$$\Delta'_{n+1} = \frac{S_1}{2^2} + \frac{2\,\Delta_2}{2^3} + \frac{3\,\Delta_3}{2^4} + \cdots + \frac{n\,\Delta_n}{2^{n+1}} + \frac{(n+2)\,\Delta_{n+1}}{2^{n+1}} \quad (26)$$

Also

$$\Delta'_n = \frac{S_1}{2^2} + \frac{2\,\Delta_2}{2^3} + \frac{3\,\Delta_3}{2^4} + \cdots + \frac{(n+1)\,\Delta_n}{2^n} \quad (27)$$

Subtracting (27) from (26) we see that

$$\Delta'_{n+1} - \Delta'_n = \frac{n+2}{2^{n+1}}\,(\Delta_{n+1} - \Delta_n) \quad (28)$$

But

$$\Delta_{n+1} - \Delta_n = \frac{(-2)^n}{n!} \quad (19)$$

Hence

$$\Delta'_{n+1} - \Delta'_n = \frac{(2+n)(-1)^n}{2n!} \quad (29)$$

Substituting (29) into (18′) there results

$$\begin{aligned} f' &= \sum_i \frac{(2+i)(-1)^i}{2i!}x^i \\ &= \sum_i \frac{(-x)^i}{i!} - \frac{x}{2}\sum_i \frac{(-x)^{i-1}}{(i-1)!} \\ &= e^{-x} - \frac{x}{2}e^{-x} = e^{-x}\left(1 - \frac{x}{2}\right) \quad (30) \end{aligned}$$

The result expressed by equation (30) is also a simple result, yet substantially different from that applying to case 1, namely, $f = e^{-2x}$. It should be noted that if $x = 1$, equation (30) gives $f' = 1/2e$ in agreement with Flory's result for that special case.

## Discussion

A certain amount of evidence as to the nature of the vinyl polymers can be obtained by seeing which of the two formulas $e^{-2x}$ or $e^{-x}(1 - x/2)$ best predicts the fraction of chlorine isolated in the mixed polymers. Preliminary evidence obtained by Marvel and Mastin[5] indicates that the former expression is the better of the two. This alone would not prove the 1–3 hypothesis, since the same result could be obtained with the random distribution, if 1–2, 1–3 and 1–4 pairs could be drawn off with equal ease and 1–5 or higher pairs not removed at all. However, agreement with the formula $e^{-2x}$ would substantiate other evidence[1] for the 1–3 hypothesis.

The author is indebted to Professor Marvel and Mr. Mastin for bringing this problem to his attention.

## Summary

By statistical methods, formulas are developed to predict the fraction of chlorine remaining in mixed vinyl chloride–vinyl acetate polymers upon treatment with zinc, assuming the acetates to be distributed in a random manner. Two cases are considered: first, 1–3 coupling throughout with the assumption that only 1–3 pairs of chlorides can be removed; second, random coupling with only 1–2 and 1–3 pairs of chlorides capable of removal by zinc, it being assumed that 1–2 and 1–3 removals are equally probable. These two cases yield the results $f = e^{-2x}$ and $f' = e^{-x}\cdot(1 - x/2)$ for the two respective cases where $x$ is the chlorine mole fraction of the substituents.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY]

# The Vapor Pressures of Certain Unsaturated Hydrocarbons

BY ARTHUR B. LAMB AND EDWIN E. ROPER

In connection with a study of the adsorption of the vapors of certain unsaturated hydrocarbons upon charcoal and other adsorbents, more accurate and extensive information as to the vapor pressures of these hydrocarbons was required than was available in the literature. The measurements of vapor pressure here presented were therefore made over a considerable range of temperature and, since our samples of hydrocarbons were of exceptional purity, with particular care.

**Materials.**—The hydrocarbons studied by us (Tables II–IV) were those used by Professor Kistiakowsky and his collaborators in their studies of the heats of hydrogenation, etc., and were prepared in part by them and in part by them and ourselves jointly. We wish to express our appreciation of this generous arrangement. A description of the methods of preparation has already been published.[1]

The high purity of these hydrocarbons has been demonstrated by the close concordance of the heats of hydrogenation, boiling points, freezing points and other physical properties of different distillation fractions of the same samples

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[1] (a) Kistiakowsky, Romeyn, Ruhoff, Smith and Vaughan, THIS JOURNAL, **57**, 65 (1935); (b) Kistiakowsky, Ruhoff, Smith and Vaughan, *ibid.*, **57**, 876 (1935); (c) **58**, 137 and (d) 146 (1936).

and of samples of the same hydrocarbons prepared by different methods. Further evidence of their high purity also has been obtained in our own work by the close concordance of the vapor pressures of successive fractions obtained in a further isothermal distillation of our samples at 0°, as will be explained later. No deterioration of these samples over the period of our measurements has been detected except in the case of 2-methylpropene which in the liquid phase was found to undergo a slow change, its vapor pressure at 0° decreasing at the rate of about 1 mm. per day. Definitive measurements of this substance were therefore made only upon freshly distilled samples.

## Apparatus and Procedure

A static method of measurement was adopted as affording the greatest promise of accuracy. A cryostat to maintain a constant, known temperature over a considerable period of time and over the temperature range of −130 to 25° was therefore required; also, a carefully standardized platinum resistance thermometer and an accurately legible manometer.

