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Estimation of Boiling Points of Organic Compounds at Various Pressures Using Recurrent Relations

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Abstract—A new approach is proposed for the estimation of boiling points (T_b) of organic compounds at reduced pressure from their values at atmospheric pressure based on the application of a recurrent relation: T_b (log P + Δlog P) = aT_b (log P) + b. Estimation of coefficients in this relation for the compounds different by their chemical nature gives the following average values: a = 1.126, b = –41.7. Successive application of this relation with Δlog P = 1 (that corresponds to 10-fold decrease in pressure) allows estimation of the T_b values at the pressure values of 100, 10 and 1 torr from the value of T_b (760 torr) by simple arithmetic calculation with an average accuracy about 8°C.

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The boiling point (T_b) belongs to the most significant physicochemical constants of organic and many inorganic compounds [1]. However, as reference values are considered only the most reproducible ones that correspond to the ambient pressure (760 torr), because the data related to another pressure values are less reliable and less accessible. On the other hand, distillation (rectification) still remains an important laboratory and industrial method for separation and purification of liquid substances [2]. A problem is that distillation at atmospheric pressure is recommended for application to the compounds with boiling temperature (T_b) not higher than 150°C, because at higher temperature a probability grows of their decomposition. In such cases the distillation at reduced pressure is preferable (0.01–20 torr). Therefore it is important to have a reliable enough estimation of boiling temperature of both organic and inorganic compounds at reduced pressure from the reference data on their normal T_b at the atmospheric pressure.

Dependence of boiling temperature on pressure follows from the Clausius–Clapeiron Eq. (1) that connects vapor pressure of an individual compound with the temperature:

$$dln\ P/dT = \Delta H/RT^2, \quad (1)$$

where P is vapor pressure, ΔH is molar enthalpy of evaporation, T is temperature (K), R is gas constant.

Integration of (1) assuming ΔH = const gives another known relation, ln P = $-\Delta H/RT + C$ (C is the integration constant) which practically is often used for the description of $T(P)$ and $P(T)$ in the form of two-parametric regression equation:

$$\ln P = A - B/T. \quad (2)$$

For some organic compounds that are used often in laboratory practice the coefficients A and B of this relation are tabulated (e.g., see [3]). Besides, for estimation of T_b nomograms can be used (e.g., see [4]) or an empirical rule: reducing the pressure by half decreases T_b approximately by 15°C [2]; however, the accuracy of such methods is not high.

The approximate character of Eq. (2) originates from the fact that it is derived with an assumption of constant ΔH value at different temperatures. But actually the $\Delta H(T)$ dependence should not be omitted [5, 6]. For example, the ΔH values for methyl acetate at 273 K and 339 K are, respectively, 478 and 411 J g^{-1} [3]. Therefore for more accurate approximation of the dependence of ΔH on temperature a three-parametric equation is recommended:

$$\ln P = A - B/(T + C). \quad (3)$$

For some organic compounds the coefficients in Eq. (3) are also tabulated, but even in this case the temperature range of application of this relation is

commonly indicated. Therewith, for different temperature ranges the sets of coefficients also are different. For example, for chloroform the following values are given [3]:

Temperature range, °C	from –15 to +135	from +135 to +263
A	6.90328	7.3362
B	1163.0	1498
C	227	276

More accurate but much more complicated method for estimation of T_b from thermodynamic relations is proposed in the reference book [1]. If ΔT is the decrease in T_b at the pressure below 760 torr, then the dependence $P(T)$ can be described with Eq. (4):

$$\log P = 2.8808 - \phi\Delta T/(273.1 + T_b - 0.15\Delta T), \quad (4)$$

where $\phi = \Delta H_{evaporation}/(2.303T_bR) - \Delta S_{evaporation}/(2.303R)$; 2.8808 = log (760).

In order to enhance the accuracy in estimation of T_b to several tenths of a degree the organic compounds are divided into eight groups depending on the free energy of evaporation $\phi(T)$.

However, the problem is complicated due to uncertainty in assignment of a compound to a certain group. Generally, the increase in the number of the group corresponds to a higher polarity of a compound: groups 1–2 include hydrocarbons, groups 7–8 correspond to alcohols and carboxylic acids. At the same time in each group are encountered numerous and unpredictable anomalies. For example, acetic acid belongs to group 4, butyric acid to 7, while benzoic acid to 5. That is why this method is not applied widely.

