ON THE APPROXIMATE CALCULATION
OF VAPOUR PRESSURES OF LIQUIDS

By

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Logarithms of the p vapour pressure of liquids (usually measured in mm-s of mercury) are linear functions of the reciprocal of T absolute temperature:

$$\log p = A - \frac{B}{T} . \tag{1}$$

If we know the vapour pressure of a liquid at two different temperatures, we can calculate the vapour pressure with this relation at any desired temperature. This relation (1) is not strictly valid owing to the simplifications applied in deriving it, and so it gives satisfactorily correct results only in relatively restricted temperature-intervals, i. e. constants A and B depend to a small extent on temperature. From relation (1) assuming that the Trouton-constant, the ratio of the molar heat of evaporation and of the absolute boiling temperature T_b, is independent of the material — equation

$$\log p = 4.6 \cdot \frac{T - T_b}{T} \tag{2}$$

can be deduced (pressures must be given in atmospheres) [1]. Equation (2) can be employed for approximate calculations if there are no data, except normal boiling point.

Besides this equation we employ at least two connected temperature-pressure data pairs for the calculation of vapour pressure with equation (1) or with one of its improved forms. Among the number of improvements and generalizations of equation (1) the Antoine equation emerges [2]

$$\log p = A - \frac{B}{t + C} \tag{3}$$

which contains one more constant than the preceding equation. This rises above the other equations containing three empirical constants and is

— according to experiences — the most exact one. If at least three connected pairs of temperature and vapour pressure were known, and if the numerical values of constants of equation (3) were determined, the vapour pressure of the liquid could be calculated at any desired temperature with sufficient accuracy. Such problems of interpolation rarely occur, but it is rather the question how it is possible to calculate the vapour pressure of a liquid from less than three measurements and still with sufficient accuracy.

Constants of equation (3) are, according to Thomson [3], monotonous functions of the number of carbon atoms in different homologous series of organic compounds. Moreover, Wiener [4] also gave formulae to calculate constants A and B of paraffinic hydrocarbons with branching chain of carbon atoms from constants A and B of normal hydrocarbons with the same number of carbon atoms. The constant C of organic liquids having a normal boiling point from 0 to 150° C can be uniformly taken at 230° C [5].

When graphically representing logarithms of vapour pressures of different liquids as functions of $\dfrac{1}{t + 230}$ we obtain according to the meaning of equation (3) straight lines, and these lines — in case of vapour pressure lines of liquids belonging to the same homologous series — have a common point of intersection. Coordinates of these points of intersection (so-called "infinite-points") i. e. values of temperature t_∞ measured in °C, and their of pressure p_∞ measured in mm Hg are tabulated by Dreisbach [6]. From these constants t_∞ and p_∞ it is possible to calculate constants of equation (3) A and B with the following formulae:

$$A = \log p_\infty + \frac{B}{t_\infty + 230}$$

$$B = \frac{(t + 230)(t_\infty + 230)}{t_\infty - t} \log \frac{p_\infty}{p}$$

where t and p are related pairs of temperature and pressure and t is measured in °C. Knowing t_∞ and p_∞ is enough to measure the vapour pressure of a liquid at any single temperature, to be able to calculate the vapour pressure of a liquid at any desired temperature.

On the basis of a previous paper [7] in which we showed that the logarithms of critical pressures could be calculated by adding atomic, group and bond increments, it could be demonstrated that constant A of the Antoine equation (3) can also be calculated by adding increments corresponding to structural elements occurring in the molecules.

Namely, according to Gutman and Simmons [8] logarithms of vapour pressures are in connection with the proportionality factor a of the pressure correction and with the volume correction b of the van der Waals equation

in the form

$$\log p = \log \frac{a}{b^2} - \frac{a}{4.57 \cdot b(t + C)} . \tag{4}$$

From the well-known correlations among the constants a and b of the van der Waals equation and the critical parameters [9]

$$a = 3p_c \cdot V_c^2 \quad \text{and} \quad b = \frac{V_c}{3}$$

it follows

$$\frac{a}{b^2} = 27 \cdot p_c. \tag{5}$$

From equations (3), (4) and (5) we obtain

$$A = \log \frac{a}{b^2} = \log 27 + \log p_c$$

and on the additivity of logarithms of critical pressures, A is also an additive quantity.

