JOURNAL OF THE
AMERICAN CHEMICAL SOCIETY

VOLUME 55 NOVEMBER, 1933 NUMBER 11

[CONTRIBUTION FROM RESEARCH AND DEVELOPMENT LABORATORIES, SOCONY-VACUUM CORPORATION]

The Vapor Pressures of Propane and Propylene

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The vapor pressure of propane has been determined in five investigations,[1] but no two of them which cover the same temperature range agree with each other within about 5% in the value of the pressure (Fig. 2). The most recent investigation[1b] would seem the most reliable, judging by the care in purifying the samples and the consistency of results; but it gives a boiling point of −42.2°, which is about two degrees higher than any other reported in the literature for this hydrocarbon (except one, −37°,[1c] which is certainly too high). The vapor pressures are correspondingly at least 6% less than any other recorded values.

Three publications on the vapor pressure of propylene[1a,d,2] are more consistent, although no two cover the same temperature range.

In a recent investigation in this Laboratory an accuracy of about 1% was required in the vapor pressures of both these hydrocarbons at ordinary temperatures. Therefore, it seemed best to redetermine them. An all-glass apparatus simple both to construct and to operate was devised for this purpose. The elaborate apparatus and technique which would be required for a higher accuracy were not justified by the importance of this phase of the problem; but, since the results show less spread than those of any previous investigation, they seem worthy of record, together with a graphical comparison of all the published data.

Preparation of Materials.—Propane obtained by purchase was purified by fractional distillation at atmospheric pressure in a Davis column.[3] The finished sample distilled constantly within 0.1° at −42.3° (corr.). None of it was absorbed by sulfuric acid in a gas analysis pipet, indicating no propylene.

Propylene was made by catalytic decomposition of pure isopropanol in a bomb. It distilled constantly between −47.5 and −47.4° (corr.). In sulfuric acid it dissolved completely except for a tiny bubble, probably air from the connecting tube, which was too small to be transferred from the buret to the absorption pipet.

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(1) (a) Burrell and Robertson, THIS JOURNAL, **37**, 2188 (1915); (b) Dana, Jenkins, Burdick and Timm, *Refrig. Eng.*, **12**, 387 (1926); (c) Hainlen, *Ann.*, **282**, 233 (1894); (d) Maass and Wright, THIS JOURNAL, **43**, 1098 (1921); (e) Olszewski, *Ber.*, **27**, 3305 (1894).

(2) Seibert and Burrell, THIS JOURNAL, **37**, 2683 (1915).

(3) Davis, *Ind. Eng. Chem.*, *Anal. Ed.*, **1**, 61 (1929).

The pentane thermometer used in these distillations was standardized at the ice point and at −50° by comparison with a standardized German thermometer, and the stem correction was computed from a previous investigation involving shifting the position of the thermometer. Barometer corrections also were applied to the boiling point readings.

Apparatus.—The apparatus consisted of a glass tube shown in Fig. 1, with a manometer on one leg and the sample confined with mercury on the other leg.

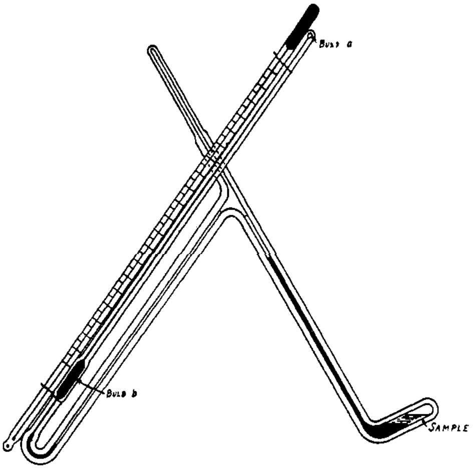

Fig. 1.—Absolute vapor pressure apparatus.