It should be noted that contemporary software ACD [7] allows estimation of T_b of various organic compounds not only at the atmospheric pressure, but also at the pressure to 0.001 torr. However, with complication of molecular structure the reliability of estimations falls and uncertainty in T_b estimates can achieve several dozens degrees.

Thus, the estimation of T_b values of organic compounds at reduced pressure is simple enough, but to some extent "unconvenient" problem for practical purposes. Precise calculations are based on the reference data known for a restricted number of compounds, while "rapid" estimations with empirical rules or nomogramms are of low accuracy. Note that in "classical" physicochemical manuals [5, 6] and on the internet sites [8] dedicated to the calculation of the properties of liquid substances the problem of estimation of T_b at reduced pressure is not considered.

In this work, we propose to carry out the calculation of T_b of organic compounds at various pressure values using the simplest linear recurrent relations that have never been used for this purpose earlier.

Recurrent Relations: Some Mathematical Properties and Application

Simplest linear (first order) recurrent equations of (5) type describe with high accuracy the changes in physicochemical constants (A) of organic compounds in homologous series [9, 10]:

$$A_{(n+1)} = aA_{(n)} + b, \quad (5)$$

where n is the homolog number (or number of carbon atoms in its molecule).

By definition, recurrent equations are applicable only to discrete functions of the arguments expressed by integer values or equidistant. The physicochemical properties of homologs are just discrete functions of the numbers of atoms in a molecule forming a sequence of integer numerical values of the argument. However, the recurrent relations can also be used for approximation of sets of continuous properties. Such possibility follows from the existence of non-recurrent algebraic solution of Eqs. (5) that is represented by a polynomial with varied power, $n \neq$ const [9, 11]:

$$A_{(n)} = ka^n + b(a^n - 1)/(a - 1). \quad (6)$$

This property allows, e.g., the application of the recurrent relations to approximation of solubility of gases and inorganic salts in water as a function of the temperature [12].

From Eq. (6) follows that specific cases of the recurrent relation (5) are arithmetical and geometric progressions [9, 11]: at $a \equiv 1$, $b \neq 1$, $A_{(n)} = k + bn$ (arithmetical progression), at $0 < a \neq 1$, $b \equiv 0$, $A_{(n)} = ka^n$ (geometric progression).

Thus, recurrent relations comprise properties of two different mathematical progressions. When a sequence of numbers form a geometric progression, then sequence of their logarithms construct arithmetical progression, and both the sequences can be approximated by the same recurrent Eq. (5). This property is important for chemical applications of the

considered approach: the same recurrent equations can be applied to approximation of either partition coefficients (K_p) and their logarithms (log K_p), of vapor pressure (P) and respective logarithms (log P) and so on. This feature of recurrent relations allowed applying them to approximation of retention time in the gas chromatography (t_R) by means of equation

$$\log (t_R - t_0) = a / T + b,$$

(t_0 is retention time of not absorbed component) with mathematical appearance similar to Eq. (2) for the temperature dependence of vapor pressure [13].

Recurrent Algorithm for Estimation of Boiling Points at the Reduced Pressure

Application of recurrent relations allows modifying and simplifying methods of obtaining estimates of T_b at reduced pressure from the data on ambient boiling temperature. More simply, they can be applied to estimation of T_b at the pressure multiple of a certain value, e.g., 10. Owing to mathematical properties of such relations they can be applied to the dependences both of $T(P)$ and $T(\log P)$, but the second turns out to be more convenient for practical purposes. The equidistant values of argument corresponding, in particular, to the pressure values 1, 10, and 100 torr, are respectively 0, 1 and 2, and the formula for calculation in this case is:

$$T_b(\log P + \Delta\log P) = aT_b(\log P) + b, \qquad (7)$$

where $\Delta\log P$ = const (for the considered pressure values $\Delta\log P = 1$, that corresponds to a 10-fold decrease in pressure).