Knowing the table of increments of constant A it can be calculated and if we know the vapour pressure of the liquid in question at another temperature, the vapour pressure of the liquid can be calculated at any desired temperature. There is no necessity for calculating B because substituting in equation (3) at first t_1, p_1 and t_2, p_2 and substracting these two equations from each other we obtain

$$\log \frac{p_1}{p_2} = A^* \left(\frac{t_1 + 230}{t_2 + 230} - 1 \right) \tag{6}$$

which contains only one constant A^*:

$$A^* = \frac{B}{t_1 + 230} = A - \log p_1$$

so if p_1 is the same constant for all liquids, A^* is also an additive quantity.

In most cases knowing the "normal" boiling point, t_b at pressure 760 mm of Hg with the greatest accuracy, it is advantageous to refer the temperature and the pressure to the normal boiling point ($t_1 = t_b$, $p_1 = 760$) and neglecting indices of p_2 and t_2, to employ equation

$$\log \frac{760}{p} = A' \left(\frac{t_b + 230}{t + 230} - 1 \right) \tag{7}$$

and to tabulate increments of the quantity

$$A' = A - \log 760$$

instead of those of constant A.

Equations of type

$$\log \frac{p_0}{p} = \Phi \left(\frac{\Theta_0}{\Theta} - 1 \right)$$

where Θ means temperatures, (p_0, Θ_0) means connected values of temperature and vapour pressure (reference state) e.g. equations (6) and (7), have been known for a long time. If Θ means the absolute temperature and the reference state is the normal boiling point we get the vapour pressure equation of Cox [10]

$$\log \frac{760}{p} = \Phi \left(\frac{T_b}{T} - 1 \right)$$

where $T_b = t_b + 230$. If the reference state is the critical state we have the reduced vapour pressure-equation of van der Waals

$$\log \frac{p_c}{p} = a \left(\frac{T_c}{T} - 1 \right)$$

[11] where p_c is the critical pressure and T_c the critical temperature.

As the critical constants are only for a few compounds known with sufficient accuracy and an extrapolation from the critical state is uncertain, it is more advantageous to calculate with equation (7) instead of the reduced vapour pressure equation.

Since important physical properties of molecules are, to a great extent, determined by bonds occurring in them; summarizing the table of increments it is more advantageous to calculate bond-increments according to the method applied recently, see increments of the molecular refraction (VOGEL [13]). But the calculation is easier and we can calculate with an improved accuracy, mainly for the case of first members of homologous series, giving increments referring to groups indicating with which kind of bond the individual groups are joined to each other.

Increments of constant A' calculated mainly from vapour pressure data collected by STULL [14] are to be seen in Table 1. (Values of increments refer to vapour pressures given in mm of Hg.)

Systems of conjugated double bonds have a special increment, corresponding to the interaction energy in these systems. In the case of naphtenic rings we have to calculate with the groups in the aliphatic compounds and we must add an increment to the naphtenic ring depending on the number of members of the ring: k and this increment is in connection with energy on closing the rings. The value of increments derivable from benzene and naphthalene depends on the total number n of the carbon atoms joining the group and

of course, on the number of hydrogen atoms m substituted by alkyl groups. Increments of elementary groups derivable from halogens can be given in terms of the number p of halogen atoms in the molecule and in terms of the main quantum number q.

On comparing the accuracy of calculation of vapour pressures from increments it may be mentioned that constant Φ of equation (8) of Cox, already mentioned above (formally analogous to (7)) is a linear function of the normal boiling point for hydrocarbons and for groups of compounds put together arbitrarily. For hydrocarbons the mean deviation of Φ from the linear function is 0.1, but the mean value of differences of the constant A' of equation (7) — determined from observed data and — calculated from increments — is e.g. for hydrocarbons only 0.068.

In Table 2 boiling points for 1 mm of mercury are summarized, measured and calculated from increments, further the difference between them and the observed boiling points.