The manometer serves to measure the pressure by application of the gas laws to the air contained in it. Deviations from the gas laws at the temperatures and pressures studied are small (less than 0.35%)[4] but these corrections were applied in the calculations. The temperature and volume of that air must be measured accurately both with the apparatus open (and a known barometric pressure) and with the apparatus sealed and an otherwise unknown pressure. The temperature was measured by the attached thermometer. The manometer consists primarily of a fine uniform capillary tube, so that volume changes of its air content are proportional to length of air column as observed by the thread of confining mercury. But since the pressures to be measured are in the range 10 to 25 atmospheres, an accuracy in reading corresponding to that of a uniform tube over 120 cm. long is obtainable with one only 25 cm. long by substituting bulbs for the upper and lower portions.

Before constructing the apparatus the manometer was calibrated by weighing the tube with various parts filled with mercury. The capillary was thus found to have a cross section of 0.256 sq. mm. uniform within 1%. The small bulb (*a*) at the upper end has a capacity of about 0.006 ml., and the large bulb (*b*) about 0.25 ml.

The apparatus was exhausted several times and refilled with dry air through a calcium chloride tube so as to eliminate water vapor in the manometer, which would make the air too compressible and give high readings for the pressures. Mercury was then introduced by means of a capillary funnel, and the amount of air in the manometer adjusted by gentle suction until, when the manometer was held vertical, one mercury level was in the short portion of fine capillary below the bulb (*b*), while at the same time there was in the wide capillary connecting tube enough mercury (about 0.3 ml.) to fill the bulb (*b*) and fine capillary when it was driven there by pressure.

Operation.—The sample bulb was filled about 75% full with mercury, which was then heated to boiling to expel any adsorbed vapors. After cooling, the sample bulb was immersed with the filling tube in a vertical position in a cold bath of acetone and dry ice, causing the mercury to freeze. Pure propylene or propane was distilled through a calcium chloride drying tube and a capillary funnel into the sample bulb until the latter was filled completely with liquid sample on top of the frozen mercury. The end of the filling tube was sealed. The apparatus was withdrawn from the bath and held with the filling tube vertical until the mercury melted, when it was tipped to the position shown in the figure, confining the sample without a bubble. The sample bulb was then

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(4) "Int. Crit. Tables," McGraw-Hill Book Co., New York, 1928, Vol. III, p. 10.

immersed in a bath of water in a four-liter beaker by hanging the apparatus over the side of the beaker. The bath was agitated with an air stream and heated with a flame as warm as possible without allowing any of the sample to spill past the mercury into the capillary filling tube, and the flame shut off. A reading was taken every five or ten minutes during spontaneous cooling of the bath, as this gave very uniform temperatures, the rate of cooling being only about 0.1° per minute. The temperature of the sample was read in most cases on a short range (30–50°) thermometer divided into fifths of a degree, by immersing it in the bath near the sample bulb. This thermometer was calibrated with fused sodium sulfate giving a reading of 32.40°. The pressure was corrected for mercury heads in the connecting tube. The observations on vapor pressure are recorded in the table.

OBSERVED VAPOR PRESSURES

Temperatures in °C. Pressures in atmospheres

Propane				Propylene			
Filling 1		Filling 2		Filling 1		Filling 2	
t	*p*	*t*	*p*	*t*	*p*	*t*	*p*
31.9	11.8	27.6	10.4	29.0	12.8	30.2	13.3
36.0	13.0	29.6	11.1	31.4	13.5	32.3	13.9
38.2	13.6	32.0	11.7	32.3	13.9	35.2	14.9
42.0	15.0	34.1	12.4	34.2	14.7	39.1	16.4
42.2	15.2	34.9	12.5	34.3	14.7	42.2	17.5
44.5	15.8	35.4	12.7	35.9	15.1	44.0	18.2
45.6	16.0	36.5	13.1	36.0	15.2	45.1	18.7
47.5	16.9	37.2	13.3	37.3	15.6	45.8	18.8
49.8	17.7	38.5	13.7	39.3	16.3	Filling 3	
51.5	18.5	39.0	13.7	42.3	17.5	29.1	12.9
53.7	19.2	40.5	14.2			33.4	14.1
57.0	20.4	40.6	14.3			33.9	14.3
57.0	20.6	42.2	14.8			35.6	14.7
58.0	21.1	43.4	15.2			37.7	15.4
58.4	21.1	43.4	15.3			41.0	16.7
61.0	22.4	45.2	16.0			41.7	17.0
63.6	23.7	46.4	16.3			42.4	17.1