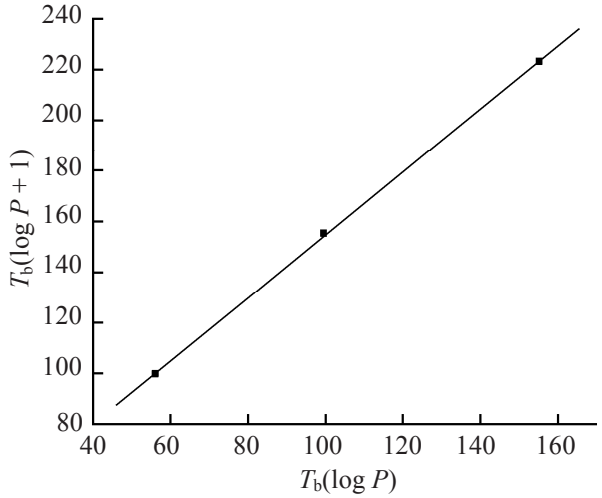

Fig. 1. Graphical illustration of recurrent approximation $T_b(\log P)$ for trichloroacetic anhydride: a = 1.245±0.017, b = 30.2±1.9, r = 0.9999, S_0 = 1.2.

Ambient atmospheric pressure does not correspond to this sequence of integer log P values because log (760) = 2.8808. But to avoid complication of computations we can tentatively assume in this procedure log (760) ≈ 3. Calculations show that such an assumption does not considerably affect the accuracy of recurrent approximation of the sets of $T(P)$ values of various compounds in the pressure region *below* 760 torr, as can be illustrated by the examples in Table 1. The correlation coefficients (r) for the plot (7) for almost all the listed compounds are above 0.999, and the values of general dispersion that characterize the average accuracy of T_b approximation in the pressure range 1–760 torr are on the average 2.2°C. Figure 1 gives graphical illustration of the linear recurrent approximation of T_b at the pressure values 760, 100, 10 and 1 torr for the trichloroacetic acid anhydride.

Note that despite the difference in molecular masses and in chemical nature of the listed compounds the variation in the value of a coefficient in Eq. (7) is relatively small (~1.2–1.3), suggesting a possibility to join the data sets $T_b(P)$ for the compounds different in their chemical nature into one array. This means that estimation of T_b of any compounds at any pressure can be carried out along a single algorithm. To verify this assumption we depicted in Fig. 2a a graphical illustration of joint linear recurrent approximation of $T_b(P)$ dependence for the compounds of one homolog series (n-alkanes C_1–C_{29}) in the range of T_b values from –206 to +422°C. The r value in this case (0.9988) naturally is slightly lower and S_0 (7.8) higher than for individual compounds (Table 1). For estimation of the effect of approximation log (760) ≈ 3 on the linear character of the recurrent approximation we showed in Fig. 2b a plot of analogous dependence for the same array of these compounds omitting T_b value at 760 torr: its parameters are only slightly better (r = 0.9993, S_0 = 5.6) that confirms the validity of this assumption. Similar results are obtained for the compounds of other homolog series. For example, the parameters of linear recurrent T_b approximation of 1-alkanols C_1–C_{18} are: a = 1.186±0.10, b = 33.0±1.1, r = 0.9987, S_0 = 4.7.

For additional characteristic of possible effect of temperature and structural features of the considered compounds on the value of the coefficients in Eq. (7) they were calculated independently for three subgroups: (1) T_b in the range 20–150°C (the best characterized compounds); (2) T_b > 150°C, compounds

Table 1. Examples of recurrent approximation of $T(P)$ dependence for various compounds

