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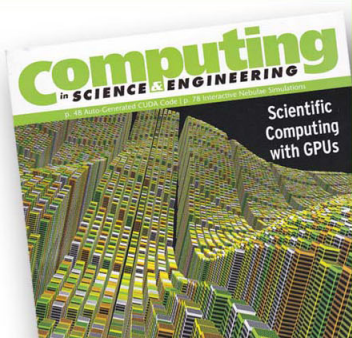
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The Heat Capacity of Benzene Vapor. The Contribution of Anharmonicity*

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The heat capacity of benzene vapor was measured at two or more pressures at each of five temperatures in the range 68° to 198°C; and values of C_p° , the heat capacity in the ideal gas state, were obtained. By assuming a moderate degree of anharmonicity of the vibrations, it was possible to obtain excellent agreement between values of C_p° calculated statistically from spectroscopic data, and the observed values. An empirical equation for the second virial coefficient of benzene vapor was obtained from the observed values of $(\partial C_p / \partial P)_T$, and heat of vaporization and vapor pressure data.

INTRODUCTION

THE Petroleum and Natural Gas Division of the U. S. Bureau of Mines is carrying on a research program to study the vapor-heat capacity of petroleum hydrocarbons and related substances. Previous publications from this laboratory^{1,2} have described the flow calorimeter currently in use, and have reported experimental results for the vapor-heat capacity of *n*-heptane, 2,2,3-trimethylbutane, *n*-hexane, and 2,2-dimethylbutane. The emphasis in this work has been on obtaining data of high accuracy. The study of the vapor-heat capacity of benzene reported in the present paper, was undertaken because the heat capacity of this substance can be calculated from spectroscopic data to the harmonic-oscillator rigid-rotator approximation. It was felt that a comparison of measured values of the heat capacity with values so calculated would give significant information about the accuracy of results obtained with the flow calorimeter. Actually, because of the inherent inaccuracies of the harmonic-oscillator rigid-rotator treatment, no direct check of the experimental measurements was possible. However, it was found that, by assuming a moderate degree of anharmonicity of the vibrations, excellent agreement between calculated and observed values of the heat capacity of benzene vapor was obtained

over the whole temperature range of the experimental measurements.

EXPERIMENTAL

The apparatus and experimental procedures have been described in detail in a recent publication¹ from this laboratory. The sample of benzene used was made available by the Chemistry and Refining Section of this station. It had been prepared for other purposes by distillation in an efficient column followed by several fractional crystallizations. From its melting-point curve,³ the sample was found to have a purity of 99.93 mole percent, assuming the impurity to be liquid-soluble, solid-insoluble. A bomb sulfur analysis⁴ (A.S.T.M. designation: D 129-44) did not indicate any significant amount of sulfur.

The vapor-heat capacity data are given in Table I. The values of C_p° were obtained by linear extrapolation to zero pressure of plots of heat capacity *vs.* pressure. For the two lower temperatures, the heat capacity was measured at three different pressures; on a plot of C_p *vs.*

TABLE I. Vapor-heat capacity of benzene;
cal./deg./mole.

1 cal. = 4.1833 int. joules; mole. wt. = 78.108; 0°C = 273.16°K					
T, °K	341.60	371.20	402.30	436.15	471.10
C_p (1 atmos.)		25.60	27.59	29.73	31.81
C_p (404 mm)	23.32	25.33			
C_p (270 mm)	23.18				
C_p (194 mm)	23.10	25.18	27.32	29.55	31.69
C_p°	22.90	25.04	27.23	29.49	31.65

* Contribution No. 8 from the Thermodynamics Laboratory of the Petroleum Experiment Station, Bureau of Mines. Published by permission of the Director of the Bureau of Mines, U. S. Dept. of the Interior.

¹ Waddington, Todd, and Huffman, J. Am. Chem. Soc. 69, 22 (1947).

² G. Waddington and D. Douslin, "Experimental vapor heat capacities and heats of vaporization of *n*-hexane and 2, 2-dimethylbutane," J. Am. Chem. Soc. (to be published).

³ Determined by Mr. H. J. Coleman of this station.

⁴ Determined by Mr. E. L. Garton and Miss Shirley Nix of this Station.

