An Empirical Equation for Calculating the Changes in the Boiling Points of Hydrocarbons with Small Changes in Pressure.

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In the separation by distillation of hydrocarbons for the purpose of identification, it is frequently necessary to calculate the change in the boiling point with pressure, even when the change in pressure may be less than 10 mm. The above statement may be fully appreciated when it is realized that a pressure change of 10 mm. corresponds to nearly 0.5°C. which is often as much as the difference between the boiling points of the compounds to be separated.

In the course of our investigations on hydrocarbon synthesis and separation of the products by distillation, we have found the following empirical equation,

$$dt_b\,{}^\circ\mathrm{C.}/dP_{\mathrm{mm.}} = 0.0345 + 0.00011\,t_b \qquad (1)$$

in which t_b is the boiling point in centigrade, $P_{\mathrm{mm.}}$ is the pressure expressed in mm. of Hg, quite convenient and sufficiently accurate for a large number of hydrocarbons commonly found in the gasoline boiling range.

The purpose of this paper is to illustrate the usefulness and the limitations of the above equation, and, at the same time, to indicate briefly justification for the linear form it assumes. A comparison of the equation with those found in the literature will be also considered.

From the thermodynamic relation,

$$(\partial S/\partial V)_T = (\partial P/\partial T)_V \qquad (2)$$

in which S, P, T, V have the usual significance, the Clausius-Clapeyron equation,

$$dP/dT = \frac{\Delta L}{T(V_g - V_l)}\,, \tag{3}$$

may be readily derived. It expresses the change in the boiling point with pressure in terms of the temperature at which the heat of vaporization is ΔL and where the liquid with a volume V_l is completely changed into vapor with a volume V_g.

Equation (3) is general, and if ΔL, T, V_l, and V_g are known, dT/dP can be determined exactly. However, it would be more convenient if dT/dP (or dt/dP) can be expressed as a simple function of the boiling point of the pure substance. For the very purpose we have found equation (1) quite adequate. We do not intend to attach any theoretical significance to the equation; our sole purpose is, as has already been mentioned above, to give a simple empirical equation which may be of use in practical application. This equation is theoretically applicable for dT/dP only at $P=760$ mm., but for a change of ±10 mm. from 760, it should still be fairly accurate.⁽¹⁾

Because of the simple form Trouton's relation takes, the Clausius-Clapeyron equation can be readily put in a much simpler form⁽²⁾ by its application, as will be illustrated below:

Writing the Clausius-Clapeyron equation in an equivalent form,

$$dP/dT = P\Delta L/RT^2 \tag{4},$$

where R is the gas constant and ΔL, P, T have the same significance as in (3), and by assuming the vapor to behave ideally, ΔL to be independent of the temperature, and the volume of the liquid to be negligible in com-

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(1) D. B. Brooks, *J. Research, NBS,* **21** (1940), 847; E. R. Smith, ibid., **26** (1941) 129. As is evident from the results, a change of 40 mm. gives a difference of 0.0016∼

P mm.	dt/dP*		
	n-Heptane	Iso-octane	**Benzene**
700	0.04779	0.04958	0.0456
760	0.04480	0.04649	0.0427
800	0.04304	0.04467	0.0411

* Calculated from dP/dT originally given in his Table.

0.0018 in dt/dP, or about 0.0004°C./10 mm. Hg., which is well within the accuracy of experimental error.

(2) By use of Trouton's rule many relations, especially those involving the heat (or energy) of vaporization, can often be reduced to simpler forms. Kimura's (O. Kimura, *J. Chem. Soc. Japan,* **63** (1942), 98) derivation of his viscosity function, $\eta = Ae^{b/\theta}$ is a good example. However, his basic idea of deriving an expression for viscosity which is applicable to all substances of the same series (paraffin) independently of the properties of the individual members of the series in terms of the reduced absolute temperature, or in its equivalent forms; in other words, when η for the members are plotted against the proper functions of the reduced absolute temperatures, all viscosities will fall on the same line, is not original. It has already been mentioned by E. P. Irany (*J. Am. Chem. Soc.,* **61** (1939), 1734.)

parison with that of the vapor, and since P is always in the neighborhood of 760 mm., we readily obtain

$$dT_b/dP = KT_b \qquad (5),$$

where T_b is the boiling point in the absolute temperature. Therefore, in terms of t_b, the boiling point in centigrade, the expression becomes

$$dt_b/dP = K(273.1+t_b) = A+Kt_b\ ,$$

which is the form relation (1) assumes.