Compound	Molecular weight	T_b (P, mm Hg) [6]				Parameters of Eq. (7)			
		1	10	100	760[a]	a	b	r	S_0
Acetonitrile	41	–47.0	–16.3	27.0	81.8	1.32±0.04	46.8±1.3	0.9995	2.1
Acetic acid	60	–17.2	17.5	63.0	118.1	1.25±0.03	39.8±1.1	0.9998	1.6
Nitromethane	61	–29.0	+2.8	46.6	101.2	1.30±0.04	41.4±1.2	0.9996	2.0
Carbon disulfide	76	–73.8	–44.7	–5.1	46.5	1.33±0.02	53.5±0.8	0.9999	0.8
Glycerol	92	125.5	167.2	220.1	290.0	1.30±0.02	3.7±2.6	0.9999	1.0
Succinimide	99	115.0	157.0	217.4	287.5	1.27±0.08	14.0±12.9	0.998	5.6
Diethylnitrosoamine	102	18.5	57.7	111.0	176.9	1.29±0.03	35.0±2.5	0.9996	2.3
Chlorotrifluoromethane	104	–84.3	–59.0	–23.0	23.7	1.35±0.04	55.2±2.1	0.9997	1.5
Anthracene	178	145.0	187.2	250.0	342.0	1.47±0.01	–26.2±1.3	0.9999	0.5
Dibenzyl	182	86.8	136.0	202.8	284	1.26±0.03	28.6±5.1	0.9996	2.8
1,2-Dibromopentane	228	19.8	58.0	110.1	175.0	1.29±0.03	33.4±2.4	0.9997	2.1
Methyl tetradecanoate	242	115.0	160.8	222.6	295.8	1.25±0.05	18.6±7.9	0.9993	3.5
Triphenylmethane	244	169.7	197.0	228.4	259.2	1.06±0.05	18.4±9.7	0.9990	2.0
Nonadecane	268	133.2	183.5	248.0	330.0	1.28±0.01	13.7±0.6	1	0.3
Dibutylphthalate	278	148.2	198.2	263.7	340.0	1.22±0.04	18.3±8.5	0.9994	3.3
Ethoxytriphenylsilane	304	167.0	213.5	273.5	344.0	1.22±0.03	10.4±7.2	0.9996	2.5
Trichloroacetic anhydride	306	56.2	99.6	155.2	223.0	1.24±0.02	30.2±1.9	0.9999	1.2

[a] The log P at P = 760 torr is tentatively taken equal to 3 for simplicity (see comments in the text).

whose T_b estimation at reduced pressure is the most actual; (3) compounds containing one or more active hydrogen atoms. The coefficients in Eq. (7) for the compounds of these groups are as follows:

Subgroup	$20 \le T_b \le 150$°C	$T_b > 150$°C	With active hydrogen atoms
Number of compound in the acquisition	164	109	80
Parameters of Eq. (7):			
a	1.227±0.005	1.133±0.006	1.133±0.005
b	44.1±0.2	40.5±0.9	36.8±0.8
r	0.996	0.995	0.997
S_0	4.6	7.9	6.6

Note the lower S_0 value for the relatively low boiling compounds (subgroup 1), that most probably is due to the higher accuracy of the experimental data. However, since no significant difference was found in the values of a and b coefficients for the three subgroups, all the data (1039 pairs of T_b values for 353 compounds) were joined to obtain common regression equation with the parameters: $a = 1.126 \pm 0.003$; $b = 41.7 \pm 0.3$; $r = 0.997$; $S_0 = 7.5$.

The general dispersion S_0 for such common acquisition is 7.5 that corresponds to an average accuracy of T_b in the pressure range 1–760 torr. Further increase in the number of compounds in the

