

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

The Vapor Pressure of Crystalline Benzene and Cyclohexene¹

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In the course of an investigation concerning symmetry calculations for molecules it was necessary to know accurately the vapor pressure of benzene and cyclohexene in the crystalline state at various temperatures. In order to fill this need the Knudsen method of measuring vapor pressure was modified to fit the requirements of low temperature, and measurements were obtained of the vapor pressure of benzene and cyclohexene in the temperature range 165–200°K.

I. Apparatus

A. Temperature Control.—For temperature control a thermostat was used which was an adaptation from that of Andrews and Southard.² A block of aluminum was machined to fit into a standard liter Pyrex Dewar flask, evacuated to about 5-mm. pressure. It was non-magnetically wound with about 80 ohms of constantan resistance wire and contained in the center a 3-cm. hole to take the tube in which the diffusion cell was hung. It also was equipped with thermocouples placed on the inside and outside.

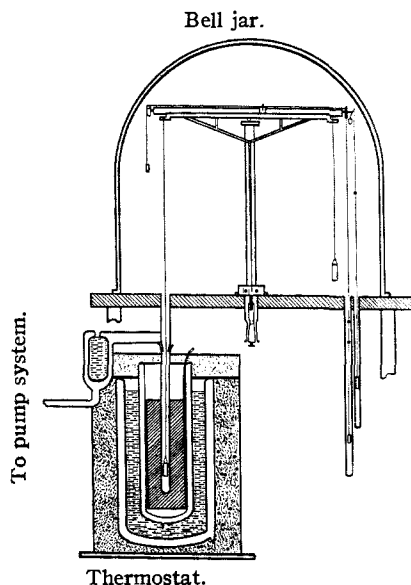


Fig. 1.

The Dewar containing the block was immersed in liquid air contained in a larger one-half gallon Dewar, see Fig. 1. After adjusting the necessary cork insulators, the assembly was raised into position by aid of an auto jack not shown in the figure.

The thermocouples functioned as follows: when the inside thermocouple showed that the temperature desired was being approached, the outside thermocouple current was opposed by the proper e. m. f. from a potentiometer circuit. Hence, when the temperature changed, the galvanometer placed in this circuit reflected a beam of light across a photoelectric cell. This regulation, properly amplified, tripped a relay which caused current to heat the aluminum block. Thus a balance between the cooling effect of the liquid air and the heating of the resistance coil produced a constant temperature. A period of about an hour was necessary before the temperature was constant. Under normal operating conditions, the heating current was on for about three

seconds out of two minutes. Temperature control of $\pm 0.05^\circ$ was readily obtained.

B. Vacuum Balance.—In the usual Knudsen method the amount of vapor escaping through a calibrated hole is determined by noting the loss in weight of the evaporating substance over a definite time interval. Because of the difficulties incident to the low

(1) From the dissertation submitted to the Johns Hopkins University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Andrews and Southard, *J. Franklin Inst.*, **207**, 323 (1929).

temperature, it appeared advisable to follow the loss of weight continuously, without removing the diffusion cell from the thermostat.

A Becker analytical balance was mounted on a steel plate and equipped with devices so that it could be operated by controls outside of the vacuum chamber, see Fig. 1. The beam was lifted off and on the knife edges by replacing the usual eccentric mechanism by a screw device. The male screw was fastened to the vertical shaft of the balance release mechanism. The female screw had a flange midway up the side, so placed as to fit into a depression in the surrounding glass tube. The bottom of the female screw fitted snugly into the stopper part of a glass ground joint. This arrangement permitted the turning of the ground-glass stopper to rotate the screw which forced the central shaft up or down.

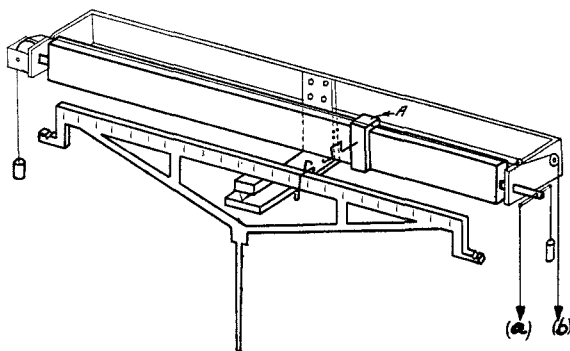


Fig. 2.—Rider adjustment.

A sufficiently heavy rider was used to measure a difference of 0.4 g. The rider was moved along by the mechanism shown in Fig. 2. The carriage A was pulled left or right by means of a solenoid arrangement. Once the carriage was pulled into place under the rider, the carriage was tilted by a second solenoid arrangement so as to pick up the rider. It was then moved into the desired position and lowered on the beam. The weighings were made by the method of swings. The usual index plate of twenty divisions was replaced by one of forty divisions, furnished by Christian Becker, Inc., New York. The moving pointer was viewed through a telescope, so that the magnification allowed one to estimate tenths of division. Under the conditions and load of the experiment the sensitivity as determined several times averaged 2.05 ± 0.10 divisions per milligram.

C. Diffusion Cell.—The substance was placed in a small brass cylinder, see Fig. 3. The platinum disk containing the calibrated hole was held between two thin lead gaskets, compressed by screwing down the top very firmly. The cylinder was threaded with 72 threads per inch. With these precautions, the amount of vapor escaping around the lead washers or down the threaded side was negligibly small.