**Cryostat.**—This (see Fig. 1) was of the type developed by Scott and Brickwedde[2] in which the bath liquid contained in an inner cylindrical Dewar flask (E) is circulated through and around a submerged vertical tube of bakelite (J) about which the heating element (H) is wound. Refrigerant (liquid air) in an outer Dewar flask surrounds the inner Dewar flask and by adjusting the pressure in its jacket the rate of cooling of the cryostat bath can be controlled. The intermittent, regulated current in the heating element is superposed upon a continuous one. The thermoregulator is of a type of which many designs have been published[2,3] which comprises a Mueller thermometer bridge, a galvanometer, a photocell, a 3-stage amplifier and a relay. The sensitivity of the regulator is such that the total, cyclical fluctuation of temperature in the center of the cryostat is 0.003°. The stirrer and gear shafts are of Monel metal and the bearings of a lead–tin alloy, high in lead; two bearings and one set of gears are immersed in the bath liquid. About one gram of finely divided graphite added to the bath liquid aids materially in lubrication at the lower temperatures. The non-inflammable bath liquid is a five-component mixture (No. 39) as recommended by Kanolt.[4] To compensate for the slow sinking of the liquid air level in the outer container during an experiment, an automatic modulator was installed which slowly increases the continuous energy input during the time that the intermittent heater is on and slowly decreases it during the time that the intermittent heat input is off.[5] For the measurements on the vapor pressure of the crystals and on the triple point of propadiene, an aneroid cryostat was utilized, which has been described in another connection.[6]

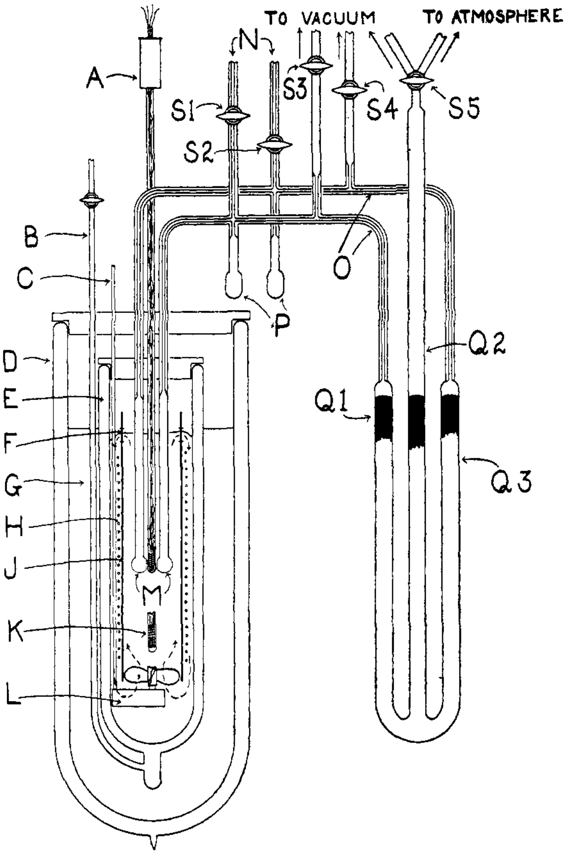

Fig. 1.—Double vapor pressure apparatus: A, measuring thermometer; B, connection for exhausting jacket of E; C, stirrer shaft; D, outer Dewar tube; E, inner Dewar tube; F, ports in J for circulating liquid; G, refrigerant; H, heating coil on J; J, bakelite tube; K, control thermometer; L, stirrer gearing; M, vapor pressure bulbs; N, gas admitted or withdrawn here; O, to manometers; P, condensing bulbs; Q, double manometer; S, stopcocks.

**The Platinum Resistance Thermometer.**—This had a resistance of 25 ohms and was of the coiled filament type.[7] It has shown a high stability over a long period. Its resistance was measured on a calibrated Mueller type Wheatstone bridge in an oil thermostat at 25.0 ± 0.1° to 0.0001 ohm, which corresponds to about 0.001° and produces a galvanometer deflection of 1.8 mm. with a measuring current in the thermometer of 1.3 ma. This thermometer assembly already has been described elsewhere.[6,8]

To obtain the constants in the quadratic calibration equation[9] of this thermometer for

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[2] Scott and Brickwedde, *Bur. Standards J. Research*, **6**, 40 (1931).

[3] Southard and Andrews, *J. Franklin Inst.*, **207**, 323 (1929).

[4] Kanolt, Bur. Standards Sci. Paper No. 520, March, 1926.

[5] Roper, *Ind. Eng. Chem., Anal. Ed.*, **12**, 113 (1940).

[6] Roper, THIS JOURNAL, **60**, 1693 (1938).

[7] Meyers, *Bur. Standards J. Research*, **9**, 807 (1932).

[8] Roper, THIS JOURNAL, **60**, 866 (1938).

[9] Burgess, *Bur. Standards J. Research*, **1**, 635 (1928).

temperatures above 0°, observations were made at three primary points: the sulfur b. p.,[9,10] the steam point[9,11] and the ice-point.[8] The thermodynamic temperature of the last was taken as 273.16°K.[12] To obtain the two additional constants of the biquadratic equation[13] for temperatures below 0°, one additional primary point, the vapor pressure of oxygen,[14a] and one secondary point, the vapor pressure of crystalline carbon dioxide,[14a] were also observed. As a check upon the accuracy of our temperature scale, three other secondary points were observed, namely, the b. p. of naphthalene,[9,15] the transition point of sodium sulfate decahydrate[9,16] and the f. p. of mercury,[9,14b] these observations indicating that the absolute accuracy was of the order of 0.01°, while the relative precision was of the order of 0.002°. In all cases more than one standardizing run was performed, bracketed in each instance with a determination of the ice-point, using material for standardization from different sources, purified by different methods. For the fixed point temperatures above 0° we took the values as defined by the International Temperature Scale[9]; for those below 0°C., the values determined by Heuse and Otto.[14b,c]

**Vapor Pressure Apparatus.**—This was a double apparatus permitting the simultaneous measurement of the vapor pressure of two samples at a given temperature-setting of the cryostat. This proved convenient, since eight of the nine hydrocarbons studied-formed well-defined pairs with boiling points close together. The bulbs (M) to contain the liquid samples were small (volume about 0.5 cc.) with thin walls and were placed close to the sensitive part of the thermometer (A). The thermometer and twin bulb assembly was wound with thin aluminum foil to facilitate thermal equilibration. The manometer was of 18, and the connecting tube (0) of 3 mm., bore (to minimize the effect of changes in room temperature). The height of the mercury was read to ±0.04 mm. with an accurate cathetometer, a correction for the meniscus being applied always and the pressures converted to millimeters of mercury at 0° and $g = 980.665$ cm./sec.[2,9] In most cases the final value for the pressure was rounded off to the nearest 0.1 mm. All stopcocks were of the type having a bulb sealed onto the base of the barrel for evacuation, giving a seating force of one atmosphere on the plug at all times. For pressures greater than 900 mm. (the length of the cathetometer scale), manometer Q2 with stopcock S5 turned to the atmosphere was utilized in conjunction with a barometric manometer read with the same cathetometer. High vacuum technique was followed in all operations.