We shall now show to what extent relation (1) is useful; at the same time a comparison will be made between it and other empirical equations for dt_b/dP found in the literature. Relation (1) has been obtained by changing the first term of the equation,(3)

$$dt_b\,{}^\circ\mathrm{C.}/dP_{\mathrm{mm.}} = 0.0350+0.00011\,t_b \qquad (6),$$

which is the equation of the line drawn through the accurate dt_b/dP points given in Table 1.

Table 1. Change in Boiling Point with Small Change in Pressure.

Hydrocarbons(8)	Formula	B.P. (°C.) at 760 mm.Hg.	dt_b°C./$dP_{\mathrm{mm.}}$ Found	dt_b°C./$dP_{\mathrm{mm.}}$ Calculated*	Deviation Found—Calculated	Ref.
3,3-Dimethyl-butene-1	C_6H_{12}	41.239	0.0397	0.0395	+0.0002	4
2,3-Dimethyl-butene-1	C_6H_{12}	55.615	0.0410	0.0411	−0.0001	4
2,3-Dimethyl-butene-2	C_6H_{12}	73.24	0.0414	0.0431	−0.0017	4
2,3,3-Trimethyl-butene-1	C_7H_{14}	77.874	0.0447	0.0436	+0.0011	4
2,3-Dimethyl-butane	C_6H_{14}	57.999	0.0412	0.0414	−0.0002	4
2,2-Dimethylbutane	C_6H_{14}	49.731	0.0407	0.0405	+0.0002	4
2,2,3-Trimethyl-butane	C_7H_{16}	80.879	0.0449	0.0439	+0.0010	4
3-Ethylpentane	C_7H_{16}	93.473	0.0446	0.0453	−0.0007	4
n-Heptane	C_7H_{16}	98.424	0.0449	0.0458	−0.0009	4
2,2,4-Trimethyl-pentane	C_8H_{18}	99.233	0.0465	0.0459	+0.0006	4
2,3,4-Trimethyl-pentane	C_8H_{18}	113.391	0.0479	0.0475	+0.0004	4
Benzene	C_6H_6	80.094	0.0427	0.0438	−0.0011	5
2,2,4,4-Tetramethylpentane	C_9H_{20}	122.281	0.0492	0.0485	+0.0007	6
Isopropylbenzene	C_9H_{12}	152.39	0.0507	0.0517	−0.0010	7
			±0.002**			

* From Eq. (6), $dt_b{}^\circ\mathrm{C}/dP_{\mathrm{mm}}=0.0350+0.00011t_b$.

** Limits of experimental error. The writer (R.N.) is unable to ascertain whether it is ±0.0020 or ±0.0002.

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(3) C. Isobe and R. Negishi, *J. Soc. Chem. Ind., Japan,* **45**(1942).

(4) D. B. Brooks, F. L. Howard, and H. C. Crafton, Jr., *J. Research NBS,* **24**(1940), 33.

(5) E. R. Smith and H. Matheson, *ibid.,* **20**(1938), 641.

(6) F. L. Howard, *J. Research NBS,* **24**(1940), 677.

(7) J. D. White and F. W. Rose, Jr., *ibid.,* **21**(1938), 151.

(8) G. Egloff, ('Physical Constants of Hydrocarbons, Reinhold Publish. Corp., (1939, 1940); Science of Petroleum, Vol. II, (1938), 1302.

Table 2 shows the results of determination and calculation made by Lamb and Roper⁽⁹⁾ on dt_b/dP (originally dP/dT_b) of 35 hydrocarbons of the paraffin series. Their results seem fairly accurate, and they serve as a good basis for some interesting comparison between our empirical relation and theirs, either derived from the Clausius-Clapeyron equation or derived empirically to agree particularly with the data given in Table 2.

