solutions of mono-, di- and trimethylamine hydrochloride have been determined experimentally at 25° in the concentration range 0.05 to 1.0 molal.

2. Heat capacities of these solutions have also been determined at 25°.

3. From these data and the activity coefficients near the freezing point reported by Jones, Spuhler and Felsing, the activity coefficients of these amine hydrochlorides in aqueous solution at 25° have been calculated.

AUSTIN, TEXAS RECEIVED AUGUST 21, 1944

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

The Heat Capacity of Gaseous 1,3-Butadiene from 0 to 100°

BY D. H. TEMPLETON[1] AND D. D. DAVIES[2] WITH W. A. FELSING

Introduction

Since there was considerable disagreement between calculated values of the heat capacity of gaseous butadiene, and a lack of direct experimental data, this Laboratory was asked to undertake the direct calorimetric determination in the temperature range 0 to 100°.

Stull and Mayfield[3] and Stull[4] have presented calculated values for C_p^0 and C_p', respectively, over a large temperature range, which values were based upon spectroscopic data. Workers at the National Bureau of Standards calculated some values[5] of such heat capacities, based upon thermodynamic properties of the liquid and solid butadiene. In another special report[6] two values based upon the heat capacity ratio, as determined by the velocity of sound method, are given, together with values calculated from spectroscopic data. These data are presented, for comparison, in Fig. 1 with the data of this investigation. After the results of the present paper were reported to the National Bureau of Standards, some direct calorimetric data, obtained in the Cryogenic Laboratory there, were reported[7] to the authors. These data are also included in Fig. 1.

Method and Apparatus

The Method.—The method used in this investigation was the constant flow method of Scheel and Heuse.[8] The apparatus was that used by Felsing and Drake[9]; only minor changes were made.

The Thermocouple.—A 10-junction copper–constantan thermocouple was calibrated by the use of two Beckmann thermometers measuring two temperatures 3 to 5° apart in the neighborhood of 25°. These Beckman thermometers were calibrated immediately before use against a platinum resistance thermometer certified by the National Bureau of Standards. An average value of 2505 degrees per volt was obtained for this 10-junction couple. At other temperatures, it was assumed that the values of $\Delta T/E$ were proportional to those calculated by means of Adams' table.[10]

Electrical Measurement.—A Leeds and Northrup Mueller bridge was used to measure the resistance of the platinum resistance thermometer and of a10-ohm resistance used in the heater current measurements. All other measurements were made with a Leeds and Northrup Type K-2 potentiometer. The Eppley standard cell had been certified recently by the National Bureau of Standards.

The Thermostat.—The temperature of the thermostat was maintained constant (±0.01°) at *one* degree below the temperature of measurement.

Temperature Elevation on Heating.—The temperature of the gas (air, butane, or butadiene) passing through the heating element increased approximately two degrees in all the experiments.

Materials Used

The heat capacities of air and *n*-butane were determined in the apparatus as a check. **Air.**—It was purified by passing over potassium hydroxide, calcium chloride, and anhydrone. **Butane.**—The sample was some of the material used by Dailey and Felsing.[11] It contained approximately 1% impurities, chiefly isobutane. It was purified further by distillation, as described below. **Butadiene.**—The 1,3-butadiene sample was furnished through the National Bureau of Standards by Mr. A. E. Buell of the Phillips Petroleum Company of Bartlesville, Oklahoma. Its quality was stated to be the same as that previously furnished to and tested by the National Bureau of Standards; it was stated to contain 0.0017 ± 0.0006 mole-fraction of impurity. The liquid butadiene in the steel cylinder contained 0.02% of butyl catechol to prevent polymerization. This inhibitor and the other impurities were essentially eliminated by the distillation procedure described below.

