suspension extracted with chloroform. Distillation of the extract gave 1.9 g. of impure bromide; b. p. 92-95° (14 mm.), $n^{25}_{\mathrm{D}}$ 1.5147 and $d^{25}_{4}$ 1.2228. The product gave no precipitate with silver nitrate and did not react with sodium methoxide in methanol at 55°.

**8-Bromocamphene.**—From 50.0 g. of camphene and 60.0 g. of bromine was obtained by the method of Langlois[8] 45.8 g. (58%) of 8-bromocamphene; b. p. 92-94° (14 mm.), $n^{25}_{\mathrm{D}}$ 1.5207 and $d^{25}_{4}$ 1.2679.

**Camphene-8-carboxylic Acid.**—The unreacted bromide from the zinc reduction was converted to a Grignard reagent on refluxing overnight with 1.0 g. of magnesium and 0.1 g. of ethyl bromide. The reaction mixture was cooled in an ice-salt-bath and an excess of dry carbon dioxide bubbled through. The resulting pasty mixture was acidified with dilute hydrochloric acid and the ether layer separated. The acidic product was extracted from the ether layer by shaking with sodium carbonate solution. Acidification of the carbonate solution gave a solid which was crystallized from ethanol, m. p. 122-123°. This material did not depress the melting point (123°) of a sample of camphene-8-carboxylic acid prepared from 8-bromocamphene.

**Bromopinene.**—$\alpha$-Pinene (50 g.) was brominated with 25 g. of NBS by the previously described procedure.[11] The yield of bromopinene after two distillations was 9.1 g. (23%); b. p. 89-90° (13 mm.), $n^{25}_{\mathrm{D}}$ 1.5120, $d^{25}_{4}$ 1.2400.

**Rate Determinations.**—The reaction rates of the bromides with sodium methoxide in methanol solution were determined at 25° by titration with standard acid of samples withdrawn from a flask held in a thermostat at 25.0 ± 0.1°. For 50 and 100° rates, 5-ml. samples were sealed in individual test-tubes to avoid loss of the solvent.

## Summary

The reaction of N-bromosuccinimide with camphene gave a mixture of monobromides of which the principal component (65%) was 8-bromocamphene.

The bromination with N-bromosuccinimide of $\alpha$-pinene was shown to give a mixture of monobromides.

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[CONTRIBUTION FROM DEPARTMENT OF PHYSICS, DUKE UNIVERSITY]

# Vapor Pressures of Naphthalene, Anthracene and Hexachlorobenzene in a Low Pressure Region[1]

BY G. W. SEARS[2] AND E. R. HOPKE

In line with a program of securing vapor pressure data on spectroscopically interesting compounds the vapor pressures of naphthalene, anthracene and hexachlorobenzene have been measured in the region 0.01–1.0 mm. The vapor pressure of naphthalene has previously been studied over a wide range. The vapor pressures of anthracene and hexachlorobenzene have only been determined in the region 10–760 mm.

**Compounds.**—The naphthalene was Eastman Kodak Co. highest purity compound. The material was purified by vacuum sublimation and the center fraction was used. The melting point range was 79.9 to 80.2°. The hexachlorobenzene was Eastman Kodak Co. best grade product. It was twice recrystallized from 95% ethyl alcohol and was dried at 115° for one hour. Its melting point range was 229.5 to 229.8°. The anthracene was also of the highest purity obtainable from Eastman Kodak Company. It was three times recrystallized from benzene and was dried at 100 for one hour. Its melting point range was 216.9 to 217.3°.

## Experimental

The vapor pressure data were measured with a Rodebush gage.[3] The calibration and experimental procedure have been previously described by the authors.[4,5] Earlier measurements have all involved compounds having vapor pressures in the operating range of the gage at temperatures below room temperature. In this investigation none of the compounds were sufficiently volatile to have a vapor pressure in the gage range below room temperature.

Consequently, the experimental procedure of earlier investigations was modified. The entire gage was placed in an asbestos box, which was heated by a pair of 500-watt heating cones supplied by a one-kilowatt variac. As in earlier work the sample chamber was placed in a cold-bath. In this case the bath was cold only with respect to the interior of the box.

