers were calibrated with care and later rechecked at the ice, steam and sulfur points in apparatus as specified by Mueller and Burgess.[7] The resistance at 0° was about 24.7 ohms. The heater, H, was a thermometer element with the potential leads shortened to bring the branch-points near the top of the jacket.

The calorimeter was mounted in an oil thermostat. The open top of the oil-bath was covered by an air thermostat regulated to within a degree of the same temperature. The calorimeter was preceded by five feet of 18 mm. tubing within the oil-bath. Re-entrant bulbs were sucked in the walls to increase the surface and decrease the free cross section. A differential thermel compared the temperature of the vapor with that of the bath to ensure sufficient preheating.

The vaporizer (see Fig. 2) consisted of a boiler F about 56 mm. in diameter with a flat immersion heater G of about 35 ohms resistance which was made from chromel wire covered with glass wool to promote smooth boiling. The spray traps D contained glass wool. The boiler was completely surrounded by a light nickel radiation shield E except for a narrow observation slit and was in a jacket

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(2) Callendar and Barnes, *Trans. Roy. Soc.* (*London*), **199A**, 55 (1902); Swann, *ibid.*, **210**, 199 (1910); *Proc. Roy. Soc.* (*London*), **82A**, 147 (199).

(3) Scott, Waddington, Smith and Huffman, *J. Chem. Phys.*, **15**, 565 (1947).

(4) "International Critical Tables," Vol. **III**, pp. 155, 156; Landolt-Börnstein, "Tabellen," 5th ed., Vol. 0, p. 460; Suppl. I, p. **214**; Suppl. IIIa, p. 399; Heilbron-Bunbury, "Dictionary of Organic Compounds," Vol. I, p. 2.

(5) Pitzer, THIS JOURNAL, **63**, 2413 (1941).

(6) Meyers, *J. Research Natl. Bur. Standards*, **9**, 807 (1926).

(7) Mueller and Burgess, U. S. Bur. Standards, Sci. Paper No. 339 (1919).

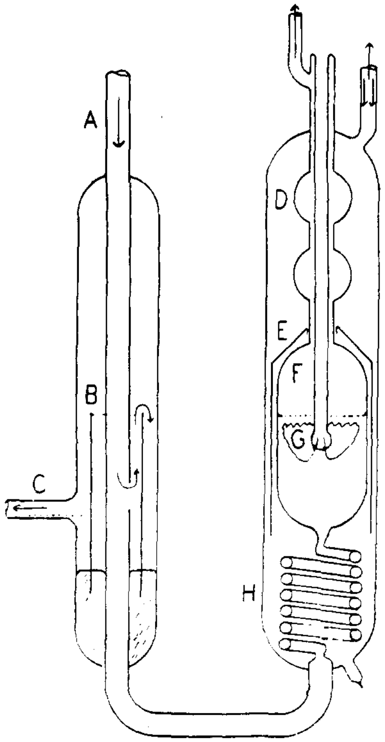

Fig. 2.—Vaporizer.

which was heated at H to boil a separate portion of the compound that was boiled in F. The liquid level in the boiler was maintained at a constant level of 1 cm. above the heater wires by supplying condensate at A from an auxiliary boiler and using an adjustable overflow B which consisted of a loose glass sleeve floating on mercury. Excess liquid was returned to the auxiliary boiler by way of C.

Before a measurement was made, the vapor was circulated through the calorimeter and returned to the auxiliary boiler. To make a measurement, the flow of the condensate was diverted by a magnetically operated valve (see Fig. 3) to a sample trap whose volume was approximately 50 ml. and which could be emptied by collecting additional liquid to start a siphon and thus permitting the liquid to flow into the auxiliary boiler. The valve consisted of a light nickel funnel whose lower end dipped about one-half cm. into one of the exit tubes, while the upper end extended at least one cm. above the drip-tip. The entire valve was enclosed in a water jacket, with a solenoid wound on the jacket at the top of the funnel and two electromagnets mounted below the solenoid, one on each side. At each operation of the valve the solenoid and one magnet are energized momentarily, lifting the funnel, swinging it to the desired position and then dropping it. The valve was rapid and precise in its action and was synchronized with an electric timer.