Lamb and Roper have derived the expression,

$$(dP/dT)_{T_b} = \frac{760 \times 20.85}{RT_b} = \frac{7975}{T_b}, \quad \text{or}$$

$$dt_b/dP = 0.03425 + 0.0001254\, t_b \qquad (7),$$

by combining the Clausius-Clapeyron equation, under the assumptions already mentioned above, with Trouton's rule, assuming 20.85 for the Trouton constant (the mean value for the 35 hydrocarbons listed in Table 2).

The line representing this equation is given in Fig. 1, where it is obvious that, even with the particular Trouton constant used, the deviation between the values of dt_b/dP calculated and found becomes appreciable at lower and higher temperatures. It clearly indicates that some of the simplifying assumptions involved in (7) are not justified.

On the other hand, relation (1) is in much better agreement with the observed values. In fact, it is even better than the equation⁽⁹⁾,

$$(dP/dT)_{T_b} = \frac{3634 \log_{10} T_b}{T_b} - 2.68 \qquad (8),$$

which takes into account the trend⁽¹⁰⁾ in Trouton constant with the boiling point, and is about as good as their so-called "general" equation,⁽⁹⁾

$$(dP/dT)_{T_b} = \frac{3461 \log_{10} T_b}{T_b} - 1.77 \qquad (9),$$

derived simply by altering the constants in relation (8) to agree better with the results in Table 2.

A comparison of the relative accuracies of the equations, (1), (7), (8), and (9) are given along with that of the "special" equation,

$$(dP/dT)_{T_b} = \frac{a_s \log_{10} T_b}{T_b} + b_s \qquad (10)$$

proposed by Lamb and Roper⁽⁹⁾, in which a_s and b_s are the constants for the particular group of hydrocarbons, in the last columns of Table 2. The results require no explanation.

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(9) A. B. Lamb and E. E. Roper, *J. Am. Chem. Soc.*, **62** (1940), 806.

(10) The fact that Trouton constant is not really a constant has long been recognized by numerous investigators, and a number of corrections—from purely empirical to semi-theoretical—have been proposed. One of the more exact and compatible with theory, yet quite simple in form, is what is known as Hildebrand's rule (J. H. Hildebrand, "Solubility," Reinhold Publish. Corp., 102 (1936)).

Table 2.(9) Change in Boiling Points with Pressure for Some of the Hydrocarbons in the Paraffin Series.