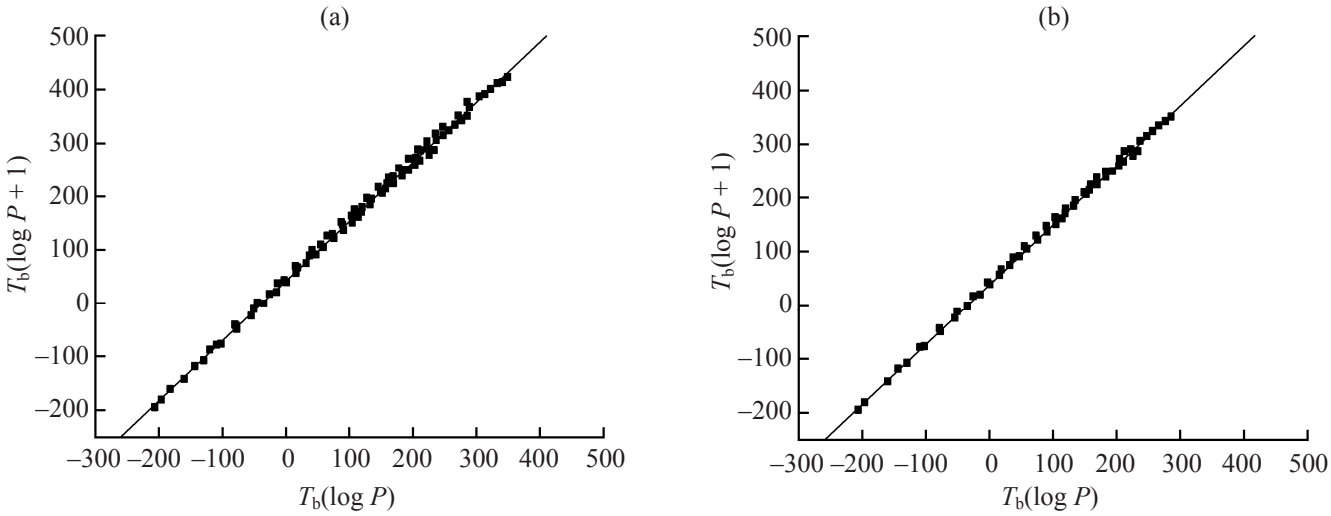

Fig. 2. Graphical illustration of recurrent approximation $T_b(\log P)$ for all *n*-alkanes C_1-C_{29}: (a) with approximate log (760) ≈ 3 (a = 1.116±0.006, b = 41.3±1.1, r = 0.9988, S_0 = 7.8) and (b) with exclusion of T_b value for the pressure 760 torr (a = 1.109±0.006, b = 38.5±0.9, r = 0.9993, S_0 = 5.6).

acquisition leads to only small changes in the coefficients of Eq. (7) and does not affect significantly the accuracy of the estimates obtained with it. The graphical illustration of linear recurrent dependence (7) for 353 compounds of different classes is shown in Fig. 3.

The value of a coefficient a = 1.126 > 1 shows that there is no restriction to T_b value of practically any compound at unlimited increase in pressure [9–11] that corresponds to the physicochemical sense of the considered constants.

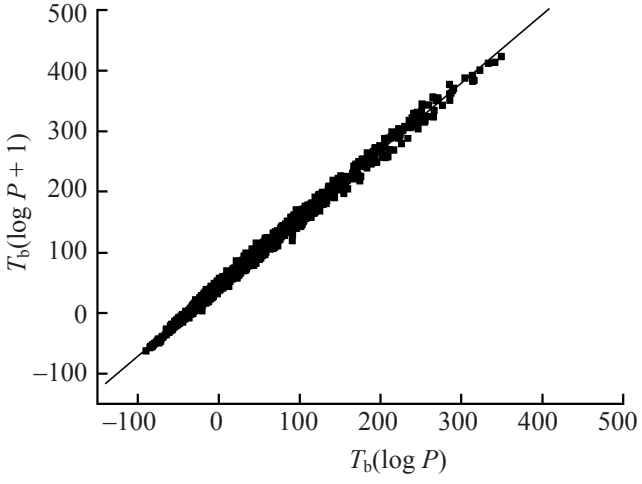

Fig. 3. Graphical illustration of recurrent approximation T_b (log P) for 353 compounds of different classes (total number of points 1039, a = 1.126±0.003, b = 41.7±0.3, r = 0.997, S_0 = 7.5).

For some compounds were found anomalous coefficients of Eq. (7). Some of them (detected with the criterion r < 0.999) can be a result of errors at experimental measuring of T_b, e.g., due to thermal decomposition of substance or due to admixtures that can lead to formation of azeotropic mixtures [14]. A specific group of compounds not matching Eq. (7) consists of polycyclic aromatic hydrocarbons and their derivatives with rigid structural fragments in their molecules formed by sp^2-hybridized carbon atoms (see the data for triphenylmethane and anthracene, Table 1). For these compounds the ratio of evaporation enthalpy ($\Delta H_{evaporation}$) and entropy ($\Delta S_{evaporation}$) differs from the ratio of these thermodynamic constants for the compounds with flexible carbon backbone. By the same reasons, in this work we exclude the compounds containing two or more aromatic fragments. The coefficients of recurrent equation for the compounds with a small number of atoms in their molecules and hence with low number of internal degree of freedom also are different (e.g., HCN: a = 1.43±0.06, b = 51.8±3.1, r = 0.9991, S_0 = 2.2, CCl_4: a = 1.32±0.04, b = 47.1±1.3, r = 0.9996, S_0 = 2.0, etc.). But the T_b estimates for such simple compounds are not actual, therefore the revealed second anomaly should not be considered as a significant restriction of the proposed algorithm.

