Vapor Pressure of Cyclohexane, 25° to 75° C.

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The vapor pressure of highly purified cyclohexane has been measured at six temperatures from 25° to 75° C. by an isolated-cell static method, temperature being measured by platinum resistance thermometer. Results agree well with the most recent equilibrium still measurements, but the difference from National Bureau of Standards results is significant. Derived latent heat of evaporation values differ from published calorimetric data by more than the estimated uncertainty.

THE VAPOR PRESSURE of cyclohexane is of particular interest because it has from time to time been suggested as a standard substance, and because many mixtures containing cyclohexane have been studied (*3, 7, 9, 11*). In fact this property has received only incidental attention since the work of Willingham *et al.* (*21*), using a controlled-pressure boiling point apparatus over the pressure range 75 to 780 torr. The earlier, equilibrium still, work of Scatchard, Wood, and Mochel (*17, 18*) gave vapor pressures about 0.1 torr below those of Willingham *et al.* between 30° and 50° C. but about 0.1 torr above between 60° and 75° C. with a similar boiling point at 80.739° C. Brown and Ewald (*7*), who used a new design of equilibrium still, observed vapor pressures which, although showing a greater scatter than those of Willingham *et al.*, have mean values 0.2 to 0.4 torr higher, with the boiling point correspondingly lower at 80.72° C. We have therefore redetermined the vapor pressure of cyclohexane, paying particular attention to purification and to temperature measurement. By using an isolated cell static technique, we have sought to minimize any errors arising from undetected temperature gradients or from atmospheric contamination.

EXPERIMENTAL

Purification. For preliminary purification, to remove aromatics, commercial grade cyclohexane was stirred for 12 hours at 10° C. with a mixture of one volume of analytical reagent grade concentrated nitric acid to two volumes of analytical reagent grade concentrated sulfuric acid. The cyclohexane was then separated, washed several times with distilled water, dried, and distilled over anhydrous calcium chloride, using a 10-plate column at 40 to 1 reflux. The middle fraction (about 50%) was redistilled under the same conditions. To remove traces of aliphatics boiling near 80° C., the final purification was by progressive freezing, using a modification of the procedure described by Dickinson and Eaborn (*10*). The cyclohexane, in closed glass tubes 45 cm. long and 3 cm. in diameter, was frozen from the top downwards at about 5 cm. per hour, until 90% was solid. The bottom 10% was rejected as liquid. This method is much more effective than freezing from the bottom upwards, owing to the action of convection currents in preventing impurity concentrating next to the solid. Eight progressive freezing passes raised the melting point from 6.19° to 6.55° C., and no further increase could be obtained. The final sample was obtained as solid from a further progressive freezing pass continued only to 50% solidification; it was transferred to a vacuum-line apparatus, degassed, and stored under its own vapor in reservoirs connected to tubes containing pure phosphorus pentoxide.

Melting points were measured to ±0.01° C. with a 0° to 10° C. mercury-in-glass thermometer calibrated against the platinum resistance thermometer described below. Densities at 25° C. were determined in a dilatometer designed to avoid atmospheric contamination [Ackermann, Cruickshank, and Giguère (*1*)]. The melting point and density of the final product are compared in Table I with previously reported values, together with the normal boiling points calculated from the Antoine coefficients given in Table II.

Temperature Measurement. The temperature of the vapor pressure cell (see below) was measured by a four-lead 25-ohm platinum resistance thermometer (Cambridge Instrument Co.) immersed in the water thermostat as close as possible to the vapor pressure cell. The thermometer resistance was measured on a Smith's difference bridge, Type 2 (*19*) calibrated by the National Physical Laboratory, Teddington, Middlesex. The thermometer and bridge combination was check-calibrated by measuring the thermometer resistance, *R*, at the water triple point and at the steam point; the triple point calibration was repeated at intervals throughout the investigation, but no slow, long persisting change was detected. Temperatures were calculated from measured resistances using the Callendar equation,

$$t(^\circ\,\mathrm{C.}) = \frac{100(R_t - R_0)}{R_{100} - R_0} + \delta\,\frac{t}{100}\left[\frac{t}{100} - 1\right] \qquad (1)$$