Electrical.—Input to the calorimeter heater was from a 2-v. lead storage cell which was constantly charged by current from the 220-v. d. c. line, stabilized by dropping resistors and two glow-discharge tubes (OA3/VR75). The current through the heater was computed from the potential drop across a calibrated manganin resistor in series with the heater. A similar calibrated resistor was in series with the vaporizer heater. The potential across the heater was measured with lead out wires separate from the current leads.

The resistances of the platinum thermometers were measured by means of a Rubicon Mueller bridge (Cat. No. 1550). All potentials were measured by means of a Rubicon Type B potentiometer. Both the bridge and the potentiometer were calibrated at the beginning of the investigation.

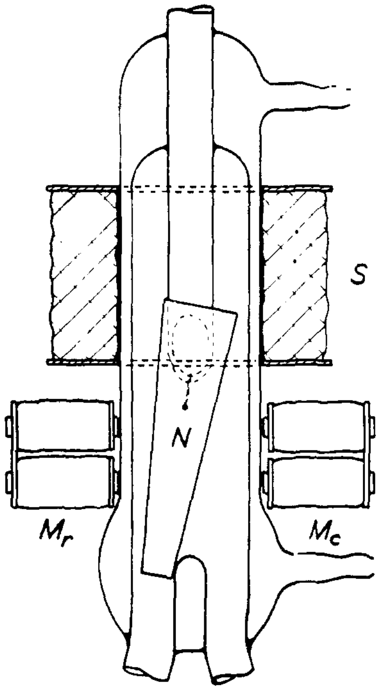

Fig. 3.—Magnetically operated valve.

Procedure.—The rate of vapor flow was first adjusted, and fifteen to thirty minutes allowed for steady state to be reached. Then a series of measurements was made of T_1 and T_2, to check relative temperature zones. The heater H in the calorimeter was next connected to its power supply, about 0.015 cal. per sec. While the temperatures were approaching the new steady state, the flow rate was checked by collecting a timed sample. The apparent heat of vaporization λ' was determined by measuring the heat input to the vaporizer five to ten times during the collection period. Finally, consecutive measurements were made over a period of about thirty minutes of the two temperatures, T_1 and T_2, the heat input to the calorimeter, and that to the vaporizer. The flow rate F during this period was calculated from the input to the vaporizer and the apparent latent heat previously determined.

In order to determine the heat of vaporization, in several runs the flow rates were measured with the vaporizer jacket pressure adjusted to equal that inside the vaporizer, which is slightly higher than that of the calorimeter manostat. The values of λ' so obtained were plotted against $1/F$ and extrapolated to λ at infinite flow, on the assumption that all major errors in λ' were inversely proportional to the flow rate.

Numerous measurements were made at two or more flow rates, and the true heat capacity was determined by extrapolating the values of the apparent heat capacity to infinite flow by plotting C'_p *vs.* $1/F$.

Results

The performance of the apparatus was tested by determining the heat capacity of benzene. From thirteen measurements at five different flow rates, the heat capacity was found to be 25.68 cal./mole/deg. at 99.2°, in excellent agreement with the value 25.67 reported by Scott, *et al.*[3] The flow rates were between 0.022 and 0.108 g./sec., the heat input was about 0.016

cal./sec., and the temperature rise varied from 0.44 to 1.84°. With a flow rate of 0.010 g./sec. and a ΔT of 3.17°, the point did not fall on the straight line. The heat of vaporization at 1 atm. (80.1°) was found to be 7360 cal./mole, compared with 7349 reported by Scott.[3]

The heat of vaporization found for acetaldehyde at 1 atm. (21°) was 139.5 cal./g., 6145 cal./mole, ±0.5% (see Fig. 4). Berthelot[8] obtained 136 cal./g. by condensation of the vapor. Roth[9] reported 137 cal./g. at 17.4°.

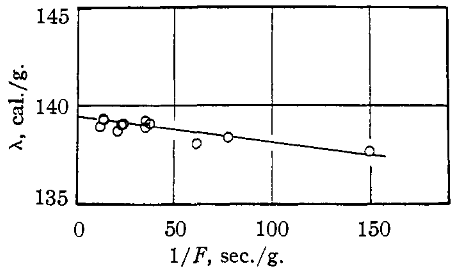

Fig. 4.—Heat of vaporization of acetaldehyde.

