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.

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 P–VT 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.

(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).

The Apparatus

The present investigation employed a calorimeter similar in design to the one proposed by Keyes and Beattie,[9] in which they had incorporated many improvements in design over older forms. In general terms, theirs was a calorimeter which allowed the vaporization process to be completely adiabatic, which minimized loss or gain of heat by radiation, convection or conduction. The vaporization process was non-turbulent, assuring a dry vapor. The vaporization was a continuous process, ensuring a series of determinations which could be averaged under conditions which practically eliminated personal errors in reading. Finally, the mass of material vaporized and the energy input could be accurately determined.

The Calorimeter.—The calorimeter followed the general design of Keyes and Beattie[9]; only changes in design will be discussed. The details are shown in Figure 1. (a) A Leeds and Northrup flat type platinum resistance thermometer, calibrated by the National Bureau of Standards, was used; it is shown at B. The entire thermometer was enclosed in the evacuated jacket C; good thermal contact with the silver coils was insured by employing Rose metal as the space filler. (b) The outer jacket C was a cylindrical iron vessel, 40 cm. long and 8 cm. in diameter; it was coated on the inside with several thin coats of glyptal resin lacquer, baked on at 150° for three hours between each coating. The junction between the two portions of the jacket was made vacuum-tight by means of a neoprene washer between two machined surfaces. (c) In order to minimize heat leakage along the electrical leads to the calorimeter, each lead was brought into good thermal contact with the outer jacket at the surface D by means of sheaves of silk-covered copper wire, baked into position by means of glyptal lacquer. (d) The heater wire, the four thermometer leads, and the two potential leads passed up through the 1 cm. glass tube and into the atmosphere through de Khotinsky cement. (e) The glass tube E was attached to the jacket by means of a brass-to-glass soldered joint, made according to the directions of McKelvey and Taylor.[10] The silver exit tube was also soldered to the jacket at its point of exit. The entire calorimeter was immersed in a thermostat kept constant at any desired temperature to ±0.01–0.02°.

The Accessory Equipment.—Platinum resistances were measured on a Mueller bridge. The calorimeter heater current was determined by measuring the voltage drop across the heater (approximately 13.5 ohms) and across the standard resistance (13.174 ohms), employing a Leeds and Northrup Type K-2 potentiometer and accessories.

The volumnometer consisted of a calibrated buret, which could be read by means of a cathetometer. The volumnometer could be immersed to any desired depth in a movable thermostat, the temperature of which could be controlled at any temperature to ±0.1°.

The loading device presented no essential changes from that described by Keyes and Beattie.[9] The operation, also, presented no marked special features.

Density measurements on the liquids were made with pycnometers of the type described by Keyes and Felsing.[11]

(9) Keyes and Beattie, THIS JOURNAL, **46**, 1753 (1924).

(10) McKelvey and Taylor, ibid., **42**, 1364 (1920).
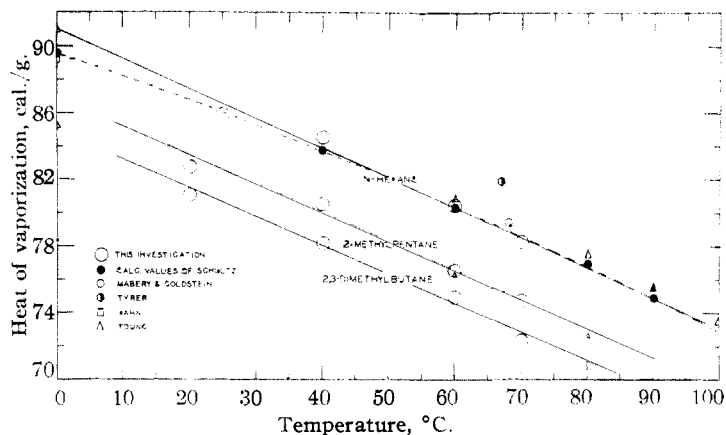
(11) Keyes and Felsing, ibid., **41**, 589 (1919).

The Materials: Normal Hexane.—This material was prepared by the procedure outlined by Kelso with Felsing[3]; it had the constants: b. p. (760 mm.), 68.70°; $n^{20}D$ 1.3750; and d^{20}_4 0.6594. **2-Methylpentane.**—This sample was obtained from Dr. Johannes H. Bruun, who stated its constants to be: b. p. (760 mm.), 60.19 ± 0.05°; $n^{20}D$ 1.3711; d^{20}_4, 0.6527. **2,3-Dimethylbutane.**—This sample was prepared by Kelso with Felsing[3] and had the following constants: b. p. (760 mm.), 57.97 ± 0.02°; $n^{20}D$ 1.3748; and d^{20}_4, 0.6615.