For thermometer-grade platinum, the constant δ correlates with the value of the ratio R_{100}/R_0, lying between 1.490 and 1.495 when this ratio is close to 1.392, as with this thermometer [Johnson, Matthey and Co. (*13*)]. We took δ arbitrarily as 1.490; correspondingly, the maximum of the systematic temperature error (at 50° C.) thus introduced is unlikely to exceed 0.0015° C., and the resulting error in the vapor pressure is always less than 0.02 torr. Thermometer resistance was measured to ±0.0001 ohm, giving temperatures to ±0.001° C.—i.e., with an over-all accuracy about ±0.002° C.

Vapor Pressure Measurement. The vapor pressure of samples of purified cyclohexane was determined at 10° intervals from 25° to 75° C. in an apparatus similar to that of Allen, Everett, and Penney (*2*), shown schematically in Figure 1.

The vapor pressure cell, *A*, was completely immersed in a water thermostat controlled by an on-off regulator actuated by a mercury-toluene thermometer, the toluene being contained in a coil of ¼-inch copper tubing sited close to the vapor pressure cell. The long-term variation of the mean thermostat temperature was usually less than ±0.001° C., with short-term oscillations (period about 1 minute) not more than ±0.003° C. The vapor pressure cell

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Table I. Physical Properties of Cyclohexane

	Freezing Point, °C.	Boiling Point, °C.	Density, d_4^{25} G./Cc.
This work	6.55 ± 0.02	80.728 ± 0.001	0.77386 ± 0.00001
(*7*)	6.54	80.720 ± 0.003	0.77390
(*21*)	6.554	80.738	0.77389
(*17*)	6.49	80.739	0.77383

was connected via the mercury cutoff, *B*, to the inside of the metal bellows, *C*, of the isolating manometer. The volume inside the bellows available to the sample vapor was made as small as possible by the hollow glass finger, *D*, whose top limited the movement of the bellows in case of accidental overload. The outer chamber, *E*, of the isolating manometer was connected to the primary mercury manometer outside the water thermostat, the pressure transfer medium being dry, oxygen-free nitrogen. The metal plate, *F*, was used to sense changes in bellows extension by the change in electrical capacitance between the two. The position of *F* was adjusted to give the maximum sensitivity consistent with keeping the proportional change in null-point capacitance (equal pressures either side) with increasing total pressure conveniently small. A Fielden proximity meter was used as a capacitance bridge. The isolating manometer was used always as a null instrument, to balance the vapor pressure and the nitrogen pressure within a few millitorr. The primary mercury manometer (in 2.4-cm. diameter, uniform-walled borosilicate glass tubing) was mounted in an air thermostat controlled to 25.0 ±0.01° C. The heights of the mercury menisci in the manometer limbs were measured by means of a 1-meter cathetometer fitted with a vernier scale reading to 0.01 mm. The calibration of the cathetometer scale was checked against a standard engraved glass scale certified by the National Physical Laboratory. Accurate vertical alignment of the cathetometer was achieved by using a set of four interconnected water levels as an artificial horizon. Allowance was made for thermal expansion of the cathetometer scale whenever room temperature differed significantly from 20° C. Manometer readings were made always with rising menisci, illuminated from behind through masked opalescent glass screens adjusted to prevent reflection from the mercury surfaces into the cathetometer telescope. All pressure measurements have been corrected to the height of the equivalent mercury column at 0° C. under standard gravity and are expressed in torr (760 torr ≡ 1 std. atm.).

