Vapor Pressures of Some High Molecular Weight Hydrocarbons

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Vapor pressures, between 5 x 10^{-6} and 10^{-1} torr., of thirteen hydrocarbons with molecular weights between 220 and 395 have been measured by an effusion method.

THE VAPOR PRESSURES of thirteen hydrocarbons with molecular weights in the range of 220 to 395 were measured by a Knudsen effusion method similar to that used by Bradley and Shellard (*2*). The hydrocarbon under examination was introduced into a glass bulb in which a small hole had been drilled. The bulb was suspended from the arm of a microbalance which was sensitive enough to detect weight changes of the order of 5 × 10^{-8} grams. The balance was then connected to a vacuum system and evacuated. The rate of effusion of the hydrocarbon through the hole was determined from rate of loss of weight from the bulb.

Each hydrocarbon was examined successively in six bulbs, the sizes of holes in which varied from 0.025 to 2 mm. diameter. The rates of effusion were so small that the cooling of the bulb by evaporation brought about a temperature change of less than 0.1° C.

The rates at which the hydrocarbon vapors effused were compared with the rates of effusion of the vapor of pure benzophenone from each of the bulbs. The vapor pressures of the hydrocarbon could then be calculated from the known vapor pressures of benzophenone (*3*). The vapor pressures were independent of the hole size.

The temperature, measured by thermometers sensitive to 0.01° C., was maintained constant to ±0.02° C. by an oil bath, which surrounded the apparatus.

The hydrocarbons were of high purity, the majority being obtained from API Project 42. They were:

Tricyclopentylmethane[a]	$C_{16}H_{28}$
9-Butylanthracene[a]	$C_{18}H_{18}$
1,6-Diphenylhexane	$C_{18}H_{22}$
1,2,3,4,4a,7,8,9,10,11,12,12a-Dodecahydrocrysene[a]	$C_{18}H_{24}$
Perhydrochrysene[a]	$C_{18}H_{30}$
1,6-Dicyclohexylhexane	$C_{18}H_{34}$
Tricyclohexylmethane[a]	$C_{19}H_{34}$
1,1-Dicyclohexylheptane[a]	$C_{19}H_{36}$
Nonadecane	$C_{19}H_{40}$
1,5-Dicyclohexyl-3-(2-cyclohexylethyl)pentane	$C_{25}H_{46}$
9-Dodecylanthracene[a]	$C_{26}H_{34}$
Heptacosane	$C_{27}H_{56}$
2,2,4,10,12,12-Hexamethyl-7-(3,5,5-Trimethylhexyl)-tridecane[a]	$C_{28}H_{58}$

[a] Obtained from API Project 42

At least 1% *w* of each hydrocarbon was vaporized from the effusion vessel before measurements were made in order to degas and dry it. Observations were continued until a constant reading was obtained; this usually took several hours. When the temperature of measurement was near its melting point special care was taken to see that the hydrocarbon was not partially melted but was either completely solid or completely liquid.

Table I. Experimental Results

Temp., ° C.	State	Vapor Press., Torr.
0.0	Liquid	9.72×10^{-5}
15.4	Liquid	5.38×10^{-4}
20.7	Liquid	9.78×10^{-4}
24.6	Liquid	1.15×10^{-3}
42.7	Liquid	9.22×10^{-3}
53.1	Liquid	2.18×10^{-2}
69.7	Liquid	8.89×10^{-2}
72.8	Liquid	1.29×10^{-1}
78.0	Liquid	1.68×10^{-1}

$A = -4065$ $B = 10.825 \pm 0.076$

Table II. Experimental Results for 9-Butylanthracene, $C_{18}H_{18}$(M.W. 228.3; M.P., 46.6–47.0° C.)