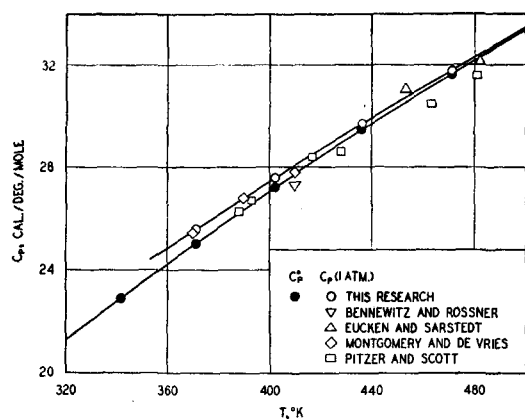


FIG. 1. C_p° and C_p (1 atmos.) of benzene as a function of temperature. The values of C_p (1 atmos.) of this research are compared with the results of other recent measurements of the vapor-heat capacity of benzene.

pressure, the observed values deviated from linearity by less than 0.05 percent. In Fig. 1 the values of C_p° and C_p (1 atmos.) are plotted as a function of temperature, and the latter are compared with the results of other recent measurements of the heat capacity of benzene vapor.⁵⁻⁸

The heat of vaporization data for benzene, obtained in the course of flow-calibration experiments with the vapor-heat capacity calorimeter, have already been reported,² but for the sake of completeness are repeated here in Table II.

DISCUSSION

In Table III the observed values of C_p° for benzene are compared with those calculated from spectroscopic data to the harmonic-oscillator rigid-rotator approximation, by use of the vibrational assignment of Herzfeld, Ingold, and Poole,⁹ and values of the fundamental constants given by Wagman, Kilpatrick, Taylor, Pitzer, and Rossini.¹⁰

As shown in the fourth column of Table III, there is a significant difference between the values of the heat capacity so calculated and those observed experimentally. It seems im-

probable that this difference could be entirely accounted for by any error in the vibrational assignment used. Lowering a single vibrational frequency would have the effect of raising the calculated heat capacity by virtually the same amount at each temperature, so that agreement with the observed values could be obtained at any one temperature but not at all five temperatures. Only an improbably drastic change of two or more vibrational frequencies would increase the slope of the calculated heat-capacity curve to agree with that observed experimentally over the entire temperature range.

If it is assumed that the vibrational assignment and the experimentally measured values of the heat capacity are correct, the difference, $C_p^\circ(\text{obs.}) - C_p^\circ(\text{calc.})$, must be attributed to the contribution to the heat capacity of the factors neglected in the harmonic-oscillator rigid-rotator treatment, namely anharmonicity, rotational stretching, and rotational-vibrational coupling. Of these factors, anharmonicity is the only one that would be expected to make a significant contribution to the heat capacity in the temperature range covered by the experimental measurements.

It is impossible at present to make a rigorous calculation of the contribution of anharmonicity to the heat capacity of benzene, as the available spectroscopic data yield only a few of the numerous anharmonicity coefficients required for such a calculation. However, it is possible to show that the difference, $C_p^\circ(\text{obs.}) - C_p^\circ(\text{calc.})$, is consistent, both in magnitude and in temperature dependence, with moderate values of the anharmonicity coefficients.

To show this, it is convenient to use the approximation, suggested by Stockmayer, Kavanagh, and Mickley,¹¹ that the anharmonicity

TABLE II. Heat of vaporization of benzene.

1 cal. = 4.1833 int. joules; mole. wt. = 78.108		
t , °C	No. expts.	ΔH_{vap} , cal./mole.
41.6	2	7868 ± 2^a
49.9	3	7755 ± 4^a
60.9	3	7606 ± 2^a
80.1	3	7349 ± 1^a

^a Maximum deviation.

¹¹ Stockmayer, Kavanagh, and Mickley, J. Chem. Phys. 12, 408 (1944).

⁵ K. Bennewitz and W. Rossner, Zeits. f. physik. Chemie B29, 126 (1938).

⁶ A. Eucken and B. Sarstedt, *ibid.* B50, 143 (1941).

⁷ J. B. Montgomery and T. DeVries, J. Am. Chem. Soc. 64, 2375 (1942).

⁸ K. S. Pitzer and D. W. Scott, *ibid.* 65, 803 (1943).

⁹ Herzfeld, Ingold, and Poole, J. Chem. Soc. (London), 316 (1946).