Table II. Constants in the Antoine Equation

	A	*B*	*C*	σ
This work	6.85875	−1212.014	223.956	0.02_4
(*7*)	6.85334	−1208.510	223.498	0.09
(*21*)	6.84498	−1203.526	222.863	

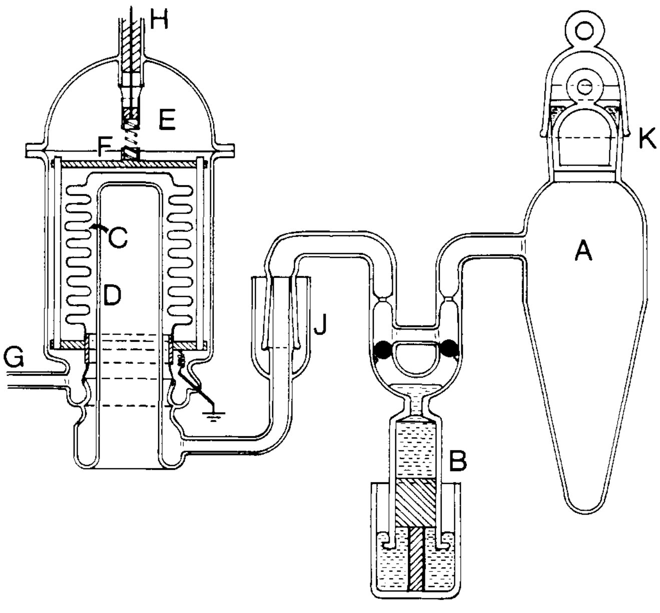

Figure 1. Schematic diagram of vapor pressure cell and isolating manometer

A. to *F.* See text
G. Connection to external manometer
H. Screened lead to proximity meter
J. Mercury-sealed joint
K. Mercury-sealed stopper and cap

The purified cyclohexane, after several vacuum redistillations to remove any residual air, was vacuum-distilled from the reservoirs to the vapor pressure cell. A series of vapor pressure measurements was then made at ascending temperatures. At each temperature, readings were taken over a period of several hours, to ensure complete equilibration. After the final measurement in each series (at about 75° C.), the thermostat was cooled to the starting temperature (about 25° C.), and the first measurement was repeated to check for inward air leak or zero-drift in the isolating manometer.

After subtracting the vapor pressure of mercury (evaporated from the cell cutoff valve), the observed vapor pressures were adjusted to the rounded temperatures using the values of dp/dt obtained from the Antoine coefficients given by Willingham *et al.* (*21*) (Table II). The temperature adjustment was never more than a few hundredths of a degree, so this procedure was accurate to better than 1 millitorr.

RESULTS

The results of five series of vapor pressure measurements, adjusted to rounded temperatures, are set out in Table III, together with the mean value, $\bar{p}$, at each temperature, the standard deviation for an individual measurement, $\sigma = [\sum(\bar{p} - p)^2/(n - 1)]^{1/2}$, and the standard error of the mean, $\sigma_a = \sigma/n^{1/2}$. The σ values are obviously consistent with the estimated experimental uncertainty arising in the measurements of temperature and pressure, which increase from ±0.03 torr at 25° C. to ±0.05 torr at 75° C.

The mean vapor pressures of Table III have been fitted by a least squares method to the Antoine (*4*) equation,

$$\log_{10} p = A - B/(C + t) \qquad (2)$$

where *t* is the Celsius temperature and *p* is in torr. Table II gives the best fit Antoine coefficients, together with those for the data of Brown and Ewald (*7*), and those quoted by Willingham *et al.* (*21*).