Hydrocarbons*	Formula	B.P. (°C.) at 760 mm.	dt_b/dP** °C./mm.	Deviation Calculated-Found (%)				
				Eq. (1)	Eq. (7)	Eq. (8)	Eq. (9)	Eq. (10)
n-Alkanes								
Methane	$C H_4$	−161.43	0.0163	−2.6	+16.5	+4.3	−3.5	−0.1
Ethane	C_2H_6	−88.69	0.0244	−1.1	+5.6	+2.4	−0.5	−0.9
Propane	C_3H_8	−42.12	0.0299	−0.1	+3.0	+3.0	+0.4	+0.3
Butane	C_4H_{10}	− 0.68	0.0341	−0.8	−0.1	+1.7	−0.5	−0.3
Pentane	C_5H_{12}	36.11	0.0388	+0.9	+0.2	+3.9	+1.4	+1.6
Hexane	C_6H_{14}	68.74	0.0421	−0.0	−1.9	+2.0	−0.4	+0.8
Heptane	C_7H_{16}	98.36	0.0447	−1.3	−4.0	+0.4	−0.8	−0.3
Octane	C_8H_{18}	125.66	0.0482	−0.2	−3.5	+1.4	+0.8	+1.1
Branched-chain Alkanes								
2-Methylpropane	C_4H_{10}	−12.10	0.0337	1.5	2.9	4.1	2.0	−0.1
2,2-Dimethylpropane	C_5H_{12}	9.46	0.0363	1.9	2.3	4.6	2.4	0.4
2-Methylbutane	C_5H_{12}	27.95	0.0380	1.1	0.7	3.5	1.6	−0.4
2,3-Dimethylbutane	C_6H_{14}	57.99	0.0414	1.4	−0.2	0.8	1.9	−0.1
2,2,4-Trimethylpentane	C_8H_{18}	99.23	0.0465	2.4	−0.4	4.2	2.9	1.0
2,5-Dimethylhexane	C_8H_{18}	109.20	0.0466	0.1	−2.9	1.5	0.6	−1.3
2,6-Dimethyloctane	$C_{10}H_{22}$	158.54	0.0521	0.4	−3.7	1.7	0.9	−0.8
n-Alkenes								
Ethene	C_2H_4	−103.81	0.0226	−2.2	6.4	0.7	−1.1	0.4
Propene	C_3H_6	−47.66	0.0291	−0.5	2.9	2.5	−0.1	0.5
1-Butene	C_4H_8	− 6.30	0.0338	−0.1	0.9	2.5	0.3	0.1
Trans-2-butene	C_4H_8	0.91	0.0350	1.0	1.8	3.7	1.5	1.2
Cis-2-butene	C_4H_8	3.53	0.0339	−2.9	−2.3	−0.4	−2.4	−2.7
1-Heptene	C_7H_{14}	93.78	0.0459	2.4	−0.1	4.4	3.0	1.2
Branched-chain Alkenes								
2-Methylpropene	C_4H_8	− 7.12	0.0344	2.1	3.3	4.9	2.6	2.5
2-Methyl-2-butene	C_5H_{10}	38.43	0.0389	0.4	−0.5	2.7	0.9	0.0
Dienes								
Propadiene	C_3H_4	−33.64	0.0300	−2.7	−0.2	0.2	−0.8	−0.5
1,3-Butadiene	C_4H_6	− 4.51	0.0340	−0.0	0.9	2.6	0.4	1.0
1,4-Pentadiene	C_5H_8	26.06	0.0376	0.4	0.1	2.9	0.9	−0.4
2-Methyl-1,3-butadiene	C_5H_8	34.08	0.0382	−0.2	−0.8	2.1	0.3	0.6
n-Alkynes								
Ethyne	C_2H_2	−85.22	0.0229	−9.5	−2.6	−5.2	−8.0	−1.0
Propyne	C_3H_4	−23.21	0.0299	−7.0	−4.7	−3.9	−6.2	−2.1
1-Butyne	C_4H_6	9.05	0.0358	0.7	1.0	−3.2	1.1	3.9
2-Butyne	C_4H_6	27.11	0.0363	−3.3	−3.6	−0.9	−2.8	−1.0
Miscellaneous								
1-Buten-3-yne	C_4H_4	5.11	0.0338	−3.1	−3.1	−1.2	−3.2	—
1,3-Butadiyne	C_4H_2	9.79	0.0351	−1.5	−1.2	1.0	−1.0	—
Cyclohexane	C_6H_{12}	80.74	0.0438	1.0	−1.2	3.0	1.5	—
1,5-Hexadien-3-yne	C_6H_6	83.50	0.0435	−0.4	−2.7	1.5	0.1	—
	Means of Values for all Hydrocarbons Listed			1.7	2.5	2.5	1.7	0.9

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* For name and carbon skeleton; see Ref. (8).

** Calculated from dP/dT.

In Fig. 1 are drawn and plotted the lines representing relations (1), (7), (9), and that representing the data given in Table 3⁽¹¹⁾, and dt_b/dPmm. values not only given in Table 2 but also in Table 4⁽¹²⁾⁽¹³⁾. Some of the compounds are given in Tables 2 and 4 to show how closely various investigators agree, or disagree, on dt_b/dP of the same substances. The "length" of the points roughly indicates the relative accuracy of the

