

Group-contribution method for the estimation of vapor pressures

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Abstract

A group-contribution method has been developed for predicting the vapor pressures of organic liquids. The parameters for 42 organic groups are derived from 5359 experimental vapor pressure data on 342 organic compounds. The various group values are presented as four-constant expressions and can be used to estimate the vapor pressures of organic liquids up to 8000 kPa. With the proposed method, vapor pressures have been calculated for 336 organic compounds, and when compared with the experimental data, this method produces an average absolute percentage deviation of 5.0%. The proposed method is quite general and relatively easy to use. The required input parameters are the group numbers and the molecular weight of that compound.

Keywords: Theory; Methods of calculation; Group contribution; Organic compounds; Vapor pressure

1. Introduction

The vapor pressure of pure liquids is a very important property in the calculations of vapor–liquid equilibria. The enthalpies of vaporization are often derived from vapor pressure data. Although experimental data can be very accurate, it is difficult to provide all the data needed for every single compound. For this reason, several methods have been developed for estimating vapor pressures (Reid et al., 1987). Many developed correlation equations, based on the classical theories of corresponding states, use critical properties as reducing parameters.

Another popular approach is to develop correlations for homologous series. This approach is the group-contribution method. Among the group-contribution methods, it is worth mentioning UNIFAC (Fredenslund et al., 1977). Although the method based on UNIFAC (Jensen et al., 1981; Yair and Fredenslund, 1983) shows some success in estimating the vapor pressures, it requires complicated calculations and input of other physical properties such as the second virial coefficient and/or normal boiling point. The applicable pressure range in the UNIFAC method

is between 1.0 and 300 kPa. Thus, a reliable and simple predictive technique for vapor pressure calculations is not only welcomed, but is a necessity in the chemical industry.

The purpose of this work is to propose a group-contribution method that will permit vapor pressures to be calculated with ease, over a broader pressure range, and with no input of other physical properties. A four-constant expression based on the Clausius–Clapeyron equation is used to develop this model for vapor pressure.

2. Group-contribution model

From the Clausius–Clapeyron equation, we obtain

$$\frac{d \ln P}{d(1/T)} = \Delta H_v / (-R \Delta Z_v) \quad (1)$$

Assuming a second order dependence on temperature for the group $\Delta H_v / (-R \Delta Z_v)$, the integration of Eq. (1) becomes

$$\ln P = A + B/T - C \ln T - DT \quad (2)$$

where A , B , C , and D are constants.

Based on the classical group-contribution concepts, the logarithm of the vapor pressure of a compound is considered as the sum of all the contributions made by the groups present in the molecule. Further, the contribution of a given group in a molecule is the same as in another molecule. Thus, Eq. (2) is rewritten for group contribution as

$$\ln P = \sum_i N_i (A_{Gi