The standard deviation of our mean vapor pressures relative to the Antoine equation is 0.024 torr, which is statistically consistent with the σ_a values of Table III. The

Table III. Vapor Pressure of Cyclohexane

(torr)

Temp., °C.	I	II	III	IV	V	Av.	σ	σ_a
25	97.80	97.77	97.78	97.83	97.86	97.81	0.03_6	0.01_7
35	150.83	150.75	150.74	150.86	150.78	150.79	0.05_1	0.02_3
45	225.06	225.07	225.08	225.11	225.07	225.08	0.01_9	0.00_9
55	326.53	326.50	326.54	326.62	326.60	326.56	0.04_4	0.02
65	461.65	461.63	461.63	461.70	461.72	461.67	0.04_1	0.01_9
75	637.61	637.66	. . .	637.71	637.59	637.64	0.05_2	0.02_3

work of Willingham *et al.* is of similar precision, while that of Brown and Ewald (single observations) gives $\sigma = \pm 0.09$ torr.

DISCUSSION

The Antoine equation is unsuitable for comparing different studies, because small differences in vapor pressure often appear as large, cooperative changes in the coefficients B and C, as is apparent in Table II. This difficulty might be avoided by using the thermodynamically correct equation

$$\log p = A + \frac{B}{T} + C \log T + DT + ET^2 + \ldots \qquad (3)$$

[Aston, Szasz, and Fink (*5*) and Clarke and Glew (*8*)]. The precision of the data here considered does not justify using more than three terms, however, and curtailing Equation 3 raises again the same difficulties as the Antoine equation. It is simpler, therefore, to compare the vapor pressures given by the Antoine coefficients of Table II. In Figure 2 the Antoine vapor pressures of the present work are taken as data (horizontal line); the vapor pressures calculated from the other sets of Antoine constants appear as curves.

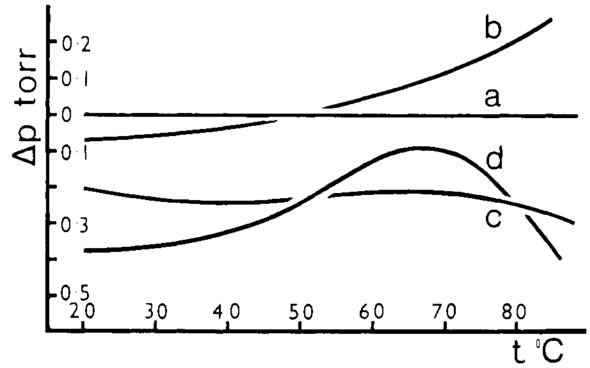

Figure 2. Comparison of vapor pressure of cyclohexane according to various authors

a. Present work
b. Brown and Ewald (*7*)
c. Willingham *et al.* (*21*)
d. Scatchard, Wood, and Mochel (*18*)

Table IV. Calculated and Experimental Heats of Evaporation

(Kilojoules per mole)

Temp., °C	20	25	54.1	73.3	80.7
This work	33.23	32.97	31.45	30.44	30.03
(*7*)	33.25	32.99	31.46	30.45	30.03
(*21*)	33.28	33.02	31.48	30.45	30.03
(*5*)	33.67	. . .	. . .	. . .	. . .
(*16*)	. . .	33.03_4	. . .	. . .	. . .
(*14*)	. . .	. . .	31.38	30.38	. . .
(*20*)	. . .	. . .	. . .	. . .	30.07

The agreement between our results and those of Brown and Ewald is satisfactory, and that between the results of Willingham *et al.* and those of Scatchard, Wood, and Mochel is fair, but the two pairs differ significantly. The detailed shapes of the curves in Figure 2 are undoubtedly imposed by using the Antoine equation, but the divergence of the four curves above 75° C., suggesting involatile contaminants, is difficult to reconcile with the roughly constant differences below 50° C. In an attempt to resolve this problem, we have calculated heat of evaporation data for intercomparison and comparison with calorimetric data.