The butane (or butadiene) cylinder was connected to the calorimeter system by means of a rubber connection. After thorough evacuation of the system, a sample from the cylinder was distilled into a glass reservoir cooled to Dry Ice temperature. Any permanent gases and a portion of the condensed phase were removed by another evacuation. From the glass reservoir, under proper temperature control, enough of the liquid sample was evaporated into the evacuated calorimeter system to fill it at the desired pressure. Thus, only a middle portion was introduced into the calorimeter.

Methods of Calculation

The rate of flow was determined in terms of volume at 25° and atmospheric pressure. Densities used in the calculations were 0.001185[12] for

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[1] Present address: 5473 Ellis Avenue, Chicago, Illinois.

[2] Present address: Pan-American Refining Corp., Texas City, Texas.

[3] Stull and Mayfield, *Ind. Eng. Chem.*, **35**, 639 (1943).

[4] Stull, *ibid.*, **35**, 1303 (1943).

[5] Scott, Rands, Brickwedde and Bekkedahl, *Special Report, Natl. Bur. Standards*, July 23, 1943, Table IV.

[6] Aston, Szasz and Brickwedde, Private Report, July 23, 1943, Tables 2 and 3.

[7] Private communication from C. S. Cragoe, July 22, 1944.

[8] Scheel and Heuse, *Ann. Physik*, **37**, 79 (1912); **40**, 473 (1913).

[9] Felsing and Drake, THIS JOURNAL, **58**, 1714 (1936).

[10] "Temperature," Amer. Inst. Physics, Reinhold Pub. Corp., New York, 1941, Table 9, p. 1306.

[11] Dailey with Felsing, THIS JOURNAL, **65**, 44 (1943).

[12] "International Critical Tables," Vol. III, pp. 3 and 10.

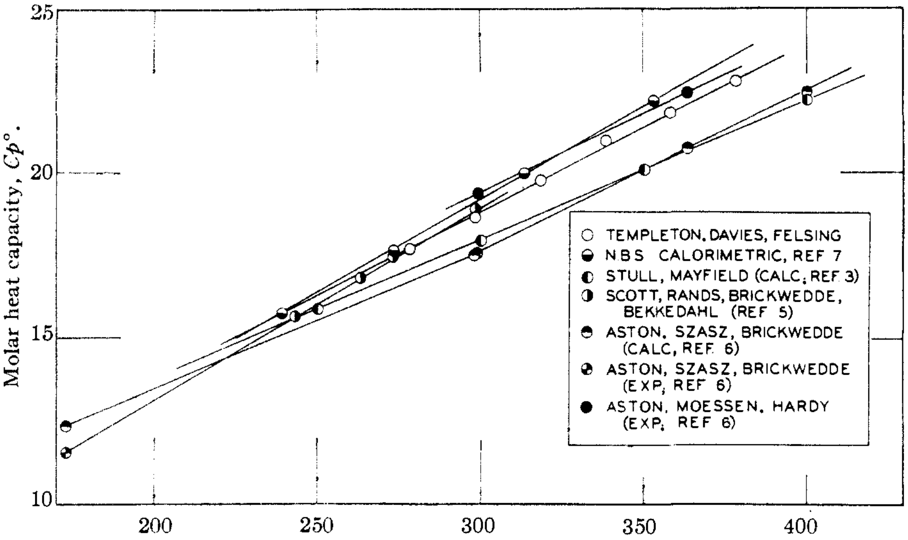

Fig. 1.—Comparison of heat capacity values for 1,3-butadiene.

air, 0.002269[13] for butadiene, and 0.002449[14] for butane at 25° and 760 mm. These values were corrected to the observed pressure by assuming Boyle's law.

