[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TEXAS]

The Heat Capacities at Higher Temperatures of Ethane and Propane[1]

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Several accurate experimental determinations of the heat capacities of gaseous ethane[3,4,5] and propane[6] at, near, or below room temperature have been made and the problem of the hindered potentials in the two gases has been studied from a number of standpoints. It seemed desirable to extend the experimental heat capacity measurements over as wide a temperature range as possible in order to test the previously determined heights and shape of these barriers and the vibrational assignment chosen for these two molecules.

The general method of determining gaseous heat capacities as developed by Bennewitz and Schulze,[7] was adopted for this investigation; certain modifications, to be described in the next section, were made in the interest of greater accuracy and ease of operation. With this adiabatic flow calorimeter, heat capacities were determined over the temperature range, 340–700°K. with an accuracy of at least one part in 100.

Design and Operation of Apparatus

In the method of Bennewitz and Schulze,[7] the heat capacity of the gas is obtained in terms of the electrical energy input of a heater which is necessary to maintain a linear temperature gradient along a thin-walled Pyrex tube, placed between two massive brass blocks maintained at a temperature difference, ΔT, through which a stream of the gas is flowing with a known velocity.

For the general design of the apparatus, the description given by Bennewitz and Schulze[7] may be consulted. Only changes in design which facilitated the ready assembly of the apparatus, which increased the sensitivity of the calorimeter, and which insured a more convenient manipulation and a more complete drying of the gases will be discussed here.

The *brass blocks* of the apparatus were connected by four symmetrically placed Pyrex glass rods cemented into place by means of sodium silicate and these blocks were bound together by means of a small split brass cylinder secured by several small screws. These blocks were bored off-center in a manner such that the Pyrex glass calorimeter lining could be slipped readily into place *after* the blocks had been assembled in rigid fashion and with the thin glass "blind tube" already in place. This tube was fashioned from the same piece of hand-drawn tubing as that of the center section of the calorimeter lining; its wall thickness was approximately 0.1 mm. The greater portion of the lining was constructed from stock tubing, selected to fit snugly into the brass blocks; its wall-thickness had been reduced to 0.1 to 0.2 mm. by treatment with aqueous hydrogen fluoride.

The differential *thermopile*, which served to detect a displacement of the linear temperature gradient along the thin-walled capillary portion of the calorimeter lining, consisted of 24 nickel–copper junctions; it was constructed on a form of thin mica strips. Bennewitz and Schulze[7] used only 13 junctions. The complete thermopile could be slipped into position between the bottom surface of the "blind tube" and the calorimeter lining. The differential *thermocouple*, used to measure the temperature difference, ΔT, of the two brass blocks, consisted of four copper–constantan junctions insulated with a winding of asbestos fibers.

All *voltage measurements* were made with a Leeds and Northrup Type K-2 potentiometer. Potentiometric measurements were substituted in this investigation for the voltmeter, ammeter, and galvanometer deflection readings of Bennewitz and Schulze,[7] because the arrangement and design of the apparatus was more compact and amenable to the more leisurely and more reliable potentiometric measurements.

The *drying* of the gas was done by the passage through two large-capacity towers; one of these contained anhydrous calcium chloride and the other Anhydrone. The two drying towers were substituted for the single calcium chloride tower of Bennewitz and Schulze, because preliminary measurements indicated that even traces of water vapor would affect seriously and adversely measurements on gases of large heat capacity. The calibrated gasometer bulb was fitted with sealed-in tungsten contact points to permit of automatic timing of the gas flow.

The three thermocouples were calibrated, while actually in operating position in the experimental oven, against a platinum resistance thermometer recently checked by the National Bureau of Standards.

At least four measurements of the heat capacity of each gas were carried out at each of seven or eight temperatures between 340 and 700°K. The determination at any one temperature, for all the gases, was made as a single series, thereby avoiding a loss of time in the attainment of a linear temperature gradient and of heat equilibrium between the various parts of the calorimeter.

Experimental.—Determinations were first made on dry air as a means of checking the apparatus and method before attempting actual determinations on ethane and propane. The heat capacity of dry air is also reasonably well-known

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(1) Constructed from a portion of a thesis presented to the Graduate Faculty of the University of Texas by Benjamin P. Dailey in partial fulfillment of the requirements for the degree of Doctor of Philosophy, August, 1942.

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(3) Eucken and Parts, *Z. physik. Chem.*, **B20**, 189 (1932).

(4) Hunsman, *ibid.*, **B39**, 23 (1938).