Heat capacities for acetaldehyde were measured at 25, 50, 100 and 150°; the results are shown in Table I and Fig. 5. The calorimetric determinations were made in two sets, at different times and with different batches of acetaldehyde. The check runs with benzene were made between the two sets of acetaldehyde runs, which eliminated any probability of a temporary systematic error. It is obvious to suspect that polymers or other products may have accumulated in the highly-reactive acetaldehyde to cause a large error, but the runs at 100° in set I were started after the acetaldehyde had been used in the calorimeter system for over a month, while the 100° runs of set II were completed within two days after the acetaldehyde was introduced into the system. Moreover, there was no drift in the measured heat of vaporization.

TABLE I

HEAT CAPACITY OF ACETALDEHYDE AT 760 MM.

Set I, Measurements made in December, 1947

t, °C.	25.4	50.3	100.2
T, °K.	298.6	323.5	373.4
c_p, cal./g./degree	0.355	0.333	0.346
C_p, cal./mole/degree	14.8	14.7	15.2

Set II, Measurements made in April, 1948

t, °C.	24.9	49.7	99.5	149.2
T, °K.	298.1	322.9	372.7	422.4
c_p, cal./g./degree	0.336	0.335	0.346	0.370
C_p, cal./mole/degree	14.8	14.8	15.2	16.3

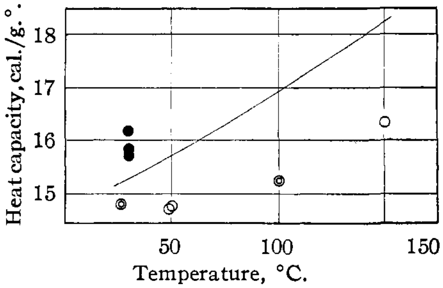

Fig. 5.—Heat capacity of acetaldehyde: this work, O; calculated from velocity of sound, ●. The solid line follows the values calculated by Smith from erroneously assigned vibrational frequencies.

The calorimetric data show a flat minimum near 50° in a manner to be expected on the assumption of association near the boiling point. This has been observed for methyl alcohol and for nitromethane.[10]

The results are lower than those computed from the velocity of sound,[11,12] which ranged from 15.7 to 16.2 cal./mole at 30°. Smith[13] has calculated C_p° at temperatures from 25 to 1227° from the spectroscopic data of Thompson and Harris,[12] obtaining 15.0 cal./mole/degree at 25°, 17.6 at 127° and 20.0 at 227°. Pitzer and Weltner[14] have resolved the disagreement between the calculated values of Smith and our data by reassigning the vibrational frequencies of acetaldehyde.

One of the authors (C. F. C.) expresses his thanks to the Purdue Research Foundation for financial assistance in the form of a research fellowship.

Summary

The heat capacity of acetaldehyde was determined at 1 atm. and 25, 50, 100 and 150°, using a direct-flow calorimeter. The vapor was heated electrically; the increase in temperature was measured with platinum resistance thermometers.

The density of acetaldehyde at 0 and 25°, and the heat of vaporization at 1 atm. were also determined.

WEST LAFAYETTE, INDIANA RECEIVED MARCH 28, 1949

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[8] Berthelot, *Ann. chim. phys.*, [5] **9**, 178 (1876). "International Critical Tables," Vol. V, p. 136.

[9] Roth, listed as unpublished data, Landolt-Börnstein, "Tabellen," 5th ed., Suppl. I, p. 805.

[10] De Vries and Collins, THIS JOURNAL, **63**, 1343 (1941); Pitzer and Gwinn, *ibid.*, **63**, 3313 (1941).

[11] Wüllner, *Ann. Physik*, **4**, 321 (1878). "International Critical Tables," Vol. V, p. 80; Müller, *Ber.*, **16**, 214 (1883); Landolt-Börnstein, "Tabellen," 5th ed., Vol. II, p. 1280; Shaha, *Indian J. Physics*, **6**, 445 (1931); Landolt-Börnstein, *op. cit.*, Suppl. IIIc, p. 2323.

[12] Thompson and Harris, *Trans. Faraday Soc.*, **38**, 37 (1942).

[13] Smith, *Trans. Am. Inst. Chem. Engrs.*, **42**, 983 (1946).

[14] Pitzer and Weltner, THIS JOURNAL, **71**, 2842 (1949).