Temp., ° C.	State	Vapor Press., Torr.
20.0	Solid	3.46×10^{-6}
30.0	Solid	1.59×10^{-5}
40.0	Solid	6.21×10^{-5}
55.0	Liquid	3.48×10^{-4}
60.0	Liquid	6.16×10^{-4}
70.0	Liquid	1.57×10^{-3}
75.0	Liquid	2.10×10^{-3}
95.0	Liquid	1.04×10^{-2}
100.0	Liquid	1.51×10^{-2}

Solid: $A = -5645$ $B = 13.818 \pm 0.133$
Liquid: $A = -4382$ $B = 9.923 \pm 0.067$

Table III. Experimental Results for 1,6-Diphenylhexane, $C_{18}H_{22}$(M.W., 238.4)

Temp., ° C.	State	Vapor Press., Torr.
20.0	Liquid	3.56×10^{-5}
31.0	Liquid	1.27×10^{-4}
36.0	Liquid	2.16×10^{-4}
46.0	Liquid	5.90×10^{-4}
57.0	Liquid	1.88×10^{-3}
78.0	Liquid	1.35×10^{-2}
82.0	Liquid	1.95×10^{-2}
95.0	Liquid	5.07×10^{-2}
100.0	Liquid	7.73×10^{-2}

$A = -4595$; $B = 11.197 \pm 0.048$

Table IV. Experimental Results for 1,2,3,4,4a,7,8,9,10,11,12,12a-Dodecahydrochrysene, $C_{18}H_{24}$(M.W., 240.4; M.P., 40.8–41.2° C.)

Temp., ° C.	State	Vapor Press., Torr.
20.0	Solid	6.20×10^{-6}
25.0	Solid	1.50×10^{-5}
30.0	Solid	3.06×10^{-5}
35.0	Solid	6.19×10^{-5}
40.0	Solid	1.34×10^{-4}
45.0	Liquid	2.21×10^{-4}
50.0	Liquid	3.81×10^{-4}
55.0	Liquid	5.26×10^{-4}
60.0	Liquid	9.67×10^{-4}
70.0	Liquid	2.35×10^{-3}
75.0	Liquid	3.97×10^{-3}
80.0	Liquid	4.94×10^{-3}
85.0	Liquid	7.32×10^{-3}

Solid: $A = -6029$; $B = 15.370 \pm 0.174$
Liquid: $A = -4396$; $B = 10.165 \pm 0.091$

Table V. Experimental Results for Perhydrochrysene, $C_{18}H_{30}$(M.W., 246.6)

Temp., ° C.	State	Vapor Press., Torr.
0.0	Liquid	7.38×10^{-6}
10.0	Liquid	3.05×10^{-5}
20.0	Liquid	8.14×10^{-5}
25.0	Liquid	1.57×10^{-4}
30.0	Liquid	2.70×10^{-4}
40.0	Liquid	7.74×10^{-4}
50.0	Liquid	2.02×10^{-3}
55.0	Liquid	3.35×10^{-3}
60.0	Liquid	4.62×10^{-3}
70.0	Liquid	1.27×10^{-2}
75.0	Liquid	1.84×10^{-2}
80.0	Liquid	2.94×10^{-2}

$A = -4298$; $B = 10.611 \pm 0.162$

Table VI. Experimental Results for 1,6-Dicyclohexylhexane, $C_{18}H_{34}$(M.W., 250.5)

Temp., ° C.	State	Vapor Press., Torr.
15.0	Liquid	3.25×10^{-5}
20.0	Liquid	6.21×10^{-5}
30.0	Liquid	1.96×10^{-4}
40.0	Liquid	5.68×10^{-4}
50.0	Liquid	1.74×10^{-3}
70.0	Liquid	9.25×10^{-3}
100.0	Liquid	1.16×10^{-1}

$A = -4474$; $B = 11.042 \pm 0.068$

Table VII. Experimental Results for Tricyclohexylmethane, $C_{19}H_{34}$(M.W., 262.5; M.P., 57.3° C.)