The difference between calculated and observed boiling points at 1 mm of Hg is suitable for characterizing the accuracy of the approximation. If we can i.e. calculate the boiling point for 1 mm of Hg by using one method with a greater accuracy than with the other, we can do so for other values of pressure too, as these differences diminish in the pressure range 1 to 760 mm Hg then they also do so in every other method.

The mean difference of calculated and observed boiling points is 3.0° C, calculated according to Dreisbach's method, and calculating on the basis of increments it is 1.8° C. Although the calculation on the basis of increments is more complicated when compared to that of Dreisbach, because for employing it we must know the structural formula of the compound too, but boiling points for small values of pressure can be calculated with the mentioned procedure with a greater accuracy, namely, an extrapolation from the "infinite point" connected with a greater temperature, resp. pressure interval can only be made having a greater error.

The calculation of the vapour pressure on the basis of increments is more advantageous also in such cases if we do not know or cannot determine Dreisbach's "infinite point" for a group of compounds, in need of sufficient data. In order to determine the "infinite point" we have to know, namely, the data of more compounds than for the determination of the corresponding increment, since vapour pressure lines referring to a homologous series usually close a small angle, and so in such cases the determination of the common intercept is rather uncertain.

In Table 3 some compounds the vapour pressure of which cannot be calculated with Dreisbach's method are summarized since we do not know the "infinite point", but the vapour pressure can be calculated with equation (7) and Table 1 with sufficient accuracy.

Summary

Logarithms of vapour pressures p (measured in atmospheres) of liquids referring to temperature T may be estimated by equation

$$\log p = 4.6 \, \frac{T - T_b}{T} \tag{2}$$

if we know only one data: the normal boiling point T_b [1]. But equation (2) only gives a rough approximation, since the ratio of the molar latent heat of evaporation and of the absolute normal boiling point, the Trouton constant is only approximately independent of the chemical composition of liquids.

Let us assume that the logarithms of vapour pressures are linear functions of the reciprocal of temperature given in units of any temperature scale, and knowing two corresponding pairs of temperature-pressure values, vapour pressures can be calculated with greatly increased accuracy.

According to Dreisbach measuring the temperature from —230° C, it is enough to know one pair of values of temperature and pressure t_∞, p_∞ to calculate the vapour pressure, to know a following, altogether two pairs of temperature-pressure data with equation

$$\log p = A - \frac{B}{t + 230} \tag{3}$$

at any desired temperature.

But the knowledge of the structural formula of the mentioned compound is also enough for this purpose. Namely, we obtain constant A of equation (3) from equation $A = A' + 2.8808$ and A' may be calculated from increments of Table 1 (vapour pressures must be given in mm of Hg).

The disadvantage of the above mentioned method for estimation of vapour pressures is, that when employed it is not sufficient to know to which group of compounds the compound belongs, but the method is more advantageous compared to that of Dreisbach, since employing it boiling points for 1 mm of Hg can be estimated with an error generally about the half of that of the former.

Table 1

CH_3-	1.6302	$CH_2=$	1.5764	$CH\equiv$	1.5674
$-CH_2-$	0.2006	$-CH=$	0.2581	$-C\equiv$	0.5969
$CH\big\langle$	—1.3004	$=C=$	0.2973		
$C\big\langle$	—2.8718	$-C=$	—1.3142		

Conjugated double bond	0.0589
k-membered napthenic ring	$-0.1268 \, k + 3.5321$
C_6H_{6-m} (derivatives of benzene)	$4.1452 - 1.3819 \, m - 0.1292 \, n$
$C_{10}H_{8-m}$ (derivatives of naphtalene)	$4.6948 - 1.7202 \, m - 0.1107 \, n$
halogens (Cl, Br, J)	$-0.0877n - 0.2342 \, p + 0.0227 \, q + 2.4670$
q: mean quantum number of halogen	
p: number of halogen atoms occurring in the compound	

NH_2-	$-0.1775 \, n + 2.8384$
$NH\big\langle$	$-0.1453 \, n + 1.2258$
$-O-$	$-0.1416 \, n + 0.9412$
$-CO$	$-0.0748 \, n + 2.2327$
$-CN$	$-0.1036 \, n + 3.6524$
$-COO$	$-0.1272 \, n + 1.4318$
$-HCOO$ (in formates)	$-0.1272 \, n + 2.7868$
$-COOH$	$-0.0990 \, n^2 + 0.7653 \, n + 1.8058$
$-OH$ (in alcohols)	$-0.0549 \, n^2 + 0.3032 \, n + 3.0254$
$-OH$ (in phenols)	$-0.1554 \, n + 0.6138$