An apparent specific heat was calculated from (1) the energy input, (2) the mass rate of flow and (3) the observed temperature rise. Several determinations (usually 5 to 7) were made at each temperature with different rates of flow; the energy input was adjusted in each case to keep the temperature rise approximately constant, within narrow limits. Since at higher rates of flow, the fraction of the heat lost to the thermostat became less, the values of C_p' (the apparent specific heat) decreased with increasing rate of mass flow. It has been found, empirically, that

$$C_p = C_p'(1 - k/M)$$

where k is a constant and M is the mass rate of flow. This may be rewritten to read

$$C_p' = k\frac{C_p'}{M} + C_p$$

A plot of C_p' *versus* C_p'/M yielded a straight line whose intercept, corresponding to infinite rate, was taken as C_p for the gas at a "calculated" pressure. The pressures for all the points were very nearly the same, decreasing slightly as the rate increased; the "calculated" pressure was obtained by fitting a straight line to the points of a large-scale plot of pressure, $p_{\text{obs.}}$, *versus* C_p'/M. The intercept, read graphically, was the "calculated" pressure—the pressure at which the value of C_p was applicable. The value of 4.1833 international joules was taken to be one calorie. After converting specific heats into molar heat capacities, C_p, the values of this quantity for the gas in the ideal state, C_p^0, were calculated by means of the relation

$$C_p^0 = C_p - \frac{81Rp_0T_c^3}{32p_cT^3}$$

where P_c is 42.86 atm. and T_c is 426°K.

The Data

In Table I are presented the values of the heat capacities of *n*-butane and of air at 25°; in Table II are given the results obtained for 1,3-butadiene.

TABLE I

MOLAR HEAT CAPACITIES OF *n*-BUTANE AND OF AIR AT 25°

	n-Butane	Air
Press. (mm.)	716	716
C_p (j. g.$^{-1}$°C.$^{-1}$)	1.684	1.011
C_p (cal. mole^{-1}°C.$^{-1}$)	23.40	7.003
$C_p - C_p°$(cal. mole^{-1}°C.$^{-1}$)	0.37	0.011
C_p^0 (cal. mole^{-1}°C.$^{-1}$)	23.03	6.992
C_p^0 (spectroscopic)	23.18[6]	6.954[15]
Difference (per cent.)	0.6	0.5

TABLE II

MOLAR HEAT CAPACITIES OF 1,3-BUTADIENE AT DIFFERENT TEMPERATURES

Temp., °C.	Press., mm.	Spec. heat (int. j. g.$^{-1}$ °C.$^{-1}$)	C_p (cal. mole^{-1} °C.$^{-1}$)	$C_p - C_p^0$	C_p^0 (cal. mole^{-1} °C.$^{-1}$)	C_p^0 (calcd. from Eq.)
5	721	1.394	18.08	0.40	17.68	17.67
25	712	1.465	18.94	.32	18.62	18.70
45	710	1.547	20.00	.26	19.74	19.73
65	702	1.636	21.15	.22	20.93	20.77
85	699	1.699	21.97	.18	21.79	21.80
105	682	1.772	22.91	.15	22.76	22.83

A graphical comparison of these data with those previously reported is presented in Fig. 1. The

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(13) Meyers, Scott, Brickwedde and Rands, "Thermal Properties of Vapor and Liquid 1,3-Butadiene," Special Report, Natl. Bureau of Standards, June 30, 1943.

(14) Calculated by assuming a compressibility factor of 0.970; *cf.* Sage, Webster and Lacey, *Ind. Eng. Chem.*, **29**, 1188 (1937).

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

equation of the straight line representing these data, obtained by the method of least squares, is

$$C_p{}^0 = 3.32 + 0.516T$$

The values obtained with this equation are given in the last column of Table II.

By comparison of the results attained with air and *n*-butane with the apparatus and technique employed, it is believed that the over-all accuracy of the 1,3-butadiene heat capacities is better than 1 part in 100.

Acknowledgment.—The authors wish to thank Dr. C. S. Cragoe of the National Bureau of Standards for his interest in the problem and for his efforts in securing the sample of butadiene. They also wish to thank the Phillips Petroleum Company of Bartlesville, Oklahoma, for the liberal sample of highly purified butadiene used in this investigation.

