## Eechnical Note

No. 4

THE VAPOR PRESSURES OF
SOME HYDROCARBONS IN THE
LIQUID AND SOLID STATE
AT LOW TEMPERATURES
by W. T. Ziegler
U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

## NATIONAL BUREAU OF STANDARDS

## Eechnical Note

4

May 1959

# THE VAPOR PRESSURES OF SOME HYDROCARBONS IN THE LIQUID AND SOLID STATE AT LOW TEMPERATURES 

by

W. T. Ziegler

# NBS Technical Notes are designed to supplement the Bureau's regular publications program. They provide a means for making available scientific data that are of transient or limited interest. Technical Notes may be listed or referred to in the open literature. They are for sale by the Office of Technical Services, U. S. Department of Commerce, Washington 25, D. C. <br> Contents were formerly <br> NBS Report 6038, issued Feb. 13, 1959 <br> DISTRIBUTED BY <br> <br> UNITED STATES DEPARTMENT OF COMMERCE <br> <br> UNITED STATES DEPARTMENT OF COMMERCE <br> Office OF TECHNICAL SERVICES <br> WASHINGTON 25, D. C. 

Price \$ 75

THE VAPOR PRESSURES OF SOME HYDROCARBONS IN THE LIQUID AND SOLID STATE AT LOW TEMPERATURES

by<br>W. T. Ziegler*<br>School of Chemical Engineering Georgia Institute of Technology

## SUMMARY

This paper presents a brief review of the literature pertaining to the vapor pressure of eleven hydrocarbons at low temperatures. These hydrocarbons are methane, ethane, propane, n-butane, isobutane ( 2 -methyl propane), n-pentane, ethylene, propylene, 1-butene, acetylene and cyclopropane. All of these except cyclopropane are encountered in the purification of hydrogen from refinery sources. Vapor pressure data are given for most of these hydrocarbons over the pressure range 0.001 to 1500 mm Hg . These data have been used to estimate the triple-point pressures of the hydrocarbons where these pressures were not found in the literature. Some data for the vapor pressures of solid methane, ethane, $n$-butane, ethylene, acetylene and cyclopropane are included.

It is recommended that vapor-pressure equations of Rossini et al. ${ }^{2}$ for ethane, propane, $n$-butane, isobutane, $n$-pentane, ethylene, propylene and 1 -butene be used for the range 1500 to 10 mm Hg , and that the data of Tickner and Lossing ${ }^{4}$ be used for all hydrocarbons except methane for the range 10 to 0.001 mm Hg . For liquid and solid methane the equations of Armstrong, Brickwedde and Scott 10 appear to be the most accurate. However, they differ only very slightly from the equations developed by Rossini et al. 2 For solid ethylene below about 0.03 mm Hg the vapor-pressure equation of Lister and McDonald ${ }^{7}$ appears to be the most accurate.

[^0]
## INTRODUCTION

A knowledge of the vapor pressure of hydrocarbons is often needed in the analysis of low-temperature processes such as the purification of hydrogen and the design of apparatus such as low-temperature distillation or scrubbing equipment, cryogenic baths, etc. It is the purpose of the present paper to collect in one place for ready reference the vapor pressures of a number of hydrocarbons often encountered in such studies. The eleven hydrocarbons included in this survey are methane, ethane, propane, n-butane, isobutane ( 2 -methyl propane), n-pentane, ethylene, propylene, l-butene, acetylene and cyclopropane. In general the range covered is from 1500 mm down to approximately 0.001 mm Hg . For the most part the data apply to the liquid range. Some data for the vapor pressure of solid methane, ethane, n-butane, cyclopropane, ethylene and acetylene are included. The data have been used to estimate the triple-point pressures where this quantity was not found in the literature.

The present survey is not intended to be a critical analysis of all of the available data. However, it is believed that most of the available data have been examined. Principal reliance has been placed on the extensive compilations of the National Bureau of Standards and the data of Project 44 of the American Petroleum Institute ${ }^{1,2}$ for the pressure range 10 to 1500 mm Hg , and the measurements of Tickner and Lossing ${ }^{3,4}$ for the range 10 to 0.001 mm Hg. A number of other papers dealing with the vapor pressure of these hydrocarbons have been examined. Several of these papers $5,6,7$ emphasize the importance of taking the Knudsen thermo-molecular pressure effect into account at pressures below about 0.01 mm Hg if precise experimental values of vapor pressure are desired. These papers will be discussed in their appropriate place.