Table 2

	A'_i	$t^{(1)}_{meas.}$	$t^{(1)}_i$	δ
Etane	3.2604	−159.5	−154.9	+4.6
propane.....................	3.4610	−128.9	−127.5	+1.4
n-butane	3.6616	−101.5	−101.6	−0.1
n-pentane	3.8622	−76.6	−77.6	−1.0
n-hexane	4.0628	−53.9	−55.2	−1.3
n-heptane	4.2634	−34.0	−34.0	0.0
n-octane	4.4640	−14.0	−13.9	+0.1
n-nonane.....................	4.6646	2.4	4.1	+1.7
2-methylpropane	3.5902	−109.2	−108.9	+0.3
2-methylbutane	3.7908	−82.9	−83.5	−1.6
2-methylpentane	3.9914	−60.9	−61.4	−0.5
3-methylpentane	3.9914	−59.0	−59.7	−0.7
2-methylhexane	4.1920	−40.4	−40.6	−0.2
3-methylhexane	4.1920	−39.0	−39.2	−0.2
3-ethylpentane...............	4.1920	−37.8	−38.3	−0.5
2-methylheptane	4.3926	−21.0	−20.1	+0.9
3-methylheptane	4.3926	−19.8	−19.3	+0.5
4-methylheptane	4.3926	−20.4	−20.0	+0.4
3-ethylhexane	4.3926	−20.0	−19.1	+0.5
2-2-dimethylbutane	3.8496	−69.3	−70.0	−0.7
2-2-dimethylpentane	4.0502	−49.0	−49.3	−0.3
3-3-dimethylpentane	4.0502	−45.9	−45.3	+0.6
2-2-dimethylhexane	4.2508	−20.7	−29.3	+0.4
3-3-dimethylhexane	4.2508	−25.8	−25.6	+0.2
3-methyl-3-ethylpentane	4.2508	−23.9	−22.4	+1.5
2-2-3-3-tetramethylbutane.......	4.0376	−17.4	−33.7	−16.3
2-3-dimethylbutane	3.9200	−63.6	−64.0	−0.4
2-3-dimethylpentane............	4.1206	−42.0	−40.8	+1.2
2-4-dimethylpentane............	4.1206	−48.0	−47.3	+0.7
2-3-dimethylhexane	4.3212	−23.0	−22.6	+0.4
2-4-dimethylhexane	4.3212	−26.9	−26.4	+0.5
2-5-dimethylhexane	4.3212	−26.7	−26.5	+0.2
3-4-dimethylhexane	4.3212	−22.1	−21.4	+0.7
2-2-3-trimethylpentane	4.1794	−29.0	−28.8	+0.2
2-2-4-trimethylpentane	4.1794	−36.5	−35.1	+1.4
2-3-3-trimethylpentane	4.1794	−25.8	−25.9	−0.1
2-3-4-trimethylpentane	4.2498	−26.3	−25.3	+1.0
2-methyl-3-ethylpentane	4.3212	−24.0	−22.5	+1.5
propylene	3.4647	−131.9	−131.7	+0.2
butene-1	3.6653	−104.8	−104.8	0.0
cis-butene-2	3.7766	−96.4	−97.4	−1.0
trans-butene-2	3.7766	−100.4	−99.0	+0.4
pentene-1	3.8659	−80.4	−81.0	−0.6
hexene-1	4.0665	−57.5	−56.7	+0.8
methylpropene................	3.5226	−105.1	−107.3	−2.2
2-methyl-2-butene	3.8345	−75.4	−76.7	−1.3
2-methyl-1-butene.............	3.7232	−89.1	−89.0	+0.1
2-methyl-2-heptene	4.4363	−16.1	−16.3	−0.2
propadiene	3.4501	−120.6	−123.7	−3.1
1-2-butadiene	3.7620	−89.0	−89.3	−0.3
1-3-butadiene	3.7279	−102.8	−102.8	0.0
1-3-pentadiene	4.0398	−71.8	−71.2	+0.6
1-4-pentadiene	3.8696	−83.5	−83.2	+0.3
2-methyl-1-3-butadiene	3.7858	−79.8	−80.9	−1.1
myrcene	4.7611	14.5	20.1	+5.6
cyclopentane	3.9064	−68.0	−69.2	−1.2