**Procedure.**—The compounds, after being freed from all water[17] and air, were stored in 5-liter Pyrex glass reservoirs connected to cocks S1, S2 (Fig. 1). The vapor was condensed into the bulbs (P) from the storage reservoirs by the use of refrigerants. The vapor pressure bulbs (M) were not visible during a measurement, but it was easy to ascertain from the pressure changes during distillation from P to M whether liquid phase was present in them. The cryostat was then adjusted to the desired temperature and after equilibrium had been established as shown by no change for ten minutes, the pressure and the temperature were read, the latter observations bracketing the former.

The measurements on propadiene were made with the aneroid cryostat and McLeod gage (except the one at 188.17°). This gage was carefully standardized and comparison of it with the U-type manometer at 2 mm. showed satisfactory correspondence. The hydrocarbon was purified by pumping for a half-hour on the liquid phase at −136° and this purging was continued until no further change in vapor pressure could by detected at this temperature. Nine separate determinations of the triple point in three different cryostats gave 136.94 ± 0.02°K. (pressure 0.1448 mm.).

For the six highest-boiling hydrocarbons studied, a test was made for the presence of impurities. For this purpose the bulbs (P) were surrounded with cracked ice in an unsilvered Dewar tube. The ice-bath was brought to 0.000 ± 0.001° by a modified White washing technique,[8] the vapor pressure of the condensed sample determined, slow isothermal vaporization

TABLE I

VARIATIONS OBSERVED IN THE VAPOR PRESSURE AT 0.000°

| Substance | Pressure, mm. Maximum | Pressure, mm. Minimum | Change observed Mm. | Change observed °K. |
|---|---|---|---|---|
| 2-Methylpropene | 989.00 | 987.78 | 1.22 | 0.035 |
| 1-Butene | 965.12 | 963.10 | 2.02 | .057 |
| *t*-2-Butene | 733.98 | 733.25 | 0.73 | .026 |
| *c*-2-Butene | 661.50 | 658.31 | 3.19 | .121 |
| 1,4-Pentadiene | 275.02 | 273.78 | 1.24 | .103 |
| 2-Methyl-2-butene | 165.21 | 164.14 | 1.07 | .140 |
| Average | | | 1.63 | .084 |

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[10] Mueller and Burgess, *Bull. Bur. Standards*, **15**, 163 (1919).

[11] Mueller and Sligh, *J. Optical Soc. Am.*, **6**, 958 (1922).

[12] Heuse and Otto, *Ann. Physik*, **2**, 1012 (1929).

[13] Van Dusen, THIS JOURNAL, **47**, 326 (1925).

[14] (a) Loomis and Walters, *ibid.*, **48**, 3101 (1926); (b) Heuse and Otto, *Ann. Physik*, **9**, 486 (1931); (c) *ibid.*, **14**, 185 (1932).

[15] Finck and Wilhelm, THIS JOURNAL, **47**, 1577 (1925).

[16] Dickinson and Mueller, *Bull. Bur. Standards*, **3**, 641 (1907).

[17] Ethene was dried by a simple bulb-to-bulb distillation; the remaining eight hydrocarbons by a physical method: Roper, *Ind. Eng. Chem., Anal. Ed.*, **9**, 414 (1937).

TABLE II

VAPOR PRESSURE OF ETHENE, PROPENE AND THE FOUR BUTENES

| $T$, °K. | $p$, mm. | (Diff., calcd. − obsd.) Mm. | °K. |
|---|---|---|---|
| | Ethene | | |
| 147.89 | 174.0 | −0.4 | −0.03 |
| 154.92 | 296.2 | +1.3 | + .06 |
| 163.13 | 523.4 | −3.2 | − .10 |
| 168.31 | 714.4 | +0.8 | + .02 |
| 170.17 | 794.7 | +2.4 | + .05 |
| 173.25 | 948.8 | −0.9 | − .02 |
| | Propene | | |
| 151.72 | 3.87 | 0.00 | 0.00 |
| 185.08 | 75.75 | − .10 | − .02 |
| 198.47 | 183.4 | + .32 | + .03 |
| 212.51 | 404.6 | − .7 | − .03 |
| 222.52 | 662.8 | +1.7 | + .05 |
| 227.58 | 834.2 | −0.2 | − .01 |
| 235.43 | 1164.2 | −1.2 | − .03 |
| | 2-Methylpropene | | |
| 216.41 | 65.44 | +0.03 | +0.01 |
| 247.86 | 357.8 | −2.1 | − .13 |
| 252.28 | 431.0 | +2.2 | + .12 |
| 265.69 | 748.5 | +1.4 | + .05 |
| 272.49 | 966.0 | −1.0 | − .03 |
| 273.16 | 987.8 | +0.6 | + .02 |
| 273.16 | 989.0 | − .3 | − .02 |
| | 1-Butene | | |
| 216.41 | 64.12 | −0.01 | −0.00 |
| 247.86 | 340.7 | − .3 | − .02 |
| 250.25 | 378.3 | + .9 | + .05 |
| 262.56 | 641.4 | − .7 | − .03 |
| 265.69 | 727.5 | −1.6 | − .05 |
| 272.49 | 941.7 | 0.0 | .00 |
| 273.16 | 963.1 | +2.3 | + .06 |
| 273.16 | 965.1 | +0.7 | + .02 |
| | *trans*-2-Butene | | |
| 204.76 | 18.46 | +0.12 | +0.09 |
| 219.95 | 53.45 | − .44 | − .01 |
| 225.67 | 75.78 | − .30 | − .07 |
| 230.11 | 97.94 | − .03 | − .01 |
| 239.51 | 163.7 | + .01 | + .00 |
| 250.93 | 287.4 | + .3 | + .02 |
| 258.50 | 403.1 | +1.6 | + .09 |
| 259.37 | 419.9 | −0.6 | − .03 |
| 266.20 | 559.5 | + .03 | + .01 |
| 273.16 | 733.4 | + .8 | + .03 |
| 273.16 | 734.0 | + .2 | + .01 |
| 276.03 | 820.2 | −2.6 | − .09 |
| 282.76 | 1047.9 | −7.1 | − .20 |
| | *cis*-2-Butene | | |
| 186.26 | 3.71 | −0.03 | −0.09 |
| 219.95 | 45.44 | − .42 | − .16 |
| 225.67 | 64.73 | + .36 | + .07 |
| 230.11 | 83.79 | + .58 | + .13 |
| 239.51 | 141.2 | + .2 | + .03 |
| 258.50 | 361.2 | −5.4 | − .33 |
| 259.37 | 373.7 | −3.7 | − .22 |
| 273.16 | 658.3 | +3.1 | + .12 |
| 273.16 | 658.9 | +2.5 | + .09 |
| 276.03 | 749.7 | −8.9 | − .32 |
| 282.76 | 951.5 | +5.1 | + .15 |