Temp., ° C.	State	Vapor Press., Torr.
28.6	Solid	6.31×10^{-5}
36.8	Solid	1.86×10^{-4}
37.7	Solid	2.38×10^{-4}
48.0	Solid	1.05×10^{-3}
59.9	Liquid	3.63×10^{-3}
68.2	Liquid	9.30×10^{-3}
70.8	Liquid	1.05×10^{-2}
85.5	Liquid	3.21×10^{-2}
91.6	Liquid	5.05×10^{-2}

Solid: $A = -6133$; $B = 16.096 \pm 0.154$
Liquid: $A = -4250$; $B = 10.366 \pm 0.126$

Table VIII. Experimental Results for 1,1-Dicyclohexylheptane, $C_{19}H_{36}$(M.W., 264.5)

Temp., ° C.	State	Vapor Press., Torr.
20.8	Liquid	6.55×10^{-5}
25.5	Liquid	1.19×10^{-4}
30.4	Liquid	2.02×10^{-4}
52.3	Liquid	2.23×10^{-3}
68.4	Liquid	9.78×10^{-3}
88.0	Liquid	5.54×10^{-2}
95.0	Liquid	8.89×10^{-2}

$A = -4585$; $B = 11.416 \pm 0.049$

Table IX. Experimental Results for Nonadecane, $C_{19}H_{40}$(M.W., 268.5; M.P., 32.1° C.)

Temp., ° C.	State	Vapor Press., Torr.
15.0	Solid	4.71×10^{-6}
20.0	Solid	1.24×10^{-5}
25.0	Solid	3.23×10^{-5}
30.0	Solid	$7,80 \times 10^{-5}$
33.0	Liquid	1.41×10^{-4}
45.0	Liquid	5.34×10^{-4}
55.0	Liquid	1.57×10^{-3}

Solid:[a] $A = -7135$; $B = 19.430 \pm 0.022$. First order phase transition at 23° C. [Table 23-2 of API Project 44 (*3*)] apparently did not take place during vapor pressure measurement.
Liquid: $A = -4776$; $B = 11.745 \pm 0.043$.

Table X. Experimental Results for 1,5-Dicyclohexyl-3-(2-cyclohexylethyl)pentane, $C_{25}H_{46}$(M.W., 346.6)

Temp., ° C.	State	Vapor Press., Torr.
45.0	Liquid	3.45×10^{-6}
65.0	Liquid	3.61×10^{-5}
85.0	Liquid	3.10×10^{-4}
105.0	Liquid	2.28×10^{-3}
125.0	Liquid	1.10×10^{-2}
145.0	Liquid	5.88×10^{-2}

$A = -5623$; $B = 12.198 \pm 0.073$

Table XI. Experimental Results for 9-Dodecylanthracene, $C_{26}H_{34}$(M.W., 346.5; M.P., 49.5° C.)

Temp., ° C.	State	Vapor Press., Torr.
80.0	Liquid	6.25×10^{-6}
90.0	Liquid	2.39×10^{-5}
95.0	Liquid	5.16×10^{-5}
105.0	Liquid	1.16×10^{-4}
115.0	Liquid	3.35×10^{-4}
125.0	Liquid	9.86×10^{-4}
130.0	Liquid	1.43×10^{-3}

$A = -6655$; $B = 13.692 \pm 0.133$

Table XII. Experimental Results for Heptacosane, $C_{27}H_{56}$(M.W., 380.7)

Temp., ° C.	State	Vapor Press., Torr.
78.1	Liquid	2.76×10^{-5}
89.5	Liquid	9.32×10^{-5}
101.0	Liquid	2.08×10^{-4}
118.5	Liquid	1.33×10^{-3}
135.4	Liquid	6.27×10^{-3}
161.6	Liquid	5.00×10^{-2}

$A = -5990$; $B = 12.441 \pm 0.167$

Table XIII. Experimental Results for 2,2,4,10,12,12-Hexamethyl-7-(3,4,5-trimethylhexyl)tridecane, $C_{28}H_{58}$(M.W., 394.7)