(5) Kistiakowsky and Rice, *J. Chem. Phys.*, **7**, 281 (1939).

(6) Kistiakowsky and Rice, *ibid.*, **8**, 616 (1940).

(7) Bennewitz and Schulze, *Z. physik. Chem.*, **A126**, 299 (1940).

from spectroscopic data. **Air.**—Ordinary air was washed by passage through distilled water, after which it was thoroughly dried by means of calcium chloride and Anhydrone. **Ethane.**—A sample of ethane from the Ohio Chemical Company, labelled "95% Pure," was carefully fractionated in a low-temperature fractionating column. From a charge of 350 cc. of liquid ethane, a middle fraction of 70 cc. was collected and stored in a previously evacuated gas storage vessel. The observed normal boiling point of this sample was −88°. **Propane.**—This material, from the Matheson Company, had a total impurities content of not more than 0.1%, the impurities being chiefly ethane and the butanes. The sample had a normal boiling point of −41.5°. It was used without further purification after thorough drying.

The Data Obtained.—The results of the heat capacity determinations are presented in Table I; the actual observations may be found elsewhere.[1] The reduction of these experimental values to the state of the ideal gas at one atmosphere is based upon Berthelot's equation. The magnitude of the correction, $C_p - C_p^0$, is so small at the temperatures of this investigation that only a small error could be introduced by the utilization of this method; in fact, the error would be considerably less than the probable calorimetric error. The heat capacities were calculated from these data by means of the following relations:

TABLE I

EXPERIMENTAL VALUES OF THE HEAT CAPACITIES OF AIR, ETHANE, AND PROPANE

Temp., °C.	C_p, Cal./deg./mole	$C_p - C_p^0$, Cal./deg./mole	C_p^0, Cal./deg./mole
	Air		
72.9	6.973	0.007	6.966
86.0	6.975	.006	6.969
114.0	6.978	.005	6.973
179.0	7.087	.003	7.084
246.9	7.202	.002	7.200
289.4	7.284	.002	7.282
332.3	7.306	.001	7.305
	Ethane		
74.5	14.14	0.06	14.08
86.6	14.49	.06	14.43
114.4	15.32	.05	15.27
178.8	17.34	.03	17.31
247.4	19.16	.02	19.14
288.5	20.64	.02	20.62
330.1	21.63	.01	21.62
	Propane		
70.5	19.80	0.14	19.66
86.9	20.48	.12	20.36
114.6	21.72	.10	21.62
179.4	25.13	.06	25.07
248.0	27.93	.04	27.89
288.8	29.13	.03	29.10
330.1	30.78	.03	30.75
420.0	33.63	.02	33.61

$$C_p = \frac{0.239\ E{\cdot}T}{\mathrm{d}n/\mathrm{d}t\ \Delta T}$$

where $E{\cdot}T$ is the electrical energy imparted by the heater, ΔT is the difference in temperature of the brass blocks, and $\mathrm{d}n/\mathrm{d}t$ is the rate of flow of the gas as determined by the relation

$$\mathrm{d}n/\mathrm{d}t = \frac{V}{82.06 \times t \times T \times 76}\left[1 - \frac{p_{\mathrm{H_2O}}}{B - h/d}\right](B - h/d)$$

Here V is the volume of the calibrated gasometer bulb; t is the time in seconds to empty the bulb; T is the average Kelvin temperature of the gas and the gasometer liquid; B is the barometric pressure; h is the height in centimeters of the gasometer entry tube; and d is the density of mercury at the temperature T.

The experimental heat capacity data are also presented graphically in Figs. 1 and 2, together with the values calculated from spectroscopic data. For air, the values calculated by Justi[8] are presented in Fig. 1; for ethane and propane, independent calculations were made and are shown in Fig. 2. The vibrational assignment of Stitt[9] was adopted for ethane and the rotational

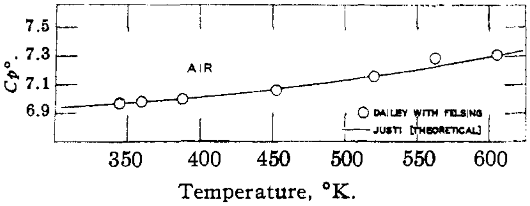

Fig. 1.