at 0° carried out until only about one-twentieth of the original sample remained in the bulbs, and the vapor pressure then re-determined. The decrease in the vapor pressure under such treatment is a partial measure of the purity of the sample.[18] Table I gives the results, and also the temperature changes corresponding to the observed decrease in vapor pressure computed from the temperature coefficient at 0°.

These slight changes between the beginning and end of the fractionation indicate that the liquids were quite pure.

However, since in the actual vapor pressure measurements during the transfer of hydrocarbon from the reservoirs to the vapor pressure bulbs and when the temperature of the cryostat was raised much of the liquid vaporized from the vapor pressure bulb, similar though perhaps not so drastic fractionation may have taken place. If this occurred, deviations similar to those in Table I, namely, of about 0.08°, would be expected. Actually the average of the apparently random deviations of our observed boiling points from those computed from our empirical vapor pressure formulas derived by least squares was about ±0.06°. This shows that our fractionation and vapor pressure data are in accord and indicates that the random deviations of our vapor pressure measurements are probably due to the presence of these slight impurities, rather than to thermometric errors.

**The Observed Vapor Pressures and Empirical Formulas.**—Tables II, III and IV contain the results of our measurements.[19]

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[18] Shepherd, *Bur. Standards J. Research*, **12**, 185 (1934).

[19] One earlier set of measurements on the liquid phase of propadiene using the Scott–Brickwedde type of cryostat where the purging was done on the solid phase gave slightly higher vapor pressures than those obtained later and listed in Table IV. We suspected inadequate purging and perhaps adsorption on the crystalline material and have not included them in our table although they agreed with certain earlier measurements recorded in the literature.[20] All measured values will, however, be found in "An Experimental Study of Various Manifestations of Van der Waals Forces in Certain Hydrocarbons," by Edwin E. Roper, a thesis submitted to the Faculty of Harvard University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[20] Livingston and Heisig, THIS JOURNAL, **52**, 2409 (1930).

TABLE III

VAPOR PRESSURE OF 1,4-PENTADIENE AND OF 2-METHYL-2-BUTENE

| | 1,4-Pentadiene | | | 2-Methyl-2-butene | | |
|---|---|---|---|---|---|---|
| $T$, °K. | $p$, mm. obsd. | Diff.: calcd. − obsd. Mm. | Diff.: calcd. − obsd. °K. | $p$, mm. obsd. | Diff.: calcd. − obsd. Mm. | Diff.: calcd. − obsd. °K. |
| 194.31 | 1.60 | 0.00 | 0.00 | 0.73 | 0.00 | 0.00 |
| 218.38 | 12.08 | − .01 | − .01 | 6.08 | + .01 | + .02 |
| 235.18 | 37.80 | − .14 | − .06 | 20.22 | − .05 | − .00 |
| 243.32 | 61.27 | − .12 | − .03 | 33.88 | − .16 | − .08 |
| 252.10 | 99.67 | − .17 | − .03 | 56.53 | − .26 | − .08 |
| 260.45 | 152.0 | + .3 | + .04 | 88.26 | + .05 | + .01 |
| 269.18 | 299.2 | + .6 | + .06 | 136.8 | − .2 | − .03 |
| 273.16 | 273.7 | + .6 | + .05 | 164.4 | + .6 | + .08 |
| 273.16 | 275.0 | − .7 | − .06 | 165.2 | − .2 | − .03 |
| 275.60 | 304.5 | + .3 | + .02 | 184.7 | − .1 | − .01 |
| 277.67 | 332.3 | + .5 | + .04 | 202.7 | − .1 | − .01 |
| 289.47 | 533.1 | − .1 | − .00 | 335.9 | −1.0 | − .08 |
| 291.23 | 572.7 | −3.2 | − .15 | 359.1 | +0.3 | + .02 |

TABLE IV

VAPOR PRESSURE OF PROPADIENE

| $T$, °K. | $p$, mm. Obsd. | $p$, mm. Calcd. |
|---|---|---|
| | Crystalline Phase Equilibria | |
| 127.0 | 0.0218 | 0.0210 |
| 129.5 | .0356 | .0351 |
| 131.2 | .0496[a] | .0496 |
| 131.3 | .0486 | .0501 |
| 132.1 | .0573 | .0585 |
| 132.1 | .0585 | .0585 |
| 132.3 | .0602 | .0615 |
| 132.8 | .0667 | .0666 |
| 134.2 | .0873 | .0873 |
| | Supercooled Liquid Phase Equilibria | |
| 134.87 | 0.1043 | 0.1050 |
| 135.71 | .1196 | .1198 |
| 136.64 | .1380 | .1383 |
| | Liquid Phase Equilibria | |
| 137.92 | 0.1670 | 0.1680 |
| 141.17 | .2702 | .2707 |
| 144.56 | .4390 | .4347 |
| 145.59 | .5015 | .4997 |
| 147.02 | .6086 | .6041 |
| 150.82 | .9832 | .9820 |
| 157.65 | 2.210 | 2.208 |
| 188.17 | 37.86 | 38.05 |

[a] Utilized in conjunction with the triple point coördinates, 136.94°K. and 0.1448 mm., to evaluate the constants in the vapor pressure equation for the crystalline phase.