The cold-bath consisted of a 400-ml. beaker filled with water in the case of naphthalene and with paraffin oil for the other two compounds. The temperature of the box was maintained at about 30° above the temperature of the bath. The temperature of the bath rose about 0.1° per minute.

To avoid error caused by local temperature differences in the bath a copper cylinder 3″ in diameter and 2″ long was supported in the bath so that its surface lay at the surface of the bath. The cylinder was provided with a hole into which the sample tube fitted and with a thermometer hole of the same depth. The experimental proof that the bath was the cold spot of the gage was the repeated observation that condensed sample was never observed elsewhere than in the sample chamber.

In the case of naphthalene a calibrated 0 to 50° mercury-in-glass thermometer was used for temperature measurement. The temperature was read directly to the nearest 0.1°. The precision of the pressure measurements did not justify any closer temperature measurements. The temperatures of the hexachlorobenzene and anthracene were measured with respect to a finely ground ice-bath using a calibrated copper–constantan thermocouple. The thermal e. m. f. was measured to 1 microvolt with a Leeds and Northrup Type K-2 potentiometer. Temperatures were then calculated from the calibration chart to the nearest 0.1°.

When hexachlorobenzene and anthracene escaped from the vapor enclosure during a pressure measurement, they condensed on the walls of the high vacuum side and effectively degraded the vacuum. To avoid this a collar of Dry Ice was placed on the vacuum walls at the point

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[1] This investigation was assisted by the Office of Naval Research under Contract N6ori-107, Task Order I, with Duke University.

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[3] Rodebush and Henry, THIS JOURNAL, **52**, 3159 (1930).

[4] Sears and Hopke, *J. Phys. Chem.*, **52**, 1137 (1948).

[5] Hopke and Sears, THIS JOURNAL, **70**, 3801 (1948).

where the vacuum line entered the asbestos box. This reduced the pressure on the high vacuum side to its original value.

Another difficulty experienced with the less volatile compounds was their condensation on the armature case. Since this continuously changed the calibration of the gage, the armature was heated by an infrared drying lamp during the measurements. The gage was recalibrated against the vapor pressure of mercury under the described conditions.

The system was thoroughly cleaned between runs by a modification of the previous procedure.[5] The compounds were removed from the experimental zone by pumping with simultaneous heating of the glassware to about 150°. The compounds were collected in the cold-trap on the high-vacuum side of the diffusion pump. Since this trap was permanently cooled with Dry Ice, the compounds were effectively removed from the experimental zone.

The solid substances were outgassed by sublimation and subsequent pumping out of evolved gases. This process was carried out repeatedly. In addition it was necessary to outgas the compounds at the temperature of the investigation for a minimum of five days to remove the volatile impurity which was always found to be present.

## Results

The vapor pressures of hexachlorobenzene and anthracene were measured over the ranges 96 to 124° and 105 to 125°, respectively. The vapor pressure of naphthalene was measured over a temperature range 19 to 35°.

The data for anthracene are represented by the equation

$$\log_{10} P \text{ (mm.)} = -(5102.0)/T + 12.002 \quad (1)$$

The data for hexachlorobenzene are represented by the equation

$$\log_{10} P \text{ (mm.)} = -(4793.6/T) + 11.397 \quad (2)$$

The data for naphthalene over the experimental range are represented by

$$\log_{10} P \text{ (mm.)} = -[108.30/(t + 27)] + 1.115 \quad (3)$$

The mean percentage errors were 1.2, 2.0 and 1.2% for anthracene, hexachlorobenzene and naphthalene, respectively. In equations (1) and (2) $T$ represents the absolute temperature where the ice-point is taken as 273.2° K. In equation (3) $t$ represents the temperature in degrees centigrade.

## Discussion

The vapor pressure of anthracene has been determined only in the region of 40–760 mm. The most recent measurements have been made by Mortimer and Murphy[6] and by Nelson and Senseman.[7] The agreement between these experimenters was quite satisfactory.