HEAT OF EVAPORATION

The Clausius-Clapeyron relation may be stated in the form

$$\Delta\text{He} = T \frac{dp}{dT} (v^g - v^l) \qquad (4)$$

where v^g and v^l are the molal volumes of the gaseous and liquid phases. Differentiating the Antoine equation [Haggenmacher (*12*)], and substituting in Equation 4 gives

$$\Delta\text{He} = \frac{2.3026\, BT}{(t + C)^2} \left[RT + (B^* - v^l)\, p \right] \qquad (5)$$

where B^* is the second virial coefficient of the vapor. B^* values were interpolated from Bottomley and Coopes (*6*) using the equation of McGlashan and Potter (*15*) with adjusted n; v^l was calculated from literature values of density. Equation 5 is inexact because of the form imposed by the Antoine equation, but the consequent errors should not exceed 20 joules per mole. Table IV compares the ΔHe values calculated from the Antoine coefficients of Table II with some of the more precise of the published calorimetric data (*5, 14, 16, 20*).

The ΔHe values from the present work and from that of Brown and Ewald differ from the calorimetric results by more than the estimated uncertainty at 20° and 25° C., and this is true also of the ΔHe from the work of Willingham *et al.* at 54.1° and 73.3° C. The uncertainty on the result of Spitzer and Pitzer (*20*) is rather larger than the others (±30 calories per mole, or ±0.12 kilojoule per mole), so that the agreement at 80.7° C. is apparently satisfactory, suggesting that at the higher temperatures the vapor pressure discrepancies may indeed arise from sample contamination. At lower temperatures, however, no such simple explanation is apparent.

ACKNOWLEDGMENT

A. J. B. Cutler acknowledges the award of an S. R. C. studentship, during the tenure of which this work was carried out.

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RECEIVED for review November 28, 1966. Accepted March 20, 1967.

Compressibility Factors and Virial Coefficients of 2-Propanol

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The compressibility factor isotherms of gaseous 2-propanol were determined by the Burnett method at 100°, 125°, 150°, 175°, and 200° C. At each temperature, vapor pressures were measured, and the second and third virial coefficients were determined by graphical methods.

THE BURNETT method (*3*) essentially consists of measuring a series of pressures obtained by making repetitive expansions of a gas from one chamber into a previously evacuated second chamber under isothermal conditions. The method and apparatus have been thoroughly discussed by Silberberg, Kobe, and McKetta (*8*). The basic equation relating the compressibility factor of the gas to the pressure and temperature of the gas after the *r*th expansion is

$$Z_r = \frac{P_r N^r / T_r}{P_0 / Z_0 T_0} = \frac{P_r N^r}{\rho_0 R T_r} \tag{1}$$

In Equation 1, the quantity N is the apparatus constant, defined as

$$N = \frac{V_{\text{I}} + V_{\text{II}}}{V_{\text{I}}} \tag{2}$$

where V_{I} is the volume of the first chamber and V_{II} is the volume of the second chamber into which the expansions are made. The zero-subscripted quantities refer to the condition of the gas before the first expansion in a particular run. The details of determining the values of N and P_0/Z_0T_0 (or ρ_0) have been discussed by Silberberg and coworkers (*8, 9*).

The experimental apparatus employed in this work was that used by Heichelheim and coworkers (*6*), with the inclusion of a platinum resistance thermometer for more accurate temperature measurement and a fused quartz Bourdon tube pressure gage for low pressure determinations. The apparatus was a modified Burnett apparatus utilizing a third chamber of small volume into which expansions could be made in order to provide closer spacing of data points within a run. During any particular run, expansions could be made into either of the two expansion chambers in any order. Equation 1 then becomes

$$Z_r = \frac{P_r \Pi_r / T_r}{P_0 / Z_0 T_0} = \frac{P_r \Pi_r}{\rho_0 R T_r} \tag{3}$$

where

$$\Pi_r = \prod_{i=1}^{r} N_i$$

and N_i is the value of the apparatus constant applicable to the *i*th expansion.

The compressibility factor can be expressed in terms of molal density by the Leiden virial expansion

$$Z = 1 + B\rho + C\rho^2 + D\rho^3 + \ldots \tag{4}$$

The coefficients B, C, and D are the second, third, and fourth virial coefficients, respectively, and are functions

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