A preliminary examination showed that the vapor pressures could be represented within the accuracy of our measurements by a three-constant equation of the form $\log p = A/T + BT + C$, equations with four and more constants affording very little improvement. Equations of this form were therefore derived for all of our data on each hydrocarbon by the method of least squares. In the case of certain of the more complex hydrocarbons (with the exception of propadiene) this disclosed a very few erratic values[19]; these were discarded and a new set of constants evaluated. The resulting constants and the temperature range covered are given in Table V.

TABLE V

CONSTANTS IN THE VAPOR PRESSURE EQUATION

$$\log_{10} p_{\text{mm}} = -A/T - BT + C$$

| Hydrocarbon | $A$ | $B$ | $C$ | Temp. range °K. |
|---|---|---|---|---|
| | Liquid Phase Equilibria | | | |
| Ethene | 907.768 | 0.0063661 | 9.31934 | 148 to 173 |
| Propene | 1195.712 | .0038733 | 9.05678 | 152 to 235 |
| Propadiene | 1318.091 | .0039204 | 9.32289 | 137 to 188 |
| 2-Methylpropene | 1503.866 | .0046649 | 9.77465 | 195 to 274 |
| 1-Butene | 1330.977 | .0017607 | 8.33816 | 195 to 274 |
| *trans*-2-Butene | 1532.745 | .0040597 | 9.58593 | 171 to 282 |
| *cis*-2-Butene | 1375.857 | .0011167 | 8.16234 | 171 to 282 |
| 1,4-Pentadiene | 1717.300 | .0040279 | 9.82523 | 194 to 291 |
| 2-Methyl-2-butene | 1773.506 | .0035747 | 9.68640 | 194 to 291 |
| | Crystalline Phase Equilibrium | | | |
| Propadiene | 1464.40 | 0.000 | 9.8545 | 118 to 137 |

The deviations of our experimental results from these empirical equations are given in columns three, four, seven and eight of Table II and columns three, four, six and seven of Table III, expressed both in mm. and in °C., the latter being obtained from the differential of the equations together with the pressure deviations. In general the over-all accuracy of the measurements is governed at the lower temperatures by the accuracy of the pressure measurements, and at the higher temperatures by the accuracy of the temperature measurements.

The constants of the empirical equation for the crystalline phase of propadiene were derived by drawing the best line through the data. Those for the liquid were derived by least squares, as usual.

**Boiling Points, Temperature Coefficients of Vapor Pressure and Heats of Vaporization.**—The boiling points and the temperature coefficients of the vapor pressures were computed from the empirical equations for the vapor pressure and from these in turn the molecular heats of vaporization were computed using the Clausius–Clapeyron equation in the form

$$\Delta H^{p}_{\text{vap}} = \frac{RT_b^2}{p}\frac{\mathrm{d}p}{\mathrm{d}T} = 0.002614T_b^2\left[\frac{\mathrm{d}p}{\mathrm{d}T}\right]_{T_b}$$

which neglects the volume of the liquid phase and assumes the saturated vapor to behave as a perfect gas. These values are listed in Table VI.

It can be seen from this table that, as would be expected, isomers exhibit very similar properties. However, it is surprising that 1-butene and 2-methylpropene are more nearly identical than are *cis*- and *trans*-2-butene.

TABLE VI

VALUES CALCULATED FROM THE VAPOR PRESSURE EQUATIONS

$T_0 = 273.16$°K. $R = 1.9877$ cal./mole/deg.

| Hydrocarbon | Normal boiling point, °C. L. and R. | Prior values | | d$p$/d$T$ at $T_b$ mm./deg. | $\Delta H^p_{\text{vap}}$ at $T_b$ cal./mole |
|---|---|---|---|---|---|
| Ethene | −103.81 | −103.70[21] | −104.1[1a] | 44.25 | 3320 |
| Propene | − 47.66 | − 47.75[22] | − 47.76[1b] | 34.37 | 4570 |
| Propadiene | − 33.64 | − 34.28[1d] | − 35.0[20] | 33.35 | 5000 |
| 2-Methylpropene | − 7.12 | − 6.6[23] | − 7.02[1b] | 29.02 | 5370 |
| 1-Butene | − 6.30 | − 6.1[24] | − 6.46[1b] | 29.62 | 5520 |
| *trans*-2-Butene | + 0.91 | + 0.96[1b] | | 28.60 | 5620 |
| *cis*-2-Butene | 3.53 | 3.73[1b] | | 29.50 | 5900 |
| 1,4-Pentadiene | 26.06 | 26.0[25] | 26.01[1d] | 26.52 | 6210 |
| 2-Methyl-2-butene | 38.43 | 38.42[26,27] | 38.60[1c] | 25.71 | 6520 |