## VAPOR PRESSURE OF HYDROCARBONS FROM 10 TO 1500 mm Hg

Rossini et al. ${ }^{2}$ have represented the vapor-pressure data for many hydrocarbons over this pressure range by means of the Antoine equation:

$$
\begin{equation*}
\log _{10} P=A-\frac{B}{t+C} \tag{1}
\end{equation*}
$$

where $A, B$, and $C$ are constants for a given hydrocarbon, $P$ is the vapor pressure in mm Hg , and t is the temperature in ${ }^{\circ} \mathrm{C}$.

If the temperature, $T$, is expressed in ${ }^{\circ} \mathrm{K}$, equation (1) may be written in the form

$$
\begin{equation*}
\log _{10} P=A-\frac{B}{T+C^{1}} \tag{2}
\end{equation*}
$$

The Antoine constants, as determined by Rossini, et al., for nine of the hydrocarbons covered in this paper are given in Table I. No vapor-pressure data are given by Rossini for acetylene and cyclopropane.

## TABLEI

> Temp. at which vapor

| Hydrocarbon | Formula | State | pressure $10 \mathrm{~mm} \mathrm{Hg},{ }^{\circ} \mathrm{C}$ | A | B | C | $C^{1}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Methane | $\mathrm{CH}_{4}$ | Solid* | -195.51 | 7.69540 | 532. 20 | 275.00 | 1.84 |
|  |  | Liquid |  | 6.61184 | 389.93 | 266.00 | -7.16 |
| Ethane | $\mathrm{C}_{2} \mathrm{H}_{6}$ | Liquid | -142.88 | 6.80266 | 656.40 | 256.00 | -17.16 |
| Propane | $\mathrm{C}_{3} \mathrm{H}_{8}$ | Liquid | -108.51 | 6.82973 | 813.20 | 248.00 | -25.16 |
| n-Butane | $\mathrm{C}_{4} \mathrm{H}_{10}$ | Liquid | -77.76 | 6.83029 | 945.90 | 240.00 | -33.16 |
| Isobutane | $\mathrm{C}_{4} \mathrm{H}_{10}$ | Liquid | -86.42 | 6.74808 | 882.80 | 240.00 | -33.16 |
| n -Pentane | $\mathrm{C}_{5} \mathrm{H}_{12}$ | Liquid | -50.1 | 6.85221 | 1064.63 | 232.00 | -41.16 |
| Ethylene | $\mathrm{C}_{2} \mathrm{H}_{4}$ | Liquid | -153.22 | 6.74756 | 585.00 | 255.00 | -18.16 |
| Propylene | $\mathrm{C}_{3} \mathrm{H}_{6}$ | Liquid | -112.11 | 6.81960 | 785.00 | 247.00 | -26.16 |
| 1-Butene | $\mathrm{C}_{4} \mathrm{H}_{8}$ | Liquid | -81.5 | 6.84290 | 926.10 | 240.00 | -33.16 |

* At the triple point $-182.48^{\circ} \mathrm{C}$, the pressure is 87.7 mm Hg .

Rossini et al. ${ }^{2}$ have used these equations to compute and tabulate the temperatures corresponding to 30 pressures over the range 10 to 1500 mm Hg . The results of these calculations are shown in Table II.