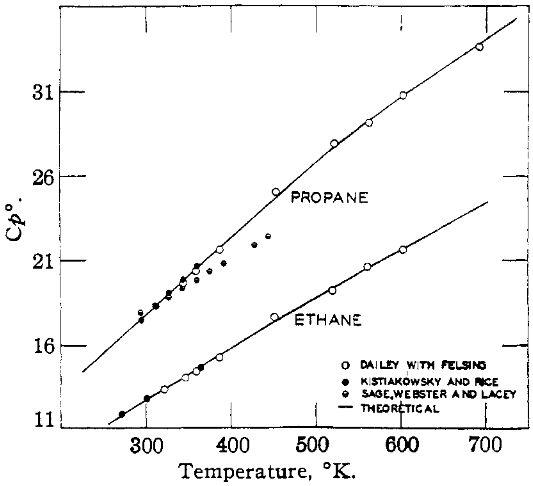

Fig. 2.

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(8) Justi, *Ann. Physik*, **29**, 302 (1938).

(9) Stitt, *J. Chem. Phys.*, **7**, 291 (1939).

heat capacity contribution was calculated by means of Pitzer's[10] tables, using for the height of the potential barrier hindering the rotation of the methyl groups the value of 2750 calories, found by Kistiakowsky[11] and co-workers. Values of the various physical constants were taken from the "International Critical Tables." A value of 2.7×10^{-40} g.-cm.^{2} was chosen for the moment of inertia, I_r. A similar procedure was followed for propane, the vibrational assignment being that of Kistiakowsky and Rice,[5] using their value, 3300 calories, for the two hindering potentials and choosing 4.4×10^{-40} g.-cm.^{2} for the reduced moment of inertia, I_r.

Discussion

The agreement between the experimental and the calculated heat capacities as shown in Figs. 1 and 2 is quite good; the deviation in every case is less than the combined errors of experiment and of the statistical calculations. The comparison is presented for air from which the carbon dioxide had not been removed. It is evident that the calorimeter of Bennewitz and Schulze, when properly modified, will yield results accurate to at least one part in 100 at temperatures up to 700°K. (or about 425°).

In the case of ethane, the agreement between experimental and calculated values again is good. While at the lower temperatures the results deviate somewhat more from the calculated values than do the values of Kistiakowsky and Rice,[5] because of a larger probable experimental error, the results for the entire temperature range, however, serve as a further confirmation of the existence of a sinusoidal hindering potential in the ethane molecule, having a height of approximately 3000 calories.

The agreement between the experimental and calculated values for propane is also satisfactory. At the lower temperatures of this investigation, there are available for comparison the conflicting data of Kistiakowsky and Rice[5] and of Sage, Webster and Lacey[12]; the agreement of the former with the results of this investigation is good, while those of the latter investigators are in less satisfactory agreement. However, the data of Pitzer[13] on *n*-pentane and of Aston, Kennedy and Schumann[14] on isobutane are likewise not in good agreement with the results of Sage, Webster and Lacey.[12]

Summary

1. Experimental values for the heat capacities of air, ethane, and propane have been determined over the temperature range 340–700°K. using a modified Bennewitz and Schulze type adiabatic flow calorimeter.
2. The results obtained have been compared with theoretical values and with the results of other investigators.
3. The Bennewitz and Schulze calorimeter has been modified to increase the ease of manipulation and to improve the accuracy of heat capacity determinations at higher temperatures.

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[10] Pitzer, *J. Chem. Phys.*, **5**, 469 (1935).

[11] Kistiakowsky, Lacher and Stitt, *ibid.*, **7**, 289 (1939).

[12] Sage, Webster and Lacey, *Ind. Eng. Chem.*, **29**, 1309 (1937).

[13] Pitzer, THIS JOURNAL, **63**, 2413 (1941).

[14] Aston, Kennedy and Schumann, *ibid.*, **62**, 2059 (1940).

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Heat Capacities of and Hindered Rotation in *n*-Butane and Isobutane[1]

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Introduction

The heights of the potential barriers to internal rotation in *n*-butane and in isobutane have been evaluated from entropy measurements by Aston and his co-workers.[3,4] On the other hand, Pitzer[5,6] has presented the results of statistical calculations using barrier heights which, in the case of *n*-butane, differ considerably from those obtained by Aston. Knowing the vibrational spectra and the moments of inertia of the two butane molecules, it should be possible to obtain values of the hindering potentials through a comparison of the calculated and the measured gaseous heat capacities reduced to the ideal gas state. Unfor-

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[3] Aston and Messerly, THIS JOURNAL, **62**, 1917 (1940).

[4] Aston, Kennedy and Schumann, *ibid.*, **62**, 2059 (1940).

[5] Pitzer, *J. Chem. Phys.*, **8**, 711 (1940).

[6] Pitzer, THIS JOURNAL, **63**, 2413 (1941).