	A_i'	$t^{(1)}_{meas.}$	$t^{(1)}_i$	δ
methylcyclopentane	4.0356	—53.7	—53.9	—0.2
ethylcyclopentane	4.2362	—32.2	—31.6	+0.6
cyclohexane	3.9695	—45.4	—50.0	—4.6
methylcyclohexane	4.0987	—35.9	—35.7	+0.2
ethylcyclohexane..............	4.2993	—14.5	—13.4	+1.4
1-1-dimethylcyclohexane	4.1575	—24.4	—23.6	+0.8
cis-1-2-dimethylcyclohexane	4.2279	—15.9	—16.1	—0.2
trans-1-2-dimethylcyclohexane ..	4.2279	—21.1	—19.8	+1.3
cis-1-3-dimethylcyclohexane	4.2279	—19.4	—19.2	+0.2
trans-1-3-dimethylcyclohexane ..	3.2279	—22.7	—21.8	+0.9
cis-1-4-dimethylcyclohexane	4.2279	—20.0	—19.3	+0.7
trans-1-4-dimethylcyclohexane ..	4.2279	—24.3	—22.3	+2.0
benzene	4.1452	—36.7	—47.0	—10.3
toluene	4.2643	—26.7	—26.7	0.0
ethylbenzene	4.3357	—9.8	—10.0	—0.2
propylbenzene	4.4071	6.3	5.4	—0.9
butylbenzene	4.4785	22.7	22.2	—0.5
heptylbenzene	4.6927	66.2	56.9	—9.3
i-propylbenzene	4.3357	2.9	—0.3	+3.2
sec.-butylbenzene	4.4071	18.6	14.0	—4.6
terc.-butylbenzene	4.2653	13.0	7.8	—5.2
sec.-amylbenzene	4.4785	27.8	18.3	—8.5
o-xylene	4.3834	—3.8	—4.1	—0.3
m-xylene....................	4.3834	—6.9	—7.3	—0.4
p-xylene	4.3834	—8.1	—7.8	+0.3
o-ethyl-toluene...............	4.4548	9.4	9.9	+0.5
m-ethyl-toluene	4.4548	7.2	7.6	+0.4
p-ethyl-toluene	4.4548	7.6	8.0	+0.4
o-diethylbenzene	4.5262	25.6	18.4	—7.2
m-diethylbenzene	4.5262	21.7	21.9	+0.2
p-diethylbenzene	4.5262	19.4	22.1	+2.7
1-2-di-i-propylbenzene	4.5262	40.0	38.3	—1.7
1-3-di-i-propylbenzene	4.5262	34.7	34.0	—0.7
3-ethylcymene	4.5262	28.3	28.5	+0.2
4-ethylcymene	4.5262	31.5	30.2	—1.3
1-2-3-trimethylbenzene	4.5025	16.8	17.6	+0.8
1-2-4-trimethylbenzene	4.5025	13.6	13.4	—0.2
1-3-5-trimethylbenzene	4.5025	9.6	10.7	+1.1
4-ethyl-1-3-xylene	4.5739	23.2	24.3	+1.1
5-ethyl-1-3-xylene	4.5739	23.2	24.6	+1.4
2-ethyl-1-4-xylene	4.5739	24.1	24.6	+0.5
3-5-diethyltoluene	4.6453	31.8	34.8	+3.0
1-2-4-triethylbenzene	4.7167	46.0	48.1	+2.1
1-3-4-triethylbenzene	4.7167	47.9	47.8	—0.1
1-3-5-trimethyl-2-ethylbenzene ..	4.6930	38.8	41.4	+2.6
1-2-4-trimethyl-5-ethylbenzene ..	4.6930	43.7	41.5	—2.2
1-2-3-4-tetramethylbenzene	4.6216	42.6	37.6	—5.0
1-2-3-5-tetramethylbenzene	4.6216	40.6	33.6	—7.0
1-2-4-5-tetramethylbenzene	4.6216	45.1	32.4	—12.4
styrene	4.3394	—7.0	—4.5	+2.5
α-methylstyrene	4.2681	+7.4	6.1	—1.3
β-methylstyrene	4.5221	17.5	19.8	+2.3
propenylbenzene..............	4.4108	17.5	17.4	—0.1
4-methylstyrene	4.4585	16.0	16.0	0.0
3-ethylstyrene	4.5299	28.3	27.6	—0.7
4-ethylstyrene	4.5299	26.0	26.1	+0.1