| $m m \mathrm{Hg}^{\text {a }}$ | Methane | Ethane | Propane | n-Butane | Isobutane | $n-P$ entane | Ethylene | Propylene | 1-Butene |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 10 | $-195.51(\mathrm{~s})^{\mathrm{b}}$ | -142.88 | -108. 51 | -77.76 | -86.42 | -50.1 | -153.22 | -112.11 | -81.5 |
| 20 | -191.77(s) | -136.69 | -100.91 | -68.93 | -77.93 | -40.2 | -147.59 | -104.75 | -72.89 |
| 30 | -189.41(s) | -132.74 | -96.07 | -63.30 | -72.52 | -33.93 | -144.00 | -100.06 | -67.41 |
| 40 | -187.66(s) | -129.78 | -92.44 | -59.08 | -68.45 | -29.22 | -141.31 | -96.55 | -63.29 |
| 50 | -186.25(s) | -127.39 | -89.51 | -55.66 | -65.16 | -25.41 | -139.13 | -93.70 | -59.96 |
| 60 | -185.06(s) | -125.36 | -87.02 | -52.77 | -62.37 | -22.18 | -137.28 | -91.29 | -57.15 |
| 80 | -183.12(s) | -122.03 | -82.94 | -48.02 | -57.79 | -16.89 | -134.24 | -87.33 | -52.52 |
| 100 | -181.45 | -119.33 | -79.63 | -44. 17 | -54.07 | -12.59 | -131.78 | -84. 12 | -48.77 |
| 150 | -178.09 | -114.12 | -73.26 | -36.76 | -46.91 | -4.33 | -127.03 | -77.95 | -41.56 |
| 200 | -175.55 | -110.19 | -68.43 | -31.16 | -41.49 | 1.92 | -123.44 | -73.27 | -36.10 |
| 250 | -173.47 | -106.98 | -64.51 | -26.59 | -37.06 | 7.01 | -120.51 | -69.46 | -31.65 |
| 300 | -171.69 | -104.25 | -61.17 | -22.71 | -33.30 | 11. 34 | -118.01 | -66.23 | -27.87 |
| 400 | -168.76 | -99.74 | -55.65 | -16.29 | -27.07 | 18.49 | -113.88 | -60.87 | -21.62 |
| 500 | -166.35 | -96.05 | -51.14 | -11.04 | -21.98 | 24.337 | -110.51 | -56.50 | -16.52 |
| 600 | -164.29 | -92.90 | -47.29 | -6.57 | -17.63 | 29.319 | -107.62 | -52.76 | -12.16 |
| 700 | -162.48 | -90.14 | -43.92 | -2.65 | -13.81 | 33.685 | -105.09 | -49.49 | -8.35 |
| 760 | -161.49 | -88.63 | -42.07 | -0.50 | -11.73 | 36.074 | -103.71 | -47.70 | -6. 26 |
| 800 | -160.86 | -87.67 | -40.90 | 0.86 | -10.40 |  | -102.83 | -46.57 | -4.94 |
| 900 | -159.39 | -85.44 | -38.17 | 4. 04 | -7.31 |  | -100.78 | -43.91 | -1.85 |
| 1000 | -158.04 | -83.38 | -35.66 | 6.95 | -4.47 |  | -98.90 | -41.48 | 0.99 |
| 1200 | -155.6 | -79.71 | -31.2 | 12. 2 | 0.6 |  | -95.53 | -37.13 | 6.1 |
| 1500 | -152.6 | -75.00 | $-25.4$ | 18.9 | 7.1 |  | -91. 20 | -31.55 | 12.6 |

VAPOR PRESSURE OF HYDROCARBONS FROM 0.001 TO 10 mm Hg
Tickner and Lossing ${ }^{3,4}$ have measured the vapor pressure of eleven hydrocarbons and $\mathrm{CO}_{2}$ as a function of temperature down to a pressure of 0.001 mm Hg using a mass spectrometer. These investigators have presented their smoothed data as temperatures for pressures of $0.001,0.002,0.005,0.01,0.02,0.05,0.1,0.2$, $0.5,1.0,2.0,5.0$ and 10.0 mm Hg . Their results for the hydrocarbons are presented in Table III.
TABLE III
Vapor Pressures of Hydrocarbons from 0.001 to $10 \mathrm{~mm} \mathrm{Hg}{ }^{\text {a }}$