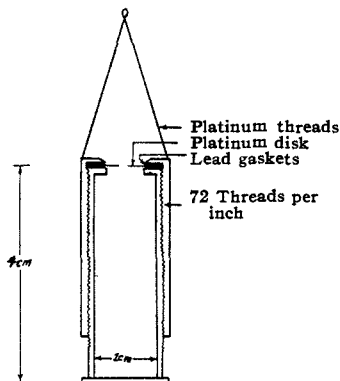


Fig. 3.—Brass diffusion cell.

The freezing point curve of the benzene used in these experiments, after purification, showed the presence of not more than 0.1% impurity, the melting point being

+5.48°. The cyclohexene was purified by Dr. J. H. Bruun of the Bureau of Standards, to whom the author is very grateful. The cooling curve showed the presence of not more than 0.5% impurity; the melting point being -104.1° .

II. Procedure

The diffusion cell containing the substance was suspended from the balance arm and the glass tube put in place surrounding it, see Fig. 1. The system was slowly evacuated with the cell at a temperature of about -20° . This permitted the water vapor to be pumped off without undue loss of benzene. The temperature was then lowered to -78° and the steel mercury diffusion pump was started. After ten hours of pumping, liquid air was placed in the trap nearest the balance. Sublimation occurred then to this trap, instead of through the apparatus to the trap near the mercury pump. The thermostat was cooled in the meantime and quickly slipped into position. While the temperature slowly attained a constant value, the zero of the balance was kept on the scale by adjusting the rider. When the temperature appeared to be constant, readings were begun.

Since preliminary experiments indicated a temperature lag between the cell and the walls of the thermostat, the outside walls of the cell (not the top) were coated with a fine soot. A thermocouple was soldered to a thin copper cylinder which was also covered with soot and placed inside touching the walls and surrounding the cell. Under these conditions the temperature distribution was uniform. A conservative estimate places the temperature control above -100° at $\pm 0.1^{\circ}$ and for lower temperatures at 0.3° .

III. Results

It is, of course, necessary to know the total resistance to flow of the vapor from the diffusion cell to the liquid air surface. This was obtained by making several runs with benzophenone and comparing the results with the data of Volmer and Kirchhoff.³ The value for the total resistance to the flow of the vapor was found to be 726 ± 20 units. There is an advantage in having the resistance at this high figure. In the work of Volmer

TABLE I

<i>t</i> , sec.	Change in scale divisions	Mass (mg.)	<i>m</i> = 1000 sec.
900	1.2	0.60	0.65
780	1.1	.55	.70
660	0.95	.45	.70
630	.85	.40	.70
800	1.15	.55	.70
1300	1.9	.90	.70
850	1.15	.55	.65

0.68 mg.

Hence $p = 7.12$ dynes

(3) Volmer and Kirchhoff, *Z. physik. Chem.*, **115**, 233 (1925).

and Kirchhoff it was shown that for rapid diffusion of the vapor the surface is cooled quite appreciably. His results show that the values obtained for $w = 17.17$ were 18% lower than for values at $w = 205$. Table I illustrates the type of data obtained for benzene at $T = 195.0^\circ\text{K}$.

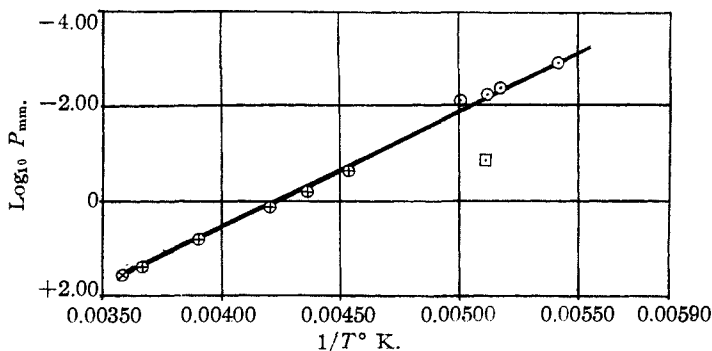


Fig. 4.—○, Deitz; ⊕, Mundel;⁴ ⊗, Young and Fortey;⁵ □, Barker.⁶

Table II summarizes the direct results for benzene and for cyclohexene. The results for benzene are shown in Fig. 4, together with those of previous investigators.⁴

TABLE II

	Temp., °K.	Pressure, dynes
Benzene (s)	200.2	10.40
Benzene (s)	195.0	7.12
Benzene (s)	193.2	5.95
Benzene (s)	184.3	1.93
Cyclohexene (l)	176.2	3.75
Cyclohexene (s)	165.0	1.20

The author wishes to take this opportunity to express his sincere appreciation to Professor D. H. Andrews at whose suggestion this work was undertaken.

Summary

The vapor pressures of crystalline benzene and cyclohexene have been measured by means of a modified Knudsen procedure. An analysis of the experimental errors entailed leads to a probable error in the vapor pressure measurements of about 4%.

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(4) Mundel, *Z. physik. Chem.*, **71**, 235 (1910).

(5) Young and Fortey, *J. Chem. Soc.*, (London) **75**, 873 (1899).

(6) Barker, *Z. physik. Chem.*, **71**, 235 (1910).