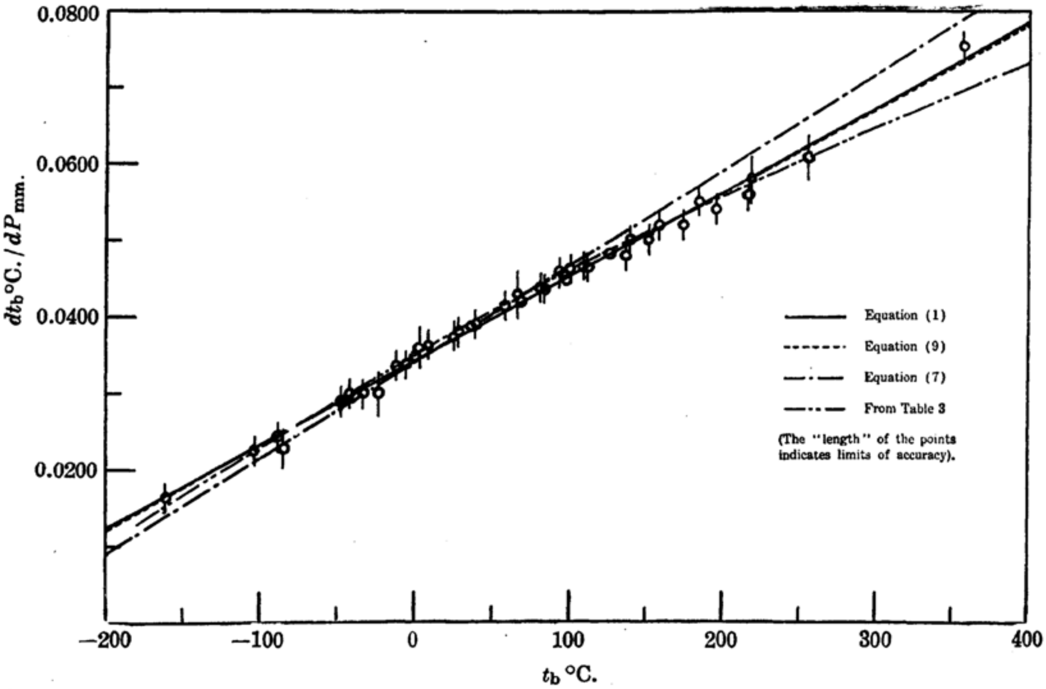

Fig. 1. dt_b°C. / $dP_{mm.}$ Vs t_b.

Table 3. Correction Factors for the Boiling Point for Small Change in Pressure*.

B.P. at 760 mm.	Correction factor °C./mm.	B.P. at 760 mm.	Correction factor °C./mm.
−100	0.023	200	0.056
− 50	0.029	250	0.061
0	0.035	300	0.065
50	0.040	350	0.069
100	0.046	400	0.073
150	0.051		

* The correction factors can be regarded as accurate over a pressure range, 760 ±50 mm Hg. (Ref. 11).

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(11) E. S. L. Beale, Science of Petroleum, Vol. II, 1281 (1938).
(12) Landolt-Boernsteins Tabellen, 2427 (1936).
(13) Landolt-Boernsteins Tabellen, 1289 (1932).

Table 4. Change in Boiling Point with Small Change in Pressure.

Hydrocarbons	Formula	B.P. (°C.) at 760 mm.	dt_b°C. / $dP_{mm.}$ Found	dt_b°C. / $dP_{mm.}$ Calculated	Diff. Found-Calculated	Ref.*
n-Pentane	C_5H_{12}	36.00	0.039	0.038	0.001	12
		36.10	0.041	0.038	0.003	12
i-Pentane	C_5H_{12}	27.95	0.037	0.037	0.000	13
n-Hexane	C_6H_{14}	68.71	0.042	0.042	0.000	12
n-Heptane	C_7H_{16}	98.35	0.045	0.045	0.000	12
n-Octane	C_8H_{18}	125.59	0.048	0.048	0.000	12
n-Nonane	C_9H_{20}	150.71	0.050	0.051	−0.001	12
n-Decane	$C_{10}H_{22}$	174.06	0.052	0.054	−0.002	12
n-Undecane	$C_{11}H_{24}$	195.84	0.054	0.056	−0.002	12
n-Dodecane	$C_{12}H_{26}$	216.23	0.056	0.058	−0.002	12
Hexene	C_6H_{12}	65.92	0.043	0.042	0.001	16
Benzene	C_6H_6	80.122	0.0428	0.0433	−0.0005	13
Toluene	C_7H_8	110.80	0.042	0.047	−0.005	13
		110.606	0.0464	0.0467	−0.0003	13
m-Xylol	C_8H_{10}	139.10	0.0490	0.0498	−0.0008	13
			0.0498	0.0498	0.0000	13
Ethylbenzene	C_8H_{10}	136.15	0.048	0.049	−0.001	13
Propylbenzene	C_9H_{12}	159.45	0.052	0.052	0.000	13
n-Butylbenzene	$C_{10}H_{14}$	183.10	0.058	0.055	0.003	13
Cyclohexane	C_6H_{12}	80.80	0.045	0.043	0.002	13
Methylcyclohexane	C_7H_{14}	101.20	0.048	0.046	0.002	13
1,2,4-Trimethyl-cyclohexane	C_9H_{18}	141.22	0.051	0.051	0.00	17
Diphenyl	$C_{12}H_{10}$	254.93	0.061	0.063	−0.002	16
Naphthalene	$C_{10}H_8$	218.	0.0592	0.0585	0.0007	16
		217.68	0.057	0.058	−0.001	16
		217.96	0.058	0.058	0.000	16

* Data given by Ref. 16 least reliable.