¹⁰ Wagman, Kilpatrick, Taylor, Pitzer, and Rossini, J. Research Nat. Bur. Stand. 34, 143 (1945).

coefficients are proportional to the sum of the frequencies, i.e., $X_{ij} = a(\nu_i + \nu_j)$, where X_{ij} is an anharmonicity coefficient, a the proportionality constant, and ν_i and ν_j the frequencies of the i th and j th modes of vibration. If the adjustable parameter, a , is given the value 9×10^{-4} , it is found that the calculated contribution of anharmonicity to the heat capacity of benzene is in excellent agreement with the values of $C_p^\circ(\text{obs.}) - C_p^\circ(\text{calc.})$ given in Table III. This is shown in Fig. 2. The maximum deviation of the points representing $C_p^\circ(\text{obs.}) - C_p^\circ(\text{calc.})$ from the calculated curve showing the contribution of anharmonicity to the heat capacity, assuming $X_{ij} = 9 \times 10^{-4}(\nu_i + \nu_j)$, is only 0.04 percent of the total heat capacity. The order of magnitude of the anharmonicity coefficients required to fit the data in this manner (0.7 cm^{-1} for the lowest frequencies to 5.5 cm^{-1} for the carbon-hydrogen stretching frequencies) seems reasonable for a molecule such as benzene.

For calculating the contribution of anharmonicity to the heat capacity, the expansion of the vibrational partition function for a polyatomic molecule given by Stockmayer, Kavanagh, and Mickley¹¹ was used. In terms of this partition function, the contribution of anharmonicity to the heat capacity, $C_p(\text{anh.})$, becomes

$$C_p(\text{anh.}) \cong R(d/dT)T^2(d/dT) \sum_{i \leq j} f_{ij},$$

where $f_{ii} = d_i(d_i + 1)X_{ii}hc/kT[\exp(\mu_i) - 1]^2$, and $f_{ij}(i < j) = d_i d_j X_{ij}hc/kT[\exp(\mu_i) - 1][\exp(\mu_j) - 1]$. In these expressions, $\mu_i = hc\nu_i/kT$ with ν_i given in cm^{-1} , and d_i is the degeneracy of the i th mode of vibration. The above equation for $C_p(\text{anh.})$ is a satisfactory approximation for the temperature range of interest here but would fail at somewhat higher temperatures.

It is rather improbable that a systematic error in the experimental heat-capacity measure-

TABLE III.

$T, ^\circ\text{K}$	$C_p^\circ(\text{obs.})$	$C_p^\circ(\text{calc.})^a$	$C_p^\circ(\text{obs.}) - C_p^\circ(\text{calc.})$
341.60	22.90	22.77	0.13
371.20	25.04	24.87	0.17
402.30	27.23	27.00	0.23
436.15	29.49	29.18	0.31
471.10	31.65	31.29	0.36

^a Harmonic-oscillator rigid-rotator approximation.

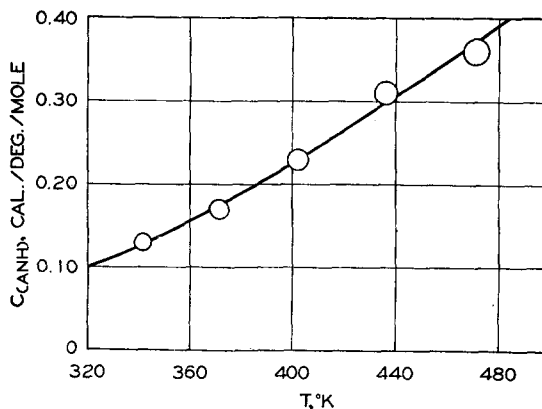


FIG. 2. Contribution of anharmonicity to the heat capacity of benzene vapor. The plotted points are the values of $C_p^\circ(\text{obs.}) - C_p^\circ(\text{calc.})$, i.e., the difference between the observed heat capacity and that calculated from spectroscopic data to the harmonic-oscillator rigid-rotator approximation. The radius of each circle is 0.05 percent of the total heat capacity. The curve shows the contribution of anharmonicity to the heat capacity calculated, assuming $X_{ij} = 9 \times 10^{-4}(\nu_i + \nu_j)$.

ments would have the same temperature dependence as the contribution of anharmonicity to the heat capacity. It seems very likely, therefore, that the values of $C_p^\circ(\text{obs.}) - C_p^\circ(\text{calc.})$ represent the true contribution of anharmonicity to the heat capacity of benzene vapor. To this extent, the results reported here are evidence of a high degree of accuracy in the experimental vapor heat-capacity measurements.