TABLE VII

RAMSAY–YOUNG RULE

| Alkenes (this research) | $T_{100}/T_{760}$ obsd. | Linear equation Δ % calcd. − obsd. | Alkanes (ref. no.) | $T_{100}/T_{760}$ | Linear equation Δ % calcd. − obsd. |
|---|---|---|---|---|---|
| | | | Methane[29] | (0.8207) | (−1.16) |
| Ethene | 0.8351 | 0.00 | Ethane[30] | .8319 | +0.05 |
| Propene | .8384 | − .01 | Propane[31] | .8374 | − .15 |
| Propadiene | .8425 | (− .76) | | | |
| 2-Methylpropene | .8394 | + .14 | *i*-Butane[32] | .8366 | + .30 |
| 1-Butene | .8391 | + .18 | *n*-Butane[33] | .8422 | − .33 |
| *trans*-2-Butene | .8410 | .00 | | | |
| *cis*-2-Butene | .8425 | − .15 | | | |
| 1,4-Pentadiene | .8428 | − .05 | *n*-Pentane[32] | .8407 | + .11 |
| 2-Methyl-2-butene | .8436 | .06 | *i*-Pentane[32] | .8416 | + .08 |
| Means (all) | .8405 | .15 | Means (omitting methane) | .8384 | .17 |
| | ± .27% | | | ± .37% | |
| Mean (omitting propadiene) | .8402 | .07 | *n*-Hexane[32] | .8450 | .00 |
| | ± .21% | | *n*-Heptane[32] | .8479 | − .07 |
| | | | *n*-Octane[32] | .8497 | .00 |
| | | | Mean of all | .8394 | .22% |
| | | | | ± .74% | |

In order to appraise the reliability of our values for the vapor pressures and boiling points of these hydrocarbons more rigorously, we have tested them by the rules of Ramsay–Young and of Dühring and by an equation giving the slopes of the vapor pressure curves at the boiling point as a function of the absolute boiling point.

**The Ramsay–Young Rule.**—This may be expressed[28] as $T_A/T_B = T'_A/T'_B$ where $T_A$ and $T_B$ are the temperatures of the saturated vapors of substances A and B at one, and $T'_A$ and $T'_B$ those at another pressure. Values for the ratio $T_{100}/T_{760}$ for the hydrocarbons studied, corresponding to a 7.6-fold change in pressure, are given in the second column of Table VII.

It can be seen that the ratios for these alkenes are indeed very constant, the average deviation from the mean being only ±0.27%. There is a a slight tendency for the ratios to increase with increasing boiling point. If allowance is made for this by expressing the ratio as a linear function of the absolute boiling point, *i. e.*, $T_{100}/T_{760} = 0.8225 + 5.66 \times 10^{-5}T_{760}$, the agreement becomes even better, the average deviation, Δ, of the calculated from the observed ratio being only 0.15%. Omitting the values for propadiene, a still better correspondence (0.07) is noted (see third column, Table VII).

A similar tabulation has been made for the corresponding saturated hydrocarbons using values calculated from the vapor pressure equations in

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[21] Egan and Kemp, THIS JOURNAL, **59**, 1264 (1937).

[22] Powell and Giauque, *ibid.*, **61**, 2366 (1939).

[23] Coffin and Maass, *Trans. Roy. Soc.* [*Can.*], **21**, 33 (1927).

[24] Coffin and Maass, THIS JOURNAL, **50**, 1427 (1928).

[25] Kogerman, *ibid.*, **52**, 5060 (1930).

[26] Norris and Reuter, *ibid.*, **49**, see p. 2633 (1927).

[27] Carr and Walter, *J. Chem. Phys.*, **4**, 756 (1936).

[28] Perry and Smith, *Ind. Eng. Chem.*, **25**, 195 (1933).

[29] Henning and Stock, *Z. Physik*, **4**, 226 (1921).

[30] (a) Burrell and Robertson, THIS JOURNAL, **37**, 1893 (1915); (b) Loomis and Walters, *ibid.*, **48**, 2051 (1926).

[31] Kemp and Egan, *ibid.*, **60**, 1521 (1938).

[32] Roper, submitted to *Ind. Eng. Chem.*

[33] Dana, Jenkins, Burdick and Timm, *Refrig. Eng.*, **12**, 387 (1926).

TABLE VIII

DÜHRING RULE

Constants in Quadratic Equation for Dühring Lines

$T_B = B_1 + B_2T_A + B_3 \times 10^{-5}T_A^2$

where $T_A$ is for the reference (propene)

| Hydrocarbon and reference no. | $B_1$ | $B_2$ | $B_3$ | Deviation, °K. Average | maximum |
|---|---|---|---|---|---|
| Propene[34] (standard) | 0.00 | 1.00000 | 0.00 | (0.00) | (0.00) |
| Ethene[21] | 3.53 | 0.6918 | 19.24 | .05 | − .17 |
| Ethene[34] | 3.56 | .6991 | 16.08 | .02 | + .08 |
| Propene[22] | 0.40 | .9954 | 0.96 | .003 | − .01 |
| 1-Butene[34] | − 9.10 | 1.27364 | − 22.29 | .07 | − .23 |
| 2-Methylpropene[34] | 6.96 | 1.12660 | 10.09 | .08 | + .24 |
| Propadiene[34] | 0.97 | 1.08451 | − 11.82 | .01 | − .02 |
| Propane[31] | 4.70 | 0.96897 | 15.25 | .05 | − .18 |
| *trans*-2-Butene[34] | 5.24 | 1.18827 | 1.82 | .03 | + .08 |
| *cis*-2-Butene[34] | −47.09 | 1.76480 | −145.15 | .69 | +1.56 |
| 1,4-Pentadiene[34] | 6.67 | 1.30848 | − 4.79 | .06 | +0.16 |
| 2-Methyl-2-butene[34] | 4.17 | 1.39734 | − 14.98 | .06 | + .13 |
| *n*-Heptane[32] | − 3.51 | 1.72956 | − 43.21 | .02 | + .05 |
| *n*-Butane[32] | − 6.41 | 1.29613 | − 26.36 | .02 | − .08 |
| | | | Average | .089 | .23°K. |
| Discarding the *cis*-2-butene value: | | | Average | .039 | .12°K. |

the literature. The results are given in the fifth column of the above table. The mean value of the ratios of comparable hydrocarbons is 0.8384 and the average deviation from the mean is ±0.37%, close to the value for the unsaturated hydrocarbons. A similar variation with the absolute boiling point is also evident here. Using the linear equation $T_{100}/T_{760} = 0.8176 + 8 \times 10^{-5}T_{760}$, values of the ratios are obtained whose percentage deviations, Δ, from the observed values average only 0.17 (omitting methane).