Temp., ° C.	State	Vapor Press., Torr.
35.0	Liquid	1.50×10^{-5}
45.0	Liquid	5.16×10^{-5}
60.0	Liquid	2.32×10^{-4}
70.0	Liquid	6.37×10^{-4}
80.0	Liquid	1.90×10^{-3}
90.0	Liquid	5.46×10^{-3}
110.0	Liquid	2.91×10^{-2}
120.0	Liquid	5.56×10^{-2}

$A = -5147$; $B = 11.869 \pm 0.108$

The experimental results for each hydrocarbon were a good fit to the equation:

$$\log_{10} P = \frac{A}{T} + B$$

where P is the vapor pressure (torr.), T is the temperature (° K.) and A and B are constants, specific for each hydrocarbon.

The values of A and B for each hydrocarbon were calculated by the method of least squares. The experimental vapor pressures obtained for each hydrocarbon together with the values of the two constants (with a confidence limit at the 95% level) are given in Tables I-XIII.

Vapor pressures reported here are in good agreement with values for higher temperatures published by API Project 4 (*1*). This is illustrated for one hydrocarbon in Figure 1.

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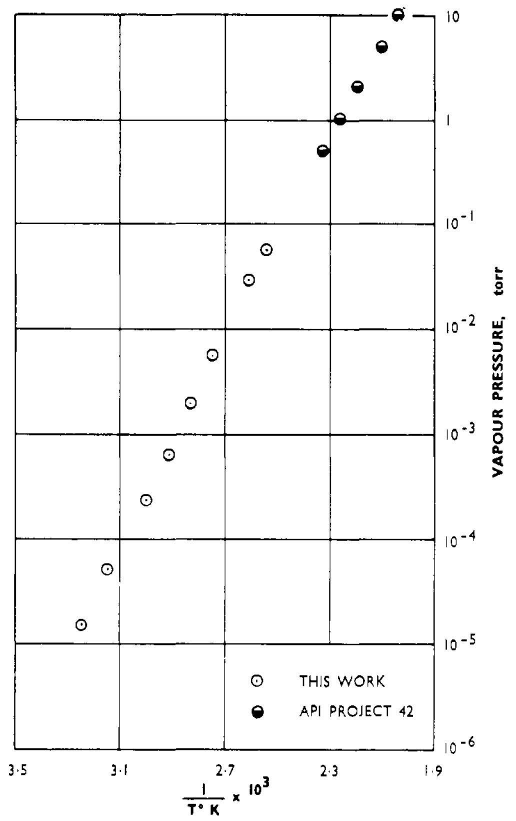

Figure 1. Vapor pressure of 2,2,4,10,12,12-hexamethyl-7-(3,5,5-trimethylhexyl)tridecane

LITERATURE CITED

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A Method for Determining the Solubility of Gases in Relatively Nonvolatile Liquids

Solubility of Methane in *n*-Decane

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FREQUENTLY, industrial operations require knowledge of the solubility of a permanent gas in an essentially nonvolatile liquid. A knowledge of the phase behavior of binary systems consisting of components of widely differing boiling points is essential in the chromatographic study of vapor-liquid equilibria (*2*, *7*). An experimental technique for obtaining such information has been developed and applied to the methane-*n*-decane binary system.

EXPERIMENTAL APPARATUS

A schematic diagram of the equipment used in this study is presented in Figure 1.

The equilibrium vessel was made of nonmagnetic 304 stainless steel 18¼ inches in length, 1.213 inches outside diameter, and 0.750 inch inside diameter. The lower end was closed and the upper end sealed to high pressure by means of an O-ring design (*2*). A ⅝-inch diameter ball bearing was placed within the vessel and used to equilibrate the mixture by raising and lowering a strong horseshoe magnet fitted directly around the cylinder body.

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