	A'_i	$t^{(1)}_{meas.}$	$t^{(1)}_i$	δ
4-i-propylstyrene	4.5299	34.7	34.4	—0.3
divinylbenzene.................	4.5336	32.7	35.5	+2.8
2-4-dimethylstyrene	4.5776	34.2	35.1	+0.9
2-5-dimethylstyrene	4.5776	39.0	29.6	+0.6
2-5-diethylstyrene	4.7202	49.7	51.3	+1.6
2-4-5-trimethylstyrene	4.6967	48.1	49.7	+1.6
2-4-6-trimethylstyrene	4.6967	37.5	40.9	+3.4
naphtalene	4.6948	85.8 (10 mm)	89.8 (10 mm)	+4.0
1-ethylnaphtalene	4.5840	70.0	69.7	—0.3
2-i-propylnaphtalene	4.6025	76.0	75.1	—0.9
methylamine	4.2911	—95.9	—96.2	—0.3
ethylamine	4.3142	—82.4	—82.1	+0.3
propylamine	4.3373	—64.4	—62.7	—1.7
i-butylamine	4.2890	—50.0	—51.4	—1.4
dimethylamine.................	4.1956	—87.7	—79.2	+8.5
di-i-butylamine	4.3850	—5.1	—7.0	—1.9
ethylcetylamine	5.0804	133.2	135.0	+1.8
ethylmethylether..............	3.9774	—91.0	—92.3	—1.3
diethyleter	4.0364	—74.3	—75.6	—1.3
methylpropylether	4.0364	—72.2	—73.0	—0.8
ethylpropylether	4.0954	—64.3	—58.8	+5.5
dipropylether	4.1544	—43.3	—41.4	+1.9
di-i-propylether	4.0116	—57.0	—51.0	+6.0
di-i-amylether	4.2476	18.6	10.4	+8.2
3-pentanone	5.5203	—12.7	—11.3	+1.4
2-pentanone	5.5203	—12.0	—11.2	+0.8
3-methyl-2-butanone	5.4489	—19.9	—21.3	—1.4
2-hexanone	5.6461	7.7	6.7	—1.0
4-methyl-2-pentanone	5.5747	—1.4	0.1	+1.5
2-heptanone	5.7719	19.3	23.6	+4.3
4-heptanone	5.7719	23.0	19.3	—3.7
ethylchloride	3.9563	—89.8	—89.0	0.0
1-chloropropane...............	4.0692	—68.3	—68.2	+0.1
i-butylchloride	4.1107	—53.8	—54.3	—0.5
methylbromid	3.8661	—96.4	—96.1	+0.3
ethylbromid	3.9790	—74.3	—74.3	+0.0
1-bromopropane	4.0919	—53.0	—53.4	—0.4
2-bromopropane	4.2048	—33.0	—33.2	—0.2
1-bromo-3-methylbutane	4.2463	—20.4	—21.2	—0.8
ethyliodide	4.0017	—54.4	—54.2	+0.2
i-iodopropane	4.1146	—36.0	—34.4	+1.6
2-iodopropane	4.0432	—43.3	—43.4	—0.1
1-iodo-methylbutane	4.2690	—2.5	—4.2	—1.7
dichlorometane	4.1586	—70.0	—70.1	—0.1
11-dichloroetane	4.1124	—60.7	—61.0	—0.3
12-dichloroetane	4.1838	—44.6	—45.0	—0.4
12-dichlorobutane	4.1628	—23.6	—21.1	+2.5
23-dichlorobutane	4.0914	—25.2	—27.0	—1.8
11-dichloro-2-metilpropane	4.0914	—31.0	—33.4	—2.4
dibromometane	4.2040	—35.1	—35.0	+0.1
14-dibromobutane	4.2796	32.0	25.5	—6.5
acetonitrile	4.0754	—47.1	—47.3	—0.2
propionitrile	4.1724	—35.0	—36.5	—1.5
butyronitrile	4.2694	—20.0	—22.4	—2.4
valeronitrile	4.3664	—6.0	—6.6	—0.6
capronitrile...................	4.4634	9.2	9.2	0.0