Summarizing, it appears that these hydrocarbons in general obey the Ramsay–Young rule closely, particularly if the rule is slightly modified. Among the hydrocarbons studied by us only propadiene shows more than the usual minimum discrepancy, suggesting that our vapor pressure data for this substance are relatively less accurate.

**Dühring Rule.**—This may be expressed[28] as $T_B = b_1 + b_2T_A$ where $T_A$ and $T_B$ have the same significance as above and $b_1$ and $b_2$ are constants characteristic of substances B. To test our results by this rule we have computed from our empirical vapor pressure equations the temperatures of the saturated vapor corresponding to nine round pressures over the range 1 mm. to 1000 mm. Taking the values for propene as standard ($T_A$) we find for the nine hydrocarbons we have studied and for four additional hydrocarbons for which sufficiently reliable data are available in the literature, that the temperatures of the saturated vapor can be represented by these linear equations (Dühring lines) over the whole range with an average deviation of only ±5% corresponding to about ±1.5° (omitting the discordant values for *cis*-2-butene).

While these lines appear almost linear, examination shows some curvature. Addition of a quadratic term giving the equation $T_B = B_1 + B_2T_A + B_3T_A^2$ suffices to reproduce them with great fidelity, as can be seen from the values in the last columns of Table VIII, where the average deviations and the average maximum deviations are only ±0.04 and 0.12°, respectively, again omitting the discordant values for *cis*-2-butene.

This agreement with the Dühring rule also encourages us to think that our vapor pressure data are reliable except perhaps in the case of *cis*-2-butene where the presence of some slight impurity is to be inferred. It should be remarked, however, that the values for propadiene which appeared to be in some doubt from the point of view of the Ramsay–Young rule show no irregularity here.

**The Temperature Differential of the Vapor Pressure.**—It follows from the Clausius–Clapeyron equation, assuming the gas to be perfect and the heat of vaporization $\Delta H_{\text{vap}}$ to be independent of the temperature, that $\mathrm{d}p/\mathrm{d}T = p\,\Delta H_{\text{vap}}/RT^2$. Combining this with Trouton's rule gives

$$\left[\frac{\mathrm{d}p}{\mathrm{d}T}\right]_{T_b} = \frac{760 \times 20.85}{RT_b} = \frac{7975}{T_b}$$

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(34) Data of this research.

TABLE IX

THE TEMPERATURE DIFFERENTIAL OF THE VAPOR PRESSURE

| Hydrocarbon | $T_b$, °K. | $dp/dT$ $\frac{\text{mm.}}{\text{deg.}}$ obs. | $\frac{dp}{dT}$, 100 $\frac{\text{calcd.} - \text{obsd.}}{\text{obsd.}}$, % | | | | Ref. |
|---|---|---|---|---|---|---|---|
| | | | Trouton | Nernst | Gen. | Spec. | |
| *n*-Alkanes, $a_s = 3409$; $b_s = -1.28$ | | | | | | | |
| Methane | 111.73 | 61.28 | +16.5 | +4.3 | −3.5 | −0.1 | 29 |
| Ethane | 184.47 | 40.95 | + 5.6 | +2.4 | −0.5 | − .9 | 30 |
| Propane | 231.04 | 33.50 | + 3.0 | +3.0 | +0.4 | + .3 | 31 |
| Butane | 272.48 | 29.29 | − 0.1 | +1.7 | −0.5 | − .3 | 33 |
| Pentane | 309.26 | 25.75 | + 0.2 | +3.9 | +1.4 | +1.6 | 32 |
| Hexane | 341.90 | 23.78 | − 1.9 | +2.0 | +0.4 | +0.8 | 32 |
| Heptane | 371.53 | 22.36 | − 4.0 | +0.4 | −0.8 | −0.3 | 32 |
| Octane | 398.82 | 20.73 | − 3.5 | +1.4 | +0.8 | +1.1 | 32 |
| Means | | | 4.4 | 2.4 | 1.0 | 0.7 | |
| Branched Chain Alkanes, $a_s = 3372$; $b_s = -1.56$ | | | | | | | |
| 2-Methylpropane | 261.06 | 29.69 | + 2.9 | +4.1 | +2.0 | −0.1 | 32 |
| 2,2-Dimethylpropane | 282.62 | 27.58 | + 2.3 | +4.6 | +2.4 | + .4 | 36 |
| 2-Methylbutane | 301.11 | 26.31 | + 0.7 | +3.5 | +1.6 | − .4 | 32 |
| 2,3-Dimethylbutane | 331.15 | 24.12 | − 0.2 | +0.8 | +1.9 | − .1 | 32 |
| 2,2,4-Trimethylpentane | 372.39 | 21.50 | − 0.4 | +4.2 | +2.9 | +1.0 | 37 |
| 2,5-Dimethylhexane | 382.36 | 21.48 | − 2.9 | +1.5 | +0.6 | −1.3 | 32 |
| 2,6-Dimethyloctane | 431.70 | 19.18 | − 3.7 | +1.7 | + .9 | −0.8 | 32 |
| Means | | | 1.9 | 2.9 | 1.8 | .6 | |
| *n*-Alkenes, $a_s = 3634$; $b_s = -3.38$ | | | | | | | |
| Ethene | 169.35 | 44.25 | + 6.4 | +0.7 | −1.1 | +0.4 | 34 |
| Propene | 225.50 | 34.37 | + 2.9 | +2.5 | −0.1 | + .5 | 34 |
| 1-Butene | 266.86 | 29.62 | + 0.9 | +2.5 | + .3 | + .1 | 34 |
| *trans*-2-Butene | 274.07 | 28.60 | + 1.8 | +3.7 | +1.5 | +1.2 | 34 |
| *cis*-2-Butene | 276.69 | 29.50 | − 2.3 | −0.4 | −2.4 | −2.7 | 34 |
| 1-Heptene | 366.94 | 21.77 | − 0.1 | +4.4 | +3.0 | +1.2 | 32 |
| Means | | | 2.4 | 2.4 | 1.4 | 1.0 | |
| Branched Chain Alkenes, $a_s = 3634$; $b_s = -3.38$ | | | | | | | |
| 2-Methylpropene | 266.04 | 29.02 | + 3.3 | +4.9 | +2.6 | +2.5 | 34 |
| 2-Methyl-2-butene | 311.59 | 25.71 | − 0.5 | +2.7 | +0.9 | −0.0 | 34 |
| Means | | | 1.9 | 3.8 | 1.8 | 1.2 | |
| Dienes, $a_s = 3895$; $b_s = -5.50$ | | | | | | | |
| Propadiene | 239.52 | 33.35 | − 0.2 | +0.2 | −0.8 | −0.5 | 34 |
| 1,3-Butadiene | 268.65 | 29.42 | + .9 | +2.6 | + .4 | +1.0 | 32 |
| 1,4-Pentadiene | 299.22 | 26.63 | + .1 | +2.9 | + .9 | −0.4 | 34 |
| 2-Methyl-1,3-butadiene | 307.24 | 26.18 | − .8 | +2.1 | + .3 | + .6 | 38 |
| Means | | | .5 | 2.0 | .6 | .6 | |
| *n*-Alkynes, $a_s = 4125$; $b_s = -6.77$ | | | | | | | |
| Ethyne | 187.94 | 43.58 | − 2.6 | −5.2 | −8.0 | −1.0 | 39 |
| Propyne | 249.95 | 33.50 | − 4.7 | −3.9 | −6.2 | −2.1 | 32 |
| 1-Butyne | 282.21 | 27.97 | + 1.0 | −3.2 | +1.1 | +3.9 | 32 |
| 2-Butyne | 300.27 | 27.55 | − 3.6 | −0.9 | −2.8 | −1.0 | 40 |
| Means | | | 3.0 | 3.3 | 4.5 | 2.0 | |
| Miscellaneous | | | | | | | |
| 1-Buten-3-yne | 278.27 | 29.58 | − 3.1 | −1.2 | −3.2 | ... | 32 |
| 1,3-Butadiyne | 282.95 | 28.52 | − 1.2 | +1.0 | −1.0 | ... | 32 |
| Cyclohexane | 353.90 | 22.81 | − 1.2 | +3.0 | +1.5 | ... | 41 |
| 1,5-Hexadien-3-yne | 356.66 | 22.97 | − 2.7 | +1.5 | +0.1 | ... | 32 |
| Means | | | 2.0 | 1.7 | 1.4 | | |
| Means of values for all hydrocarbons listed | | | 2.5 | 2.5 | 1.7 | 0.9 | |

