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).

AUSTIN, TEXAS RECEIVED OCTOBER 13, 1942

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

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

BY BENJAMIN P. DAILEY[2] WITH W. A. FELSING

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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(1) Constructed from a portion of the 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.

(2) Present address: N. D. R. C., 4800 Forbes Street, Pittsburgh, Pa.

(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).

tunately, the previously published data on the experimental heat capacities of *n*-butane and isobutane are limited to those of Sage, Webster and Lacey.[7] The calculated heat capacities of neither Aston nor of Pitzer are in good agreement with these experimental data.

Hence, it was thought to be of interest to measure these heat capacities over the range 340–700°K., using the calorimeter described in a previous paper.[8]

The Materials Used

***n*-Butane.**—The sample used was obtained from the Matheson Company.[9] Their analysis indicated the presence of approximately 1% of impurities, chiefly isobutane. The normal boiling point was determined in this Laboratory to be −0.7°. **Isobutane.**—This sample was also obtained from the Matheson Company. The observed normal boiling point was found to be −11.5°. The manufacturer's analysis indicated a maximum impurity of 2%, but vapor density determinations in this Laboratory indicated its purity to be at least 99%.

The Heat Capacity Determinations

The apparatus and the method employed have been described in a previous paper.[8] The heat capacity results are presented in the accompanying table and figure.

TABLE I

HEAT CAPACITIES OF *n*-BUTANE AND ISOBUTANE

Temp., °K.	C_p, cal./deg./mole	C_p^0, cal./deg./mole
	n-Butane	
344.9	26.67	26.43
359.6	27.68	27.47
387.5	29.27	29.10
451.6	33.09	32.98
521.0	36.88	36.81
561.3	38.84	38.78
600.8	40.76	40.71
692.6	44.45	44.42
	Isobutane	
347.6	26.41	26.21
359.4	27.09	26.90
387.5	28.73	28.59
452.5	32.86	32.75
520.9	36.64	36.55
561.7	38.60	38.55
605.3	40.60	40.56
692.7	44.29	44.26

Discussion of Results

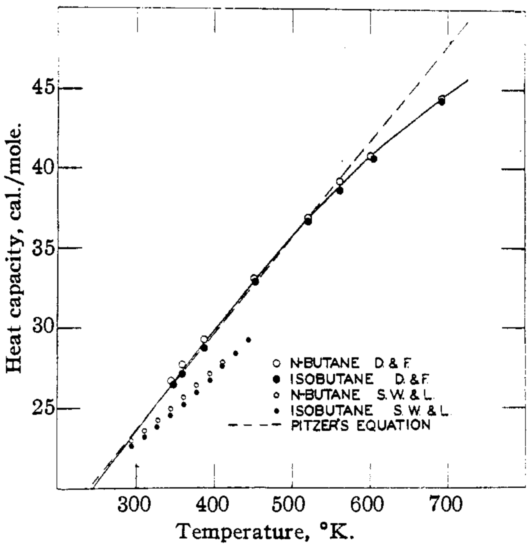

Fig. 1.

In the calculation of the heat capacities of *isobutane*, the frequency assignment taken was that of Pitzer.[5,6] Using the value of 3870 cal./mole for the potential hindering the rotation of the three methyl groups in isobutane, obtained by Aston and co-workers,[3,4] there were obtained values which agree with the experimental values to within the estimated maximum experimental error (1%). Calculations making use of the Aston value of 950 cm.$^{-1}$ for the lower group of hydrogen bending frequencies, instead of Pitzer's value of 1090 cm.$^{-1}$, yield values which appear to be somewhat too large. The experimental values of Sage, Webster and Lacey[7] for isobutane fall considerably below the experimental results of this investigation, as shown in the figure, and are not in agreement with the calculated results. Their agreement with the calculated results of Aston and co-workers is even less satisfactory.

Calculations of the gaseous heat capacity and other thermodynamic functions of *n-butane* have been presented by Pitzer.[5] He used a value of 3300 calories for the potentials hindering the rotation of the end methyl groups, 3600 calories for the potential hindering the rotation of the two ethyl groups, and a value of 1000 cm.$^{-1}$ for the lower group of hydrogen bending frequencies. The experimental data of this investigation are in good agreement with these assumptions regarding the butane molecule. The agreement with Pitzer's revised calculations,[10] using the value of 1090 cm.$^{-1}$ for the doubtful hydrogen bending frequencies, is even better. Aston and Messerly,[3] however, have obtained an entropy value for *n*-butane which indicates a potential barrier of approximately 30,000 calories for the rotation of the ethyl groups in *n*-butane. They used a

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(7) Sage, Webster and Lacey, *Ind. Eng. Chem.*, **29**, 1309 (1937).