	A_i'	$t_{meas.}^{(1)}$	$t_i^{(1)}$	δ
enantonitrile	4.5604	21.0	24.1	+3.1
caprylonitrile	4.6574	43.0	38.5	—4.5
methylformate	4.1626	—74.2	—75.1	—0.9
methylacetate	4.3106	—57.2	—57.6	—0.4
ethylformate	4.2360	—60.5	—60.8	—0.3
ethylacetate	4.3840	—43.4	—44.7	—1.3
methylpropionate	4.3840	—42.0	—43.1	—1.1
propylformate	4.3094	—43.0	—43.4	—0.4.
i-propylformate	4.2380	—52.0	—52.4	—0.4
ethylpropionate	4.4574	—28.0	—30.1	—2.1
propylacetate	4.4574	—26.7	—28.5	—1.8
methylbutirate	4.4574	—26.8	—28.2	—1.4
i-propylacetate	4.3860	—38.3	—37.5	+0.8
methyl-i-butyrate	4.3860	—34.1	—35.3	—9.2
butylformate	4.3830	—26.4	—27.2	—0.8
i-butylformate	4.5120	—32.7	—29.7	+3.0
sec.-butylformate	4.5120	—34.4	—32.5	+1.9
terc.-butylformate	4.2968	—32.7	—33.7	—1.0
methyl-i-valerate...........	4.4594	—19.2	—19.4	—0.2
ethylbutyrate...............	4.5308	—18.4	—15.5	+2.9
ethyl-i-butyrate	4.4594	—24.3	—23.3	+1.0
propylpropionate............	4.5308	—14.2	—14.5	—0.3
i-butylacetate	4.4594	—21.2	—18.6	+2.6
i-amylformate	4.5854	—17.5	—13.0	+4.5
methylcaproate	4.6042	5.0	3.8	—1.2
ethyl-i-valerate	4.5328	—6.1	—7.3	—1.2
propylbutyrate	4.6042	—1.6	—0.7	+0.9
propyl-i-butyrate	4.5328	—6.2	—7.6	—1.4
i-propyl-i-butyrate	4.4614	—16.3	—17.0	—0.7
i-butylpropionate	4.5328	—2.3	—5.7	—3.4
i-amylacetate	4.5328	0.0	—2.6	—2.6
methanol	4.9039	—44.0	—44.4	—0.4
ethanol	5.2430	—31.3	—31.0	+0.3
propanol	5.1726	—15.0	—15.2	—0.2
i-propanol	5.5192	—26.1	—24.6	—1.5
butanol	5.5918	—1.2	—0.7	+0.5
sec-butanol	5.6384	—12.2	—11.9	+0.3
i-butanol	5.5204	—9.0	—7.9	+1.1
amylalcohol	5.6015	13.6	12.9	—0.7
pentanol-2	5.6481	1.5	1.6	+0.1
hexanol-1	5.5014	24.4	24.0	—0.4
hexanol-2	5.5480	14.6	13.4	—1.2
2-methylpentanol-1............	5.4300	15.4	16.9	+1.5
acetic acid	4.5706	—17.2*	—16.5	+0.7 *[16]
propionic acid	5.0415	+4.6*	6.2	+1.6
n-butyric acid	5.3144	25.5*	25.1	—0.4
phenol......................	5.3771	40.2	38.2	—2.0
hydrochinone	6.6945	132.5	130.9	—1.6
2-cresol....................	5.3408	38.2	43.3	+5.1
3-cresol....................	5.3408	52.0	51.1	—0.9
4-cresol....................	5.3408	53.0	50.5	—2.5
2-ethylphenol	5.2568	46.2	52.6	+6.4
3-ethylphenol	5.2568	60.0	56.8	—3.4
4-ethylphenol	5.2568	59.3	60.0	+0.7
23-xylenol..................	5.3045	56.1	60.3	+4.2
24-xylenol..................	5.3045	51.8	56.1	+4.3