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(36) Aston and Messerly, THIS JOURNAL, **58**, 2354 (1936).

(37) Smith and Matheson, *J. Research Natl. Bur. Standards*, **20**, 641 (1928).

(38) Bekkedahl, Wood and Wojciechowski, *ibid.*, **17**, 883 (1936).

(39) "International Critical Tables," Vol. III, 208, 230 (1928).

(40) Heisig and Davis, THIS JOURNAL, **57**, 339 (1935).

(41) Scatchard, Wood and Mochel, *ibid.*, **61**, 3206 (1939).

where 20.85 is the Trouton constant (the mean value for the 35 hydrocarbons listed in Table IX) and $T_b$ the absolute boiling point at 760 mm. pressure. Values of $[dp/dT]_{T_b}$ computed from our measurements and for some 26 additional hydrocarbons for which accurate vapor pressure data are available are in good agreement with this equation, the average deviation being 2.5%. Trouton's rule often can be replaced advantageously by the equation of Nernst[35] $\Delta H_{vap} = 9.5 \log T_b - 0.007\ T_b$. Our equation then becomes

$$\left[\frac{dp}{dT}\right]_{T_b} = \frac{3634 \log_{10} T_b}{T_b} - 2.68$$

The differences between the values of $[dp/dT]_{T_b}$ computed from this equation and from the empirical equations (observed values) are listed in the fifth column of Table IX. The average percentage deviation is, however, still 2.5%.

Since the deviations were in general positive, we have altered the constants in the above equation slightly to obtain the general equation

$$\left[\frac{dp}{dT}\right]_{T_b} = 3461\ \frac{\log T_b}{T_b} - 1.77$$

Using this equation we find the deviations listed in the sixth column of the above table, averaging 1.7%.

Finally, since a constitutive influence is evident we have framed special equations of the general type

$$\left[\frac{dp}{dT}\right]_{T_b} = a_s\ \frac{\log_{10} T_b}{T_b} + b_s$$

for each group of hydrocarbons and the resulting deviations are listed in the seventh column of the table. It can be seen that an even better agreement is attained, particularly with the alkanes and alkenes, the deviations averaging on the whole 0.9%.

Here again we find that the values of *cis*-2-butene show a considerably greater discrepancy than any of the other alkenes or alkanes, which confirms our previous inference that our data for this substance are less reliable than our other data.

## Summary

1. Measurements have been made of the vapor pressures of very pure samples of liquid ethene, propene, 2-methylpropene, 1-butene, *cis*-2-butene, *trans*-2-butene, 1,4-pentadiene and 2-methyl-2-butene over the approximate range 10 to 1000 mm. by the static method. Equations with three constants have been derived by the method of least squares from the results of these measurements expressing the vapor pressure as a function of the temperature. The vapor pressure of liquid and of crystalline propadiene its triple point temperature and pressure also have been ascertained.

2. From the least square equations the normal boiling points and the slopes of the vapor pressure curves at these points as well as the heats of vaporization of these substances as perfect gases have been computed.

3. Our vapor pressures, with one or two exceptions, have been found to agree excellently with the Ramsay–Young and the Dühring rules, particularly when in each rule an additional constant is introduced. A general equation has been derived expressing the temperature differential of the vapor pressure at the absolute boiling point as a function of the absolute boiling point. With this equation, too, our data are found to be in excellent agreement.

CAMBRIDGE, MASS. RECEIVED JANUARY 30, 1940

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(35) Nernst, "Theoretical Chemistry," Eng. ed. transl. by Tizard, Macmillan and Co., Ltd., London, 1916 'p. 295.