By the same reasons, application of Eq. (7) with the average coefficients leads to certain systematic overestimation of T_b value at reduced pressure for

carbo- and heterocyclic compounds. Such compounds if necessary can be excluded into a separate group with independently calculated coefficients for achieving higher accuracy of the results.

Examples of Estimation of Boiling Points

Once the coefficients of the joint recurrent Eq. (7) are determined for any organic compounds, the following algorithm can be proposed for estimation of T_b values at the pressure 100, 10, 1, etc., torr proceeding from the T_b^{760} (at ambient pressure).For calculation of T_b^{100} (at 100 torr) the following arithmetic operations should be processed:

$$T(\log P - 1) = [T(\log P) - b]/a,$$

$$a = 1.126 \text{ and } b = 41.7.$$

For example, for enanthic acid which has T_b^{760} = 221.5°C [1] we obtain: T_b^{100} = (221.5 – 41.7) / 1.126 ≈ 159.7°C (reference value: T_b^{100} = 160.0°C [1]).

For estimation of T_b^{10} (at 10 torr) the same arithmetic calculations should be processed twice, for 1 torr triple. When necessary, this procedure can be extended by the same way for calculation of T_b at the pressure 0.1, 0.01 torr and below.

Finding the T_b^{10} of 4-tolylhydrazine includes two similar sequences of calculations: (T_b^{760} 242.0°C decomp. [1]). T_b^{100} = (242.0 – 41.7)/1.126 ≈ 177.89, T_b^{10} = (177.89 – 41.7)/1.126 ≈ 120.9°C (reference value: T_b^{10} = 123.8°C [1]).

Triple application of the same cycle is illustrated by the example of estimation of T_b^1 for *p*-toluidine (T_b^{760} = 200.4°C [1]). T_b^{100} = (200.4 – 41.7) / 1.126 ≈ 140.94; T_b^{10} = (140.94 – 41.7) / 1.126 ≈ 88.14; T_b^1 = (88.14 – 41.7) / 1.126 ≈ 41.2°C (reference value: T_b^1 = 42.0°C [1]).

Additional examples of estimation of T_b value at 100, 10 and 1 torr for the compounds not used as a data source at the calculation of the coefficients of Eq. (7) (so-called test data access), are listed in Tables 2–4. The proposed method is applicable also for the calculation of T_b values much below 0°C. To the Table 4 we included additionally an example of 1-pentene: its T_b estimate at the pressure 1 torr is –78°C (reference value: T_b^1 = –80.4°C [1]). A restriction of the proposed approach is the impossibility of T_b estimations at the pressure different from 10^n (n = 0–2). However, such estimation for not integer values can be achieved by solving Eqs. (6). Moreover, mathematical properties of recurrent relations allow an additional possibility of recalculation of the coefficients of Eq. (7) to provide possibility of estimation T_b at the pressure differing from 10^n (that is, not at $\Delta\log P = 1$).

The coefficients a_1 = 1.126 and b_1 = 41.7 correspond to the discrete values of the argument of Eq. (7) $\Delta\log P = 1$. For obtaining T_b estimates at lower discreteness of the argument, $\Delta\log P = k < 1$, a simple rule can be applied that follows from the conditions $b_k/(1 - a_k)$ = const and $b_k = kb_1$ [10]. Than for the coefficient a at $\Delta\log P = k < 1$ we obtain: $(1 - a_k) = k(1 - a_1)$, hence $a_k = ka_1 - k + 1$. For example, with $\Delta\log P$ = 0.25 the coefficients of Eq. (7) for T_b estimation at the respective pressure values are: b = 0.25×41.7 ≈ 10.4 and a = 0.25×1.126 – 0.25 + 1 ≈ 1.032. With $\Delta\log P$ = 0.1, b = 4.2, and a = 1.013. This increment in variation of the argument corresponds to the following pressure values in the range 10–100 torr:

log P	2.0	1.9	1.8	1.7	1.6	1.5	1.4	1.3	1.2	1.1	1.0
P, mm Hg	100	79	63	50	40	32	25	20	16	13	10

Hence, for the calculation of T_b^{40} from the value of T_b^{100} the same arithmetical operations should be repeated four times with the other values of the coefficients of Eq (7). For example, for cyclohexanone (T_b^{100} = 90.4°C [1]) the following sequence of $T_b(P)$ values can be obtained: 90.4 (100) → 85.1 (79) → 79.8 (63) → 74.7 (50) → 69.6 (40) (experimental value: T_b^{40} = 67.8°C [1]).