Densities of these samples at other temperatures were determined and expressed by means of equations found below.

Fig. 1.

The Data Obtained

The experimentally determined data may be found elsewhere[1]; the final results, only, are presented here.

The densities of the three hexanes were determined over a range of 0° to approximately their normal boiling points under their own vapor pressures. These densities are represented by the following equations, which reproduce the experimental values to better than 0.0001 g./ml. and which agree well with literature values such as listed by Egloff.[12]

n-Hexane at 0–70°:
d(g./ml.), $0.82882 - 2.6348 \times 10^{-4}T - 1.0714 \times 10^{-6}T^2$

2-Methylpentane at 0–40°: d(g./ml.), $0.91947 - 0.00091T$

40–80°: d(g./ml.), $0.82161 - 2.530 \times 10^{-4}T - 1.100 \times 10^{-6}T^2$

2,3-Dimethylbutane at 0–30°: d(g./ml.), $0.92540 - 0.0009T$

30–80°: d(g./ml.), $= 0.85026 - 3.871 \times 10^{-4}T - 8.749 \times 10^{-7}T^2$

The heats of vaporization at the different temperatures are presented in Table I; each value listed is the average of several closely agreeing determinations.

TABLE I

HEATS OF VAPORIZATION AT DIFFERENT TEMPERATURES

Temp., °C.	Heats of vaporization, cal./g.		
	n-Hexane	2-Methylpentane	2,3-Dimethylbutane
20	..	82.7	81.0
25	85.9	..	..
40	84.5	80.5	78.1
60	80.4	76.5	74.9
80	78.2	74.7	72.3

A comparison of the above values with the data available in the literature is given in Fig. 2.

(12) Egloff, "Physical Constants of Hydrocarbons," Reinhold Publishing Corp., New York, N. Y., 1939, Vol. 1, p. 37.

Fig. 2.

values for 2,3-dimethylbutane differ from those of Young[5] by about the same amount in the same direction. No comparison is possible for the 2-methylpentane values.

A consideration of all the possible sources of error points to a maximum over-all error of $\pm 1.0\%$, though it is believed the probable error is somewhat less. In Fig. 2, the diameters of the circles for our experimental values correspond to a deviation of $\pm 0.005\%$ from the average value. Straight lines were drawn through the data points, since it is believed that the data do not warrant a curvilinear relationship. The curved dotted line represents, for n-hexane, the values calculated by Schultz,[14] based upon the data of Young.[5]

The position of the lines in Fig. 2 indicates the effect of branching upon the value of the heat of vaporization; the greater the branching, the smaller the heat of vaporization. It will be interesting to ascertain if this generalization will hold when the other two hexanes are investigated.

The values listed in the table have been corrected for the Joule–Thomson cooling of the vapor due to the drop in pressure in going from the calorimeter to the volumnometer; the correction was evaluated by means of the relation Q (calories) = $\mu C_p \Delta p$, where μ is the Joule–Thomson coefficient and Δp is the observed difference in pressure. The Joule–Thomson coefficients for these hexanes were evaluated from critical data and the relation[13] $\mu = (2a/RT - b)/C_p$ where a and b are the van der Waals constants.

Discussion of Results

It may be noted from a study of Fig. 1 that the experimental values of the heats of vaporization for n-hexane tend to be somewhat lower than the heretofore generally accepted values recorded in the literature, more particularly those of Young.[5] In no case is the difference greater than 1% and the average deviation is less than 0.5%, which is less than the probable experimental error. Our

Summary

1. The densities of liquid n-hexane, 2-methylpentane, and 2,3-dimethylbutane have been determined over a temperature range of 0° to approximately their normal boiling points.

2. The heats of vaporization of these three hexanes have been determined over a temperature range of 20° to their normal boiling points.

3. The effect on the heats of vaporization of increased branching of the chain has been noted.

(13) Taylor and Glasstone, "Treatise on Physical Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1942, Vol. I, p. 459.

(14) Schultz, Ind. Eng. Chem., 21, 557 (1929).