|  | Temperature in ${ }^{\circ} \mathrm{C}$ |  |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| mm Hg | Methane | Ethane | Propane | n-Butane | Isobutane | $n-P e n t$ ane | Ethylene | Propylene | 1-Butene | Acetylene | Cyclopropane |
| $10.0{ }^{\text {b }}$ | -195.51(s) ${ }^{\text {c }}$ | -142.88 | -108.51 | -77.76 | -86. 42 | -50.1 | -153.22 | -112.11 | -81.5 |  |  |
| 10.0 | -195.5(s) | -142.5 | -108.4 | -77.3 | -86.1 | -49.8 | -152.6 | -111.9 | -81.0 | -128.0(s) | -100.2 |
| 5.0 | -199.0(s) | -147.6 | -115.0 | -84.7 | -93.6 | -58.1 | -157.7 | -118.3 | -88.1 | -132.9(s) | -107.1 |
| 2.0 | -203.1(s) | -154.1 | -123.2 | -93.9 | -102.5 | -68.2 | -163.3 | -126.2 | -97.2 | -139.0(s) | -115.5 |
| 1.0 | -206.0(s) | -158.5 | -128.8 | -100.3 | -108.4 | -75.0 | -167.4 | -131.4 | -103.3 | -143.5(s) | -121.3 |
| 0.5 | -208.5(s) | -162.6 | -134.0 | -106.2 | -113.9 | -81.7 | -170.7(s) | -136.7 | -108.8 | -147.4(s) | -126.8 |
| 0.2 | -211.6(s) | -167.8 | -140.3 | -113.3 | -120.7 | -89.7 | -174.9(s) | -142.9 | -115.9 | -152.4(s) | -132.3(s) |
| 0.1 | -213.8(s) | -171.3 | -144.8 | -118.4 | -125.8 | -95.8 | -178.0(s) | -147.3 | -120.8 | -155.9(s) | -136.2(s) |
| 0.05 | -215.8(s) | -174.6 | -148.8 | -123.2 | -130.2 | -101.0 | -180.8(s) | -151.2 | -125.6 | -159.1(s) | -140.0(s) |
| 0.02 | -218.3(s) | -178.7 | -153.9 | -128.9 | -136.0 | -107.5 | -184.1(s) | -156.3 | -131.3 | -163.4(s) | -144.9(s) |
| 0.01 | -220.1(s) | -181.8 | -157.4 | -133.2 | -139.9 | -112.0 | -186.4(s) | -159.6 | -135.4 | -166.2(s) | -148.0(s) |
| 0.005 | -221.6(s) | -184.4(s) | -160.7 | -137.3 | -143.8 | -116.4 | -188.7(s) | -163.1 | -139.1 | -168.9(s) | -150.9(s) |
| 0.002 | -223.6(s) | -187.7(s) | -164.9 | -142.0(s) | -148.3 | -121.8 | -191.5(s) | -167.2 | -143.9 | -172.3(s) | -155.1(s) |
| 0.001 | -225.0(s) | -189.8(s) | $-167.8$ | -145.5(s) | $-151.5$ | -125.7 | -193.7(s) | -169.9 | -147.3 | -174.6(s) | -157.7(s) |
| After Tickner and Lossing, Ref. 4. |  |  |  |  |  |  |  |  |  |  |  |
| Temperatures from Table II for comparison, Ref. 2. |  |  |  |  |  |  |  |  |  |  |  |
| c (s) re | fers to solid. |  |  |  |  |  |  |  |  |  |  |

The vapor-pressure data report ed by Ticicner and Lossing agree quite well with the tabulations of Rossini et al. ${ }^{2}$ in the region of overlap ( 10 to 80 mm Hg , as judged from their plotted data).

In their experiments Tickner and Lossing ${ }^{4}$ used a 1.6 cm diameter tube connecting the low-temperature equilibrium chamber with the mass spectrometer. They recognized the existence of the Knudsen thermo-molecular pressure effect for pressure below about 0.01 mm Hg but did not take it into account in their experiments. Liang, ${ }^{5}$ using a technique which he had previously employed ${ }^{6}$ with solid Kr and Xe, remeasured the vapor pressures of methane, ethylene and acetylene at $77.5^{\circ}$ and $90.0^{\circ} \mathrm{K}$ taking into account thermal transpiration. From these measurements he concluded that small corrections should be applied to the data of Tickner and Lossing for these gases at the lowest temperatures but that for the other hydrocarbons the corrections were probably smaller than the uncertainty in the reported temperatures $\left( \pm 0.3^{\circ} \mathrm{C}\right.$ at or above $\left.-196^{\circ} \mathrm{C}\right)$.

The more recent measurements by Lister and McDonald ${ }^{7}$ of the vapor pressure of solid ethylene, in which allowance was made for thermal transpiration, agree to within $2 \%$ with the measurements of Tickner and Lossing down to about $85^{\circ} \mathrm{K}$ (about 0.005 mm ). Below $85^{\circ} \mathrm{K}$ the values of Tickner and Lossing for ethylene are progressively higher than those reported by Lister and McDonald, being about $10 \%$ higher at $80^{\circ} \mathrm{K}$.