Summary

1. The heat capacities of *n*-butane and of air were determined, for calibration purposes, at 25°.

2. Six values of the molar heat capacities of 1,3-butadiene were determined over the range 5 to 105°.

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[CONTRIBUTION NO. 975 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

The Crystal Structure of Biphenylene

BY JURG WASER AND CHIA-SI LU

In an earlier paper,[1] which reported on the electron diffraction of biphenylene molecules, $C_{12}H_8$, the configuration of the carbon atoms in these molecules, as suggested by Lothrop's synthesis,[2] was confirmed, and values for various interatomic distances were assigned. In addition resonance energy and bond strengths were calculated. The present investigation deals with the crystal structure of biphenylene, and provides further proof that the compound investigated is indeed dibenzcyclobutadiene.

Unit Cell and Space Group

It was found that sublimation of biphenylene under controlled conditions resulted in sharp needles, which were, however, much too thin for X-ray work. Recrystallization from *n*-propyl alcohol gave satisfactory crystals. They were prisms, 0.25–0.5 mm. thick and 2–3 mm. long, with side faces belonging predominantly to the forms {110}, {310}, {100} and {010}. The straw-colored crystals had no distinct cleavage and showed no abnormal birefringence. Due to their appreciable vapor pressure at room temperature, their faces disappeared within a few hours on standing in open air, and the crystals evaporated completely within a few days.

All X-ray photographs showed a rather large temperature factor. Rotation and Weissenberg photographs about the three crystallographic axes led to the following dimensions of the monoclinic unit cell: $a_0 = 19.60 \pm 0.03$ Å., $b_0 = 10.50 \pm 0.02$ Å., $c_0 = 5.84 \pm 0.02$ Å., $\beta = 91°20' \pm 20'$. The absence of $(h0l)$ reflections with odd h and of $(0k0)$ reflections with odd k indicates $C_{2h}^5 - P2_1/a$ as the probable space group. Rough density measurements by flotation in an aqueous solution of potassium iodide gave $\rho = 1.24$ g./cc. Hence there are six molecules per unit cell, the calculated density being $\rho = 1.25$ g./cc.

Intensities of $(hk0)$ and $(h0l)$ reflections were estimated from Weissenberg photographs taken with unfiltered Cu K radiation, using the multiple film technique.[3] The specimens chosen for diffraction work were small enough to make absorption corrections unnecessary. It was very difficult to obtain satisfactory visual intensity correlations between different $(h0l)$ reflections due to their varying sizes, as for these reflections the axis of rotation of the crystal was perpendicular to the needle axis. It was not possible to cut a crystal sufficiently short so that its length would approximate its thickness Since there is no similar difficulty for $(hk0)$ reflections, the intensity values obtained for them should be much more reliable than the ones for $(h0l)$ reflections. No quantitative intensity data for $(0kl)$ reflections were collected, since a Fourier projection along the a axis was not expected to show any resolution.

The relative intensities obtained were corrected for the Lorentz and polarization factors with Lu's chart[4] and the scale of their square roots was adjusted to approximately absolute scale by comparison with the values calculated from the final structure. These experimental structure factors are recorded in the second columns of Tables I and II in the order of decreasing spacing, except that the values for $(h0\bar{l})$ and $(h0l)$ have been grouped together.

Determination of the Structure

In the space group $C_{2h}^5 - P2_1/a$ there are four sets of two-fold positions with the point symmetry

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[1] J. Waser and V. Schomaker, THIS JOURNAL, **65**, 1451 (1943).

[2] W. C. Lothrop, *ibid.*, **63**, 1187 (1941); **64**, 1698 (1942).

[3] J. J. De Lange, J. M. Robertson and I. Woodward, *Proc. Roy. Soc.* (London), **A171**, 398 (1939).

[4] C. S. Lu, *Rev. Sci. Inst.*, **14**, 331 (1943).