All the results of this investigation together with all published determinations of the vapor pressures of these two hydrocarbons (except those below −70° and one other) are plotted in Fig. 2. The abscissas are plotted as $1000/T$, but the lines indicate actual temperature centigrade. In order to decrease the slope of lines plotted and so permit a much larger scale, the ordinates are $(1000/T) + \log P$ instead of merely $\log P$, as is customary. A wavy line is drawn to separate the points for the two hydrocarbons, since the fields containing the points almost overlap.

Our own values do not cover a sufficient temperature range to determine the exact slope of the vapor pressure curves. It seems preferable to include the normal boiling points to determine the slope. Our observation on propane, −42.3°, agrees well with that of Dana, Jenkins, Burdick and Timm,[1b] −42.2°, and is much higher than three others in the literature, −44.1°,[1a] −44.5°[1d] and −45.0°.[1e] Our value for propylene, −47.5°, is nearly the mean of three recorded in the literature, −47.0°,[1d] −47.8°,[1a] and −47.6° (corr.).[3]

The best straight lines are drawn in the figure through the points corresponding to these boiling points and those for vapor pressures. They correspond to the equations for propane $\log P_1 = 4.375 - (1010/T)$ and for propylene $\log P_2 = 4.357 - (983/T)$.

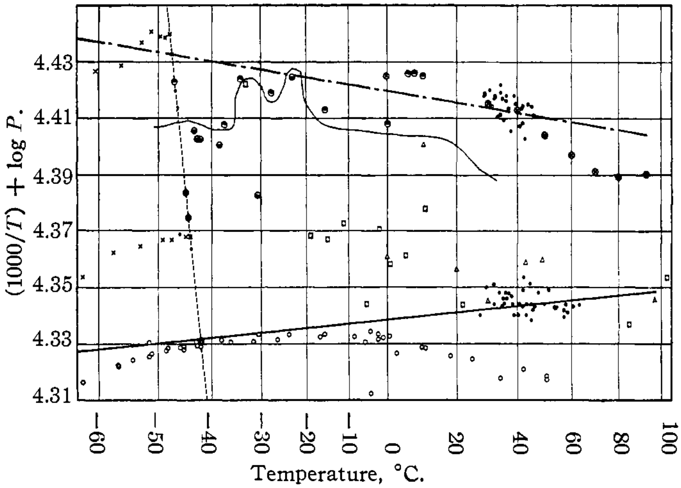

Fig. 2.—Vapor pressures of propane and propylene: propane———; propylene——— –; locus of normal boiling points– –; Burrell and Robertson, ×; Dana, Jenkins, Burdick and Timm, ⊙; Francis and Robbins, ●; Hainlen, □; Maass and Wright, propane, ◒, propylene, ◓; Olszewski, △; Seibert and Burrell, ⊗.

The former line agrees within about 1% with most of the determinations of Dana, Jenkins, Burdick and Timm[1b] up to 0°, but their values for higher temperatures diverge considerably. A plot of their points gives a line of much greater curvature than would be expected for a non-polar substance like propane.

The straight line for propylene agrees as well as any other with the various determinations in the literature.

Summary

An all-glass apparatus was devised for determining vapor pressures above atmospheric.

The vapor pressures of propane and propylene have been determined in the same apparatus for the first time above 0°. The determinations cover a temperature range of 27 to 64° for propane and 29 to 46° for propylene.

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RECEIVED MARCH 8, 1933
PUBLISHED NOVEMBER 7, 1933