SECOND VIRIAL COEFFICIENT OF BENZENE

The second virial coefficient, B , in the equation of state $PV = RT + BP$ is related to the variation of the vapor-heat capacity with pressure by the equation $(\partial C_p / \partial P)_T = -T(\partial^2 B / \partial T^2)_P$. Also values of the second virial coefficient may be obtained from heat of vaporization and vapor pressure data by use of the relation

$$B = [\Delta H_{\text{vap}} / T(dP/dT)] - RT/P + v_1, \quad (1)$$

obtained by substituting the above equation of state into the exact Clapeyron equation, $\Delta H_{\text{vap}} = T(V - v_1)dP/dT$.

The values of $(\partial C_p / \partial P)_T$ and ΔH_{vap} for benzene found in this work, in conjunction with the Antoine equation for the vapor pressure given in the A.P.I. Tables¹² were used to obtain an em-

¹² American Petroleum Institute Research Project 44 at the National Bureau of Standards. Selected Values of

TABLE IV. Second virial coefficient and $(\partial C_p/\partial P)_T$ for benzene.

$t, ^\circ\text{C}$	B, cc	
	From ΔH_{vap} and vapor pressure	Calc., Eq. 3
25.0	-1570	-1496
41.6	-1272	-1296
49.9	-1213	-1214
60.9	-1138	-1121
80.1	-994	-989
110.0	-847	-840

$t, ^\circ\text{C}$	$(\partial C_p/\partial P)_T$ cal./deg./mole./atmos.	
	Obs.	Calc., Eq. 3
68.44	0.78	0.81
98.04	.55	.53
129.14	.37	.35
162.99	.24	.24
197.94	.17	.17

irical equation for the second virial coefficient, of the form¹³

$$B = b - c \exp(a/T). \quad (2)$$

On the basis of this empirical equation, the variation of heat capacity with pressure is given by $(\partial C_p/\partial P)_T = c(a^2/T^3 + 2a/T^2) \exp(a/T)$; values of the constants c and a were selected to fit the $(\partial C_p/\partial P)_T$ data. To evaluate the remaining constant, b , values of the second virial coefficient were calculated by means of Eq. (1), using the heat of vaporization data of Table II and the Antoine equation for the vapor pressure. Substituting these values of B , and the previously obtained values of c and a into Eq. (2) gave

Properties of Hydrocarbons, Table No. 5k (Part 1), alkyl benzenes, C_6 to C_8 , vapor pressure and boiling points, at 10 to 1500 mm-Hg, dated June 30, 1944.

¹³ Hirschfelder, McClure, and Weeks, J. Chem. Phys. 10, 201 (1942).

four closely agreeing values of b , and the mean of these was taken as the final value. The resulting empirical equation for the second virial coefficient is

$$B = -202 - 53.5 \exp(950/T) \text{ cc}. \quad (3)$$

Values of B calculated with this equation are compared in the first part of Table IV with those obtained from heat of vaporization and vapor-pressure data. The value at 25° is calculated from the heat of vaporization determined by Osborne and Ginnings,¹⁴ and that at 110° from the heat of vaporization reported by Fiock, Ginnings, and Holton.¹⁵ At the other four temperatures the heat of vaporization data of Table II were used. Equation (3) may be further compared with the vapor density measurements of Magnus and Schmid,¹⁶ and of Eucken and Meyers.¹⁷ The twelve vapor density determinations reported by Magnus and Schmid, all at approximately 373°K , give values of B ranging from -614 cc to -972 cc , with a mean of -747 cc . For this same temperature, the value of B from Eucken and Meyer's equation, corrected to 1941 atomic weights, is -922 cc . The value given by Eq. (3) is -884 cc at 373°K .

The values of $(\partial C_p/\partial P)_T$ calculated from Eq. (3) are in satisfactory agreement with those found experimentally; this is shown in the second part of Table IV.

¹⁴ N. S. Osborne and D. C. Ginnings, Nat. Bur. Stand., unpublished data.

¹⁵ Fiock, Ginnings, and Holton, J. Research Nat. Bur. Stand. 6, 881 (1931).

¹⁶ A. Magnus and E. Schmid, Zeits. anorg. allgem. Chemie 120, 232 (1922).

¹⁷ A. Eucken and L. Meyers, Zeits. physik. Chemie B5, 452 (1929).