Since Mortimer and Murphy fitted their data for solid anthracene to an equation, this equation was extrapolated downward for comparison with the present data at the top of its range (129°). The values are 0.353 mm. (M. and M.) compared to 0.207 mm. for the present data.

Mortimer and Murphy took no account of the increase of heat of vaporization with decreasing temperature. This would have the effect of causing any values obtained by extrapolation from their equation to be too high. The present datum agrees as to order of magnitude with their extrapolated value and lies below as would be expected. The long extrapolation region between the two sets of data prevents more than a qualitative comparison.

The vapor pressure of naphthalene has been studied over a wide range by a variety of methods.[6,7,8,9,10] In the pressure range of the present investigation Barker[8] and Swan and Mack[10] have made very careful measurements using a dynamic and an effusion method, respectively. Table I gives a comparison of the three determinations. The pressures are given in microns.

TABLE I

| $T$, °C. | $P$ (S. and M.) | $P$ (B.) | $P$ (S. and H.) |
|---|---|---|---|
| 10 | 17.4 | 30.5 | 15.4 (extr.) |
| 20 | 64.8 | 64.5 | 64 |
| 30 | 177 | 163 | 164 |

It should be mentioned that Swan and Mack found a value of 0.164 mm. at 30° when they used Barker's method of purification by recrystallization. When they used a precipitation method for further purification, their value at 30° rose to 0.177 mm. It is hard to understand why the removal of a presumably small amount of additional impurity should raise the vapor pressure as much as they noticed.

No value for the vapor pressure of naphthalene at 10° has been inserted from interpolation of Barker's data. Barker considers his data at 0 and 10.5° to be unreliable and neglects them. This offers sufficient reason for the present investigators to do likewise.

A consideration of equation (3) giving the vapor pressure of naphthalene shows that the heat of vaporization approaches infinity as the temperature approaches −27°. It was also noticed that the data of both Barker and Swan and Mack also show unusual curvature on a log $P$ *vs.* $1/T$ plot in the neighborhood of 20°. Although no other evidence is available in support of this contention it is suggested tentatively that a crystal transformation occurs in that region.

The vapor presssure of hexachlorobenzene is to be found in Stull's[11] recent compilation of vapor pressures of organic compounds. His data were taken from Dow Chemical Company files. The present data are lower than the compiled data by an order of magnitude. At 114.4° Stull lists the value 1 mm.; in the present investigation a value of 0.109 mm. was obtained.

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[6] Mortimer and Murphy, *Ind. Eng. Chem.*, **15**, 1140 (1923).

[7] Nelson and Senseman, *ibid.*, **14**, 58 (1922).

[8] Barker, *Z. physik. Chem.*, **71**, 235 (1910).

[9] Andrews, *J. Phys. Chem.*, **30**, 1497 (1926).

[10] Swan and Mack, THIS JOURNAL, **47**, 2112 (1925).

[11] Stull, *Ind. Eng. Chem.*, **39**, 517 (1947).

## Summary

1. The vapor pressures of anthracene, naphthalene and hexachlorobenzene were measured in the region 0.01–1.0 mm. by a Rodebush manometer.

2. The data were fitted to vapor pressure equations.

3. Only in one case (naphthalene) was a quantitative comparison with previous workers possible. The agreement was satisfactory.

Durham, North Carolina Received August 2, 1948

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[Contribution No. 14 from the Thermodynamics Laboratory, Petroleum Experiment Station, Bureau of Mines]

# Cycloöctatetraene: Low-Temperature Heat Capacity, Heat of Fusion, Heat of Vaporization, Vapor Pressure and Entropy

By D. W. Scott, M. E. Gross, G. D. Oliver[1] and H. M. Huffman

During the past decade Reppe and his coworkers made extensive studies of acetylene chemistry, and one of the interesting results of these studies was a method for the synthesis of cycloöctatetraene.[2] This compound is of considerable interest, both to the theoretical chemist and to the industrial chemist. Because of this it appeared desirable to make accurate determinations of its thermodynamic properties.