	A'_i	$t^{(1)}_{meas.}$	$t^{(1)}_i$	δ
25-xylenol	5.3045	51.9	56.1	+4.2
34-xylenol	5.3045	66.2	65.0	—1.2
35-xylenol	5.3045	62.1	61.3	—0.9
2-i-propylphenol	5.1014	56.6	54.1	—2.5
3-i-propylphenol	5.1014	62.0	62.6	+0.6
4-i-propylphenol	5.1014	67.0	62.8	—4.2
4-i-butylphenol	5.0174	72.1	66.7	—5.4
4-sec-butylphenol	5.0174	71.4	69.9	—1.5
2-terc-butylphenol	4.8756	57.4	57.9	+2.5
4-terc-butylphenol	4.8756	70.0	64.2	—5.8

Table 3

	A'_i	$t^{(1)}_{meas.}$	$t^{(1)}_i$	δ
Acetylene	4.1348	—143.0	—154.0	—11.0
propyne	3.7945	—111.1	—112.5	—1.4
butyne-1	3.9951	—92.5	—91.3	+1.2
butyne-2	4.4542	—73.1	—73.8	—0.7
1-3-butadiyne	4.3286	—34.0*	—30.8*	+3.2
butenyne	3.9988	136.8	136.8	0.0
1-5-hexadien-3-yne	4.8628	—45.1	—32.8	+12.3
cyclopropane	3.8040	—116.8	—118.2	—1.4
methylcyclopropane	3.9332	—96.0	—94.6	—1.4
cyclobutane	3.8273	—48.4**	—47.9**	+0.5
cyclobutene	3.9423	—99.1	—95.7	+3.4
dicyclopentadiene	4.1900	34.1***	29.6***	—4.5
tetralin	4.4384	38.0	35.1	—2.9
cis-decalin	4.5466	22.5	29.9	+7.4
trans-decalin	4.5466	—0.8	25.1	+25.9
indene	4.6087	16.4	23.5	+7.1
acenaphtylene	4.3323	114.8***	107.5***	—7.3

* 100 mm, ** 40 mm, *** 5 mm.

Literature

1. ERDEY-GRÚZ, T., SCHAY, G.: Elméleti fizikai kémia Ed. 2. (Tankönyvkiadó, Budapest) 1955. Vol. 1. p. 535.
2. ANTOINE: Compt. Rend. **107** 681, 836 (1888).
3. THOMSON, G. M.: Chem. Rev. **38** 1 (1946)
4. WIENER, H.: J. Phys. Chem. **52** 425 (1948)
5. DREISBACH, R. R.—SPENCER, R. S.: Ind. Eng. Chem. **41** 176 (1949).
6. DREISBACH, R. R.: Pressure-Volume-Temperature Relationships of Organic Compounds. Ed. 3. (Sandusky, Ohio) 1952.
7. MÓRITZ, P.: Acta Chim. Hung. **11** 271 (1957)
8. GUTMANN, F.—SIMMONS, L. M.: J. Chem. Phys. **18** 696 (1950).
9. e.g. PARTINGTON, J. R.: An Advanced Treatise on Physical Chemistry (Longmans, London) 1949. Vol. 1. p. 672.
10. COX, E. R.: Ind. Eng. Chem. **28** 613 (1936).

11. see. e.g. 9. p. 697.
12. VOGEL, A. J.: Chemistry and Industry **1950** 358.
13. VOGEL, A. J.: J. Chem. Soc. **1948** 1842.
14. STULL, D. R.: Ind. Eng. Chem. **39** 517 (1947).
15. CRAGOE, C. S.: International Critical Tables (Washburn E. W.) New York. 1926. vol. 3. p. 246.
16. HODGMAN, CH. D.: Handbook of Chemistry and Physics (Chemical Rubber Publ. Co. Cleveland, Ohio) 1954.

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