Delaplace ${ }^{8}$ has also reported measurements of the vapor pressures of ethane, propane, isobutane, $n$-butane, ethylene, propylene, isobutylene, 1 -butene and acetylene down to about $-196^{\circ} \mathrm{C}$. Unfortunately, no units are given in this paper for the tabulated pressures. If one assumes with Lister and McDonald ${ }^{7}$ that the units used by Delaplace are baryes, then one finds approximate agreement with the data of Tickner and Lossing for ethane, propylene and acetylene and large discrepancies for the other hydrocarbons.

Almost no other data exist with which the data of Tickner and Lossing may be compared. Such limited data as do exist will be discussed in the final section of this paper where additional comments are made for the individual hydrocarbons.

The author is of the opinion that the data of Tickner and Lossing can be used with considerable confidence down to about 0.01 mm Hg . Below this pressure level the pressures reported by them may be somewhat high because of neglect of thermal transpiration.

## ESTIMATION OF TRIPLE-POINT PRESSURES

The triple-point pressures of only four of the hydrocarbons discussed in this paper appear to have been measured. ${ }^{2,9}$ The data of Tickner and Lossing 4 given in Table III have been used to estimate the triple-point pressure either by interpolation or extrapolation of the data using an empirical equation of the form

$$
\begin{equation*}
\log _{10} P=a-\frac{b}{T} \tag{3}
\end{equation*}
$$

where the pressure is expressed in mm Hg and the temperature is in ${ }^{\circ} \mathrm{K}$. The constants a and b in the appropriate equation were obtained using data points taken from Table III immediately preceding the triple point.

The triple-point temperatures and pressures are summarized in Table IV. The calculations are discussed in more detail under the individual hydrocarbons in the next section. It is recognized that the estimated triple-point pressures of propane, propylene and l-butene may be considerably in error.

## TABLE IV

## Triple-Point Temperatures and Pressures

| Hydrocarbon | Triple Point Temperature |  | Triple Point Pressure | Reference |
| :---: | :---: | :---: | :---: | :---: |
|  | ${ }^{\circ} \mathrm{C}$ | ${ }^{\circ} \mathrm{K}$ | mm Hg |  |
| Methane | -182.48 | 90.68 | 87.7 | 2 |
|  |  | 90.66 | $87.50 \pm 0.10$ | 10 |
| Ethane | -183. 27 | 89.89 | $6 \times 10^{-3}$ | 9 |


|  |  | $6.94 \times 10^{-3}$ | Calc. Eq. (3) |  |
| :--- | :---: | :---: | :---: | :---: |
| Propane | -187.69 | 85.47 | $4.07 \times 10^{-6}$ | Calc. Eq. (8) |
| n-Butane | -138.35 | 134.81 | $4.05 \times 10^{-3}$ | Calc. Eq. (9) |
| Isobutane | -159.60 | 113.56 | $1.52 \times 10^{-4}$ | Calc. Eq. (11) |
| n-Pentane | -129.72 | 143.44 | $4.66 \times 10^{-4}$ | Calc. Eq. (12) |
| Ethylene | -169.15 | 104.01 | 0.9 | 9 |


| 0.854 | Calc. Eq. (1) |
| :--- | :--- |
| 0.729 | Calc. Eq. (3) |


| Propylene | -185.25 | 87.91 | $1.14 \times 10^{-5}$ | Calc. Eq. (14) |
| :--- | :---: | :---: | :---: | :---: |
| 1-Butene | -185.35 | 87.81 | $1.0 \times 10^{-8}$ | Calc.Eq. (15) |
| Acetylene | -81.5 | 191.66 | 900 | 9 |
| Cyclopropane | -127.53 | 145.63 | 0.454 | Calc. Eq. (16) |

## COMMENTS ON VAPOR PRESSURE RELATIONS

 FOR INDIVIDUAL HYDROCARBONS*It is recommended that the vapor-pressure equations of Rossini et al. ${ }^{2}$ for ethane, propane, $n$-butane, isobutane, $n$-pentane, ethylene, propylene and l-butene be used for the range 10 mm to 1500 mm Hg , and that the data of Tickner and Lossing ${ }^{4}$ be used for all hydrocarbons except methane for the range 10 to 0.001 mm Hg . For liquid and solid methane the equations of Armstrong et al. ${ }^{10}$ appear to be the most accurate. However, they differ only slightly from the equations developed by Rossini et al. 2 For solid ethylene below about 0.03 mm Hg the vapor-pressure equation of Lister and McDonald ${ }^{7}$ appears to be the most accurate. Sondak and Thodos ${ }^{12}$ have represented the vapor pressure of many saturated aliphatic hydrocarbons from "the triple to the critical point" by a four-constant equation. They appear not to have considered the work of Tickner and Lossing. ${ }^{3,4}$ The triple-point pressures of ethane and propane estimated from these equations are approximately $20 \%$ greater than the values obtained from the data of Tickner and Lossing.