This paper presents the results of low-temperature thermal studies and vapor-pressure measurements which yield a value for the entropy of cycloöctatetraene vapor. This entropy value will aid in the eventual decision as to the structure of the cycloöctatetraene molecule, since any proposed structure must have moments of inertia, symmetry number, and vibrational frequencies consistent with the observed entropy.

## Experimental

**The Material.**—The cycloöctatetraene used in this investigation was a composite sample purified by the Chemistry and Refining Section of this station. A batch of approximately 90 cc. having a boiling range of about 5° was obtained from the General Aniline & Film Co. through the courtesy of Dr. P. G. Stevens. The second 60 cc. lot was obtained by Dr. Karl Kammermeyer at the I. G. Farbenindustrie plant at Ludwigshafen, Germany, and transmitted to this Bureau through the courtesy of Dr. Julius Alsberg of the Office of Technical Service, U. S. Department of Commerce.

The crude material, after preliminary distillation under reduced pressure, was purified by repeated fractional crystallization from *n*-pentane, followed by a second distillation under reduced pressure to remove residual solvent. A detailed description of the purification process will be given in another publication from the Chemistry and Refining Section of this station.

During the course of the low-temperature studies, a routine investigation was made of the melting point of this material. The data obtained in this investigation are given in Table I. If Raoult's law is obeyed, a plot of the equilibrium temperature against the reciprocal of the fraction melted should give a straight line. The data obtained in this study do not follow this straight-line relation, as shown by the lack of agreement between $T_{\text{calcd.}}$ and $T_{\text{obs.}}$ Hence any conclusions drawn from the data are somewhat arbitrary. An analysis of the data on the basis of the phase rule showed that the presence of a small amount of water, less than saturation concentration, could account for the observed behavior. In fact, in the vapor pressure measurements, an anomalous behavior was observed which disappeared after the material was dried by passing the vapors over magnesium perchlorate. For this reason a second study of the melting point was made with a sample dried in this manner. Unfortunately these measurements were made on a small sample, because the bulk of the material had been returned to the donors, and the results were too erratic to yield reliable values for the melting point and mole fraction of impurity. However, the general trend of this second set of measurements leads one to believe that the melting point and mole fraction of impurity given in Table I are reasonably reliable. The small amount of water that may have been present in the first sample would not have affected the heat-capacity measurements by any significant amount.

Table I

Melting Point Summary, 0°C. = 273.16°K.

| Melted, % | T, °K. Obs. | T, °K. Calcd. |
|---|---|---|
| 18.8 | 268.337 | 268.257 |
| 37.9 | .387 | .368 |
| 57.1[a] | .405 | .405 |
| 76.3 | .417 | .423 |
| 90.7[a] | .432 | .432 |
| 100 | | .436 |
| Pure | | .478 |
| Triple point | | 268.48 ± 0.05 |

$N_2/F^b = 0.0188\Delta T$

$N_2 = 0.0008 \pm 0.0005$

[a] Calculation based on these points. [b] $F$ = fraction of sample in liquid form.

Under the conditions of these heat capacity experiments some polymerization occurred, as was evidenced by the inability to remove all of the sample from the calorimeter by distillation. The amount polymerized, approximately 0.04%, was so small that it is believed to have had no significant effect on the thermal measurements.

**Apparatus and Methods.**—The low-temperature measurements were made in the apparatus described by Ruehrwein and Huffman.[3] Very briefly, the method is as follows: About 0.44 mole of the material under investigation was contained in a sealed copper calorimeter, which was mounted in the adiabatic calorimetric system. A measured amount of electrical energy was supplied to the calorimeter, and at all times the temperature of the environment was maintained at that of the calorimeter to prevent

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(1) Present address: Carbide and Carbon Chemical Corp., Oak Ridge, Tenn.

(2) Reppe, (a) "Cyclopolyolefins," BIOS Final Report No. 137; (b) "Polymerization of Acetylene to Cycloöctatetraene," FIAT Final Report 967, Appendix 5.

(3) Ruehrwein and Huffman, This Journal, 65, 1620 (1943).