(8) Dailey with Felsing, THIS JOURNAL, **65**, 42 (1943).

(9) The Matheson Company, Inc., East Rutherford, N. J.

(10) K. S. Pitzer, private communication.

method of calculation which ignores the so-called "steric factor" of Pitzer's calculations.

The difference between the experimental heat capacity, as determined, and the calculated heat capacity neglecting hindered rotation should yield a possible value for the rotational heat capacity; a comparison of this value may be made with the values of rotational heat capacities calculated, using Pitzer's tables, on the basis of the two conflicting barrier heights. However, the comparatively large probable experimental error of this investigation (up to 1%) in comparison with the magnitude of the contribution of this hindered rotation to the heat capacity prevents any positive decision as to the correct barrier height. However, the shape of the experimental heat capacity–temperature curve is in better agreement with the values based upon the lower barrier height of approximately 3600 calories. Pitzer[6] has presented arguments which seem to cast some doubt upon the correctness of Aston and Messerly's interpretation of the experimental data. Again, the data of Sage, Webster and Lacey[7] are not in good agreement with the results of either this experimental study or the theoretical treatment of Pitzer. The agreement of their data with the interpretation of Aston and Messerly is even less satisfactory.

Pitzer[6] has presented a general equation for the calculation of the gaseous heat capacities of hydrocarbons, stated to be applicable at temperatures up to 450°K. The results of this investigation are in good agreement with this equation up to approximately 500°K. (see figure). At higher temperatures, the experimental heat capacities are less than predicted by Pitzer's general linear equation.

In this investigation, the heat capacity of *n*-butane was found to be consistently slightly higher than the heat capacity of the isobutane at corresponding temperatures. This observation is in general agreement with the results of Sage, Webster and Lacey[7]; they also observed higher values for *n*-butane than for isobutane. However, the calculated values differ in the opposite direction. Since the difference in heat capacities of these isomers is well within the combined theoretical and experimental errors in every case, no special significance is attached to these results.

Summary

1. The gaseous heat capacities of *n*-butane and isobutane have been measured over a range of 340 to 700°K. and have been presented tabularly and graphically.

2. The structure of these two molecules has been discussed in the light of these results.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS]

The Heats of Vaporization of Some Hexanes[1]

BY JOE FRED LEMONS[2] WITH W. A. FELSING

Introduction

This Laboratory has been carrying on a program of determining reliable data on the thermodynamic properties of pure hydrocarbons, such as $\tilde{P}$—$\tilde{V}T$ relations[3] and heat capacities.[4] This investigation deals with the determination of heats of vaporization of *n*-hexane, 2-methylpentane, and 2,3-dimethylbutane over a temperature range, 20° to approximately 80°.

Values of the heats of vaporization for *n*-hexane are given by Young[5] (0 to 234.8°), by Jahn[6] (at 0°), by Mabery and Goldstein[7] (at 68°), and by Tyrer[8] (at 66.88°). For 2,3-dimethylbutane, under the name di-isopropyl, Young[5] gave values from 0 to 227.35°. For 2-methylpentane no data were found. A comparison of the data of the literature with that of those investigation will be made later.

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(1) Constructed from a portion of a dissertation presented to the graduate faculty of the University of Texas by Joe Fred Lemons in partial fulfillment of the requirements for the degree of Doctor of Philosophy, August, 1942.

(2) Present address: The Tennessee Valley Authority, Florence, Alabama.

(3) Kelso with Felsing, THIS JOURNAL, **62**, 3132 (1940); *Ind. Eng. Chem.*, **34**, 161 (1942); Kelso, Wash, Horeczy, Shive with Felsing, THIS JOURNAL, **63**, 2273 (1941).

(4) Dailey with Felsing, THIS JOURNAL, **65**, 42 (1943), and *ibid.*, **65**, 44 (1943).

(5) S. Young, *Sci. Proc. Roy. Dublin Soc.*, **12**, 374 (1910), through Mills, THIS JOURNAL, **31**, 1099 (1909).

(6) Jahn, *Z. physik. Chem.*, **11**, 787 (1893).

(7) Mabery and Goldstein, *Am. Chem. J.*, **28**, 66 (1902).

(8) Tyrer, *J. Chem. Soc.*, **99**, 1633 (1911).