(17) J. D. White and A. R. Glasgow, Jr., J. Research NBS, **22** (1939), 137.

measurement. For the results given in Table 2, ±0.002(14) has been assumed except for normal pentane, hexane, heptane, and octane for which ±0.0005(15); for ethyne, propyne, and cis-2-butene ±0.003. Most of the results given in Table 4 are given a weight of ±0.002(14). From Fig. 1 it seems to the author that the values of dt_b/dP for decane, undecane, and dodecane, though given a relative accuracy of ±0.002, deviate much more than that, and they seem to be too low.

It may be of some interest to mention in passing that dt_b/dP observed and calculated by relation (1) for mercury, sulfur, and sodium are as given in Table 5.

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(14) There is no real basis for the value assumed except for isopropylbenzene, $dt_b/dP = 0.0507 \pm 0.002$ (Ref. 7).

(15) The results of various measurements given in Tables 1, 2, and 4 do not differ more than ±0.0005 from the mean.

Some of them are definitely lower than ±0.002; probably ±0.004.

Table 5.

	B.p. (°C.)	dt_d/dP (°C./mm.) Obs.	dt_d/dP (°C./mm.) Calc.	Ref.*
Mercury	356.8	0.0754	0.0735	16
Sulfur	444.53	0.0820	0.0830	16
	444.55	0.0908		
Sodium	878	0.153	0.131	12

* Accuracy uncertain.

From the results given in this paper, some plausibility is lent to the following statements: (a) Relation (1) is, for practical purposes, accurate for expressing the change in the boiling point with a small change in pressure for most of the hydrocarbons over a wide range of temperature (from -160 to 300°C); (b) Relation (1) is just as accurate as the "general" equation, or (9), but it has the great advantage that its expression is very much simpler and linear; (c) The correction factors given in Table 3 are also quite good, but they seem to be inadequate at temperatures above 300°C.

The first constant term in relation (1) has been reduced by 0.0005 from the original 0.0350 found in (6) for the simple reason that, by this change, the deviations between calculated and observed for the hydrocarbons given in Table 2 are reduced materially. In view of the fact that the accuracy of the determination itself may not be greater than ± 0.002, the above change may not be significant; however, there seems to be evidence from the results of Tables 1 and 2 that there is a real difference, which amounts to about 0.0005, between dt_b/dP for branched and unbranched compounds. Unfortunately the available data are not sufficiently accurate to warrant a further discussion on this point.

As is obvious from Fig. 1, the lines representing the "general" equation (9), and relation (1) almost coincide with each other although the former is not a linear equation. This is due to the circumstance that $\log_{10} T_b$ changes only from 2.23830 to 2.75820 for the change in T_b from 173.1 to 573.1°K.

dt_b°C.$/dP_{mm.}$ for other compounds, containing halogen, nitrogen, and oxygen, have been similarly treated, and it is indicated that relation (1) is applicable not only to hydrocarbons but also to most of the substances without hydrogen bonding. A more detailed discussion of the problem will be given later.

Summary.

An empirical relation,

$$\frac{dt_b\,°\mathrm{C.}}{dP_{\mathrm{mm.}}} = 0.0345 + 0.00011\, t_b\,,$$

for calculating the change in the boiling point with a small change in

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(16) Landolt-Boernsteins Tabellen, 1327 (1923).

pressure has been derived. It has been found that the equation is applicable to most of the hydrocarbons, with their boiling points ranging from −160 to 300°C., with a maximum deviation of about ±0.002.

A comparison of this equation with the others found in the literature has been made, and it has been found that the relation is just as accurate as some of the more complicated ones proposed.

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