This approach to T_b estimation when necessary can be extended over the region of the pressure above atmospheric. However, its application is restricted due to the absence of experimental data. For example, there are reference data on T_b of some compounds at the pressure 1, 2, 5, 10, 20, 40 and 60 atm [1], but not forming sequence of equidistant log P values.

For an additional illustration of advantage of the considered method we compare accuracy in T_b estimation at various pressure values obtained by other methods. For example, according to empirical rule (decrease in pressure to a half reduces T_b by 15°C [2]) for the compounds with T_b^{760} ≈ 180°C the value of T_b at 95 torr (760/2/2/2) should be about 135°C (180–3×15), that is noticeably overestimated. The value calculated with Eq. (7) T_b^{100} = 123.7°C. Using a nomogram [4] leads to underestimated value about 110°C.

Application of the considered algorithm seems reasonable for the characterization of various industrial products, including petroleum hydrocarbons. The obtaining of quite reliable T_b estimates at reduced

Table 2. Estimation of boiling temperature (°C) of some organic compounds at the pressure 100 torr by single application of recurrent Eq. (7)

Compound	Molecular weight	T_b^{760}, °C	T_b^{100}, °C		ΔT, °C
			calculated	experimental	
Glycerol	92	290	220.5	220.1	+0.4
Resorcinol	110	276.5	208.5	209.8	–1.3
1-Hexanol	102	157.0	102.4	102.8	–0.4
Adipic acid	146	337.5	262.7	265	–2.3
Cinnamic acid	148	300.0	229.4	232.4	–3.0
Thymol	150	231.8	168.8	164.1	+4.7
Undecan-2-ol	172	232.0	169.9	167.2	+1.8
N-Phenyldiethanolamine	181	377.8	263.0	260.6	+2.4
Triisobutylamine	185	179.0	121.9	119.7	+2.2
α-Ionon	192	250.0	185.0	181.2	+3.8
Tripropyleneglycol	192	267.2	200.3	199.0	+1.3
2-Butyl-2-ethylbutane-1,3-diol	204	255.0	189.4	191.9	–2.5
Tetraethyleneglycol chlorohydrine	212	281.5	213.0	214.7	–1.7
Hexamethylcyclotrisiloxane	222	134.0	82.0	78.4	+3.6
Tripropyleneglycol monoisopropyl ether	234	256.6	190.0	187.8	+2.2
Triethoxyphenylsilane	240	233.5	170.3	167.5	+2.8
1-Iodononane	254	219.5	157.9	159.8	–1.9
(1,2-Dibromoethyl)benzene	262	254.0	188.5	186.3	+2.2
				Average value $\lvert\Delta T\rvert$, °C	2.3

pressure in a wide range can be illustrated by the following examples: 2-methylheptadecane: T_b^{760} = 306.5°C [1]; T_b^{100} = 235.2°C (experimental value 231.5°C), T_b^{10} = 171.8°C (168.7), T_b^{1} = 115.6°C (119.8); 1-hexadecene: T_b^{760} = 274°C [1]; T_b^{100} = 206.3°C (205.3°C); 2,2,3,3-tetramethylpentane: T_b^{760} = 106.3°C [1]; T_b^{100} = 57.3°C (54.8°C); 2,5-dimethylstyrene: T_b^{760} = 193°C [1]; T_b^{100} = 134.4°C (124.7°C).

The last example demonstrates the above noted systematic overestimation of the data for cyclic compounds.

Thus, application of linear regression relations allows us to propose a new simple method for estimation of boiling temperature for organic compounds (T_b) at a reduced pressure from the respective T_b value at the ambient pressure based on the following equations:

$$T(\log P + \Delta\log P) = a\,T(\log P) + b,$$

where $\Delta\log P = 1$, $a = 1.126\pm0.003$, $b = 41.7\pm0.3$, $r = 0.997$, $S_0 = 7.5$.

For the estimation of T_b at the pressure 100, 10 and 1 torr from T_b at 760 torr is necessary one or successively twice or thrice repeat simple arithmetical calculations $T_b(P) \approx (T_b - b)/a$.