## Methane

Armstrong, Brickwedde and Scott ${ }^{10}$ have presented a review of the vapor-pressure data available for both liquid and solid methane. This paper should be consulted for a bibliography and critical discussion. This paper includes extensive experimental data for the deuteromethanes as well as for methane, including careful measurements of the triple-point temperatures and pressures.

Liquid. Armstrong et al. ${ }^{10}$ have represented the vapor pressure of liquid methane above the triple point by two equations

$$
\begin{equation*}
\log _{10} P=6.61184-\frac{389.93}{T-7.16} \tag{4}
\end{equation*}
$$

and

$$
\begin{align*}
\log _{10} P= & 10.68631-\frac{595.546}{T}-0.0348066 \mathrm{~T} \\
& +1.3338 \times 10^{-4} \mathrm{~T}^{2}-1.7869 \times 10^{-7} \mathrm{~T}^{3} \tag{5}
\end{align*}
$$

[^1]They recommend that equation (4), which is identical with that proposed by Rossini et al. ${ }^{2}$ (see Table I), be used from the triple point to 760 mm and that equation (5) be used for the remainder of the liquid region to the critical point. Armstrong et al. have tabulated the vapor pressure at one-degree intervals over the liquid range.

Solid. Armstrong et al. ${ }^{10}$ have adjusted the constants of the empirical equation of Rossini et al. ${ }^{2}$ (see Table I) very slightly to give a fit with their choice of the triple-point temperature and pressure $\left(90.66 \pm 0.01^{\circ} \mathrm{K}, 87.50 \pm 0.10 \mathrm{~mm} \mathrm{Hg}\right)$. The revised equation is:

$$
\begin{equation*}
\log _{10} P=7.69540-\frac{532.20}{T+1.842} \tag{6}
\end{equation*}
$$

This equation is based on experimental data of Brickwedde and Scott ${ }^{10}$ down to $54^{\circ} \mathrm{K}$. The equation is in excellent agreement with the data of Tickner and Lossing ${ }^{4}$ down to 0.01 mm Hg. However, at 0.001 this equation gives a pressure about $6 \%$ higher than that found by Tickner and Lossing.

Armstrong et a1. have tabulated the vapor pressure of solid methane at one-degree intervals down to $51^{\circ} \mathrm{K}$.

## Ethane

Solid. The triple-point pressure, calculated from equation (3), and temperature given in Table IV, together with the experimental data at 0.001 mm Hg in Table III, have been used to obtain the following equation for the vapor pressure of solid ethane below the triplepoint temperature:

$$
\begin{equation*}
\log _{10} P=8.5812-\frac{965.40}{T} \tag{7}
\end{equation*}
$$

This equation has been used to estimate the vapor pressures given in Table $V$.

## TABLE V

Temperature
$\mathbf{o}_{\mathrm{K}}$

| Vapor Pressure, mm Hg |  |
| :--- | :--- |
| Obs. | Calc. |
| Ref. 4 | Eq. (7) |


| $89.89^{\mathrm{a}}$ |  | $6.94 \times 10^{-3}$ |
| :--- | :--- | :--- |
| 88.76 | $5 \times 10^{-3}$ | $5.9 \times 10^{-3}$ |
| 85.46 | $2 \times 10^{-3}$ | $1.93 \times 10^{-3}$ |
| 83.36 | $1 \times 10^{-3}$ | $1.00 \times 10^{-3}$ |
| 80 |  | $3.25 \times 10^{-4}$ |
| 77.4 |  | $1.28 \times 10^{-4}$ |
| 70 |  | $6.16 \times 10^{-6}$ |

a Triple point

## Propane

Liquid. The vapor-pressure data of Tickner and Lossing (Table III) for liquid propane at 0.1 and 0.001 mm Hg have been used to obtain the empirical equation

$$
\begin{equation*}
\log _{10} P=8.16173-\frac{1176.0}{T} \tag{8}
\end{equation*}
$$

For $T=115.76^{\circ} \mathrm{K}$ this equation gives $P=0.01006 \mathrm{~mm} \mathrm{Hg}$ which may be compared with the measured pressure of 0.01 mm Hg . This equation has been used to estimate the triple-point pressure given in Table IV.
n-Butane
Liquid. The vapor-pressure data of Tickner and Lossing (Table III) at 0.5 and 0.005 mm Hg have been used to obtain the empirical equation

$$
\begin{equation*}
\log _{10} P=8.47062-\frac{1464.52}{T} \tag{191}
\end{equation*}
$$

This equation has been used to obtain the triple-point pressure, $4.05 \times 10^{-3} \mathrm{~mm} \mathrm{Hg}$, given in Table IV.

Solid. The triple-point pressure and temperature given in Table IV, together with the experimental data at 0.001 mm Hg in Table III, have been used to obtain the empirical equation

$$
\begin{equation*}
\log _{10} P=8.4460-\frac{1461.2}{T} \tag{10}
\end{equation*}
$$

Equation (10) has been used to estimate the vapor pressure of solid n-butane at lower temperatures as shown in Table VI.

## TABLE VI

$\mathrm{Temper}_{\mathrm{K}}$

| Vapor Pressure, mm Hg |  |
| :--- | :--- |
| Obs. | Calc. |
| Ref. 4 | Eq. $(10)$ |

$134.81^{a}$
$4.05 \times 10^{-3}$
127.66
$1 \times 10^{-3}$
$1 \times 10^{-3}$
120
$1.86 \times 10^{-4}$
110
$1.45 \times 10^{-5}$

100
$6.8 \times 10^{-7}$
a
Triple point

## Isobutane

Liquid. The data of Tickner and Lossing given in Table III at 0.01 and 0.001 mm Hg have been used to obtain the empirical equation

$$
\begin{equation*}
\log _{10} P=8.48776-\frac{1397.6}{T} \tag{II}
\end{equation*}
$$

This equation has been used to estimate the triple-point pressure, $1.52 \times 10^{-4} \mathrm{~mm}$ Hg given in Table IV.

Solid. No data for the vapor pressure of solid isobutane were found.

## n-Pentane

Liquid. The data of Tickner and Lossing given in Table III at 0.02 and 0.001 mm Hg have been used to obtain the empirical equation

$$
\begin{equation*}
\log _{10} P=8.84223-\frac{1746.26}{T} \tag{12}
\end{equation*}
$$

This equation has been used to estimate the triple-point pressure given in Table IV.

Solid. No data for the vapor pressure of solid n-pentane were found.

## Ethylene

Liquid. It is felt that the empirical relation of Rossini et al. ${ }^{2}$ given in Table I adequately represents the vapor-pressure data down to the triple point. A short extrapolation of this equation down to the triple point of $104.01^{\circ} \mathrm{K}$ gave a triple-point pressure of 0.854 mm Hg (see Table IV).

The data of Tickner and Lossing given in Table III for 10 and 1 mm Hg were used to evaluate the constants of equation (3). Extrapolation to the triple-point temperature gave a triple-point pressure of 0.729 mm Hg .

Solid. Lister and McDonald ${ }^{7}$ have measured the vapor pressure of solld ethylene over the temperature range $77.52^{\circ}$ to $90.09^{\circ} \mathrm{K}$ corres ponding to a pressure range of $0.432 \times 10^{-3}$ to $27.8 \times 10^{-3} \mathrm{~mm} \mathrm{Hg}$. They represented their data by the equation*

$$
\begin{array}{r}
\log _{10} P \times 10^{3}=1.5477-1038.1\left(\frac{1}{\mathrm{~T}}-0.0110\right) \\
+16537\left(\frac{1}{\mathrm{~T}}-0.0110\right)^{2} \tag{13}
\end{array}
$$

These investigators made a careful study of the thermal transpiration effects and corrected their measurements accordingly. Comparison of their work with the measurements of Tickner and Lossing ${ }^{4}$ showed that the two sets of measurements agree to within $2 \%$ above $85^{\circ} \mathrm{K}$ ( $\mathrm{P}>6 \times 10^{-3} \mathrm{~mm} \mathrm{Hg}$ ). Below this temperature the disagreement becomes progressively larger reaching about $10 \%$ at $80^{\circ} \mathrm{K}$, the values of Tickner and Lossing being higher, presumably because they did not correct their measurements for thermal transpiration.

The measurements of Liang ${ }^{5}$ at $77.5^{\circ} \mathrm{K}$ and $90.0^{\circ} \mathrm{K}$ differ significantly from those of Lister and McDonald and Tickner and Lossing as may be seen from Table VII taken from the paper of Lister and McDonald. 7

| TABLE VII <br> Temperature | Vapor Pressure <br> mm Hg x $10^{3}$ |  |
| :---: | :---: | :---: |
| Lister and Tickner and <br> McDonald <br> Lossing | Liang |  |
| 90.09 | 27.87 | 26.9 |

[^2]
## Propylene

Liquid. The data of Tickner and Lossing given in Table III for 0.1 and 0.001 mm Hg were used to obtain the empirical relation

$$
\begin{equation*}
\log _{10} P=8.13809-\frac{1150.12}{T} \tag{14}
\end{equation*}
$$

This equation has been used to estimate the triple-point pressure of $1.14 \times 10^{-5} \mathrm{~mm} \mathrm{Hg}$ given in Table IV.

Solid. No data for the vapor pressure of solid propyl ene were found.

## 1-Butene

Liquid. The data of Tickner and Lossing given in Table III for 0.1 and 0.001 mm Hg were used to obtain the empirical equation

$$
\begin{equation*}
\log _{10} P=8.49889-\frac{1447.25}{T} \tag{15}
\end{equation*}
$$

This equation has been used to estimate the triple-point pressure of $1.0 \times 10^{-8} \mathrm{~mm}$ Hg given in Table IV.

Solid. No data for the vapor pressure of solid 1-butene were found.

## Acetylene

Solid. Tickiner and Lossing ${ }^{4}$ compared their measurements with those of Bourbo 11 who has measured the vapor pressure of solid acetylene over the range $89.65^{\circ}$ to $169.5^{\circ} \mathrm{K}$. Unfortunately, the papers of Bourbo were not available. However, Tickner and Lossing stated that their vapor-pressure values were in good agreement with the values obtained by Bourbo, but were slightly lower for a given temperature.

## Cyclopropane

Liquid. No search was made for the vapor pressure of liquid cyclopropane. The data of Tickner and Lossing given in Table III for 10.0 and 0.5 mm Hg was used to obtain the empirical equation

$$
\begin{equation*}
\log _{10} P=8.15832-\frac{1238.1}{T} \tag{16}
\end{equation*}
$$

This equation has been used to estimate the triple-point pressure of 0.454 mm Hg given in Table IV.

Solid. The dat a of Tickner and Lossing given in Table IV may be used to obtain the vapor pressure of the solid down to approximately $115.5^{\circ} \mathrm{K}$ where the vapor pressure is 0.001 mm Hg . No other vapor-pressure data for solid cyclopropane were found.

1. Selected Values of the Properties of Hydrocarbons, Nat1. Bur. Stds. Cir. 461, F. D. Rossini et al. (1947).
2. Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds, F. D. Rossini et al., Carnegie Press, Pittsburgh, Pa. (1953).
3. A. W. Tickner and F. P. Lossing, J. Chem. Phys. 18, 148 (1950).
4. A. W. Tickner and F. P. Lossing, J. Phys. and Colloid Chem. 55, 733 (1951).
5. S. C. Liang, J. Phys. Chem. 56, 660 (1952).
6. S. C. Liang, J. Appl. Phys. 22, 148 (1951).
7. B. A.J. Lister and L.A. McDonald, Atomic Energy Res. Establishment Report C/R 1122, Harwell, Berks. (1955).
8. R. Delaplace, Compt. rend. 204, 493 (1937).
9. Selected Values of Chemical Thermodynamic Properties,
10. G. T. Armstrong, F. G. Brickwedde and R. B. Scott, J. Research, Natl. Bur. Stds. 55, 39 (1955).
11. P. S. Bourbo, J. Phys. Chem. (U.S.S.R.) 18, 253 (1944); J. Phys. 7, 286 (1943), (see Chem. Abstr. 39, 850 (1944)).
12. N. E. Sondak and G. Thodos, A.I. Ch. E.J. 2, 347 (1956).
/


[^0]:    * Consultant, NBS Cryogenic Engineering Laboratory, Summer 1958.

[^1]:    * All temperatures referred to in this section are in ${ }^{\circ} \mathrm{K}$ and pressures in mm Hg .

[^2]:    * The equation given by Lister and McDonald appears to contain two typographical errors.