EXPERIMENTAL

The values of T_b at the pressure 760, 100, 10 and 1 torr with accuracy 0.1–1°C are taken from reference book [1] without comparison with the data from other

Table 3. Estimation of boiling temperature (°C) of some organic compounds at the pressure 10 torr otained by the double application of recurrent relation (7)

Compound	Molecular weight	T_b^{760}, °C	T_b^{10}, °C		ΔT, °C
			calculated	experimental	
Resorcinol	110	276.5	149.2	152.1	–3.9
2-Cyclohexylethanol	128	205.4	92.1	90.0	+2.1
Dimethyl malonate	132	180.7	72.5	72.0	+0.5
3-Phenylpropan-1-ol	136	235	115.4	116.0	–0.6
Tetraethyleneglycol monobutyl ether	162	231.2	112.4	107.8	+4.6
Undecan-2-ol	172	232.0	113.1	112.8	+0.3
N-Phenyldiethanolamine	181	377.8	196.5	195.8	+0.7
Triisobutylamine	185	179.0	71.3	69.8	+1.5
α-Ionon	192	250.0	127.3	123.0	+4.3
Tripropyleneglycol	192	267.2	140.8	140.5	+0.3
Tetraethyleneglycol chlorohydrine	212	281.5	152.1	156.1	–4.0
Tripropylenglycol monoisopropyl ether	234	256.6	132.5	127.3	+5.2
Triethoxyphenylsilane	240	233.5	114.2	112.6	+1.6
Pentachlorobenzene	248	276	147.8	144.3	+3.5
(1,2-Dibromoethyl)benzene	262	254.0	130.4	129.8	+0.6
				Average value $\lvert\Delta T\rvert$, °C	2.2

Table 4. Estimation of boiling temperature (°C) of some organic compounds at the pressure 1 torr obtained by the triple application of recurrent relation (7)

Compound	Molecular weight	T_b^{760}, °C	T_b^{1}, °C		ΔT, °C
			calculated	experimental	
Pent-1-ene	70	30.1	–78.0	–80.4	+2.4
Diethyl carbonate	118	125.8	–11.0	–10.1	–0.9
Octanenitrile	125	204.5	44.1	43.0	+1.1
2-Chloroaniline	127	208.8	47.1	46.3	+0.8
Ethyl 3-oxobytanoate	130	180.0	27.5	28.5	–1.0
Acetanilide	135	303.8	113.7	114.0	–0.3
2,6-Dimethylhepta-2,5-dien-4-one (phorone)	138	197.2	39.0	42.0	–3.0
Nonan-2-one	142	195.0	37.5	32.1	+5.4
Phthalic anhydride	148	284.5	100.1	96.5	+3.6
2-Isopropyl-5-methylphenol (tymol)	150	231.8	63.2	64.3	–0.9

Table 4. (Contd.)

Compound	Molecular weight	T_b^{760}, °C	T_b^l, °C		ΔT, °C
			calculated	experimental	
Diisoamyl ether	158	173.4	22.3	18.6	+3.7
Propyl levulinate	158	221.2	55.8	59.7	–3.9
3-Acetyl-2-hydroxy-6-methyl-2*H*-pyran-4-one (dehydracetic acid)	168	269.0	89.3	91.7	–2.4
Azobenzene	182	293.0	106.1	103.5	+2.6
Bornyl formate	182	214.0	50.8	47.0	+3.8
2-Ethylhexyl acrylate	184	216.0	52.2	50.0	+2.2
(1-Phenylethyl)-(2-chloroethyl) ether	184	235.0	65.5	62.3	+3.2
Diethyl glutarate	188	237.0	66.9	65.6	+1.3
Diethyl ethylmethylmalonate	202	207.5	46.2	44.7	+1.5
Diethylphthalate	222	294.0	106.8	108.8	–2.0
Chloromethyldiphenylsilane	232	295.0	107.5	105.0	+2.5
Tripropyleneglycol monoisopropyl ether	234	256.6	80.6	82.4	–1.8
Dipropyl tartrate	234	303.0	113.1	115.6	–2.5
				Average value $\lvert\Delta T\rvert$, °C	2.3

sources. The data for thermally unstable compounds with not reliable T_b values and data for the compounds characterized with the T_b intervals above 2°C are excluded from the consideration.

Calculations of the parameters of recurrent regression equations were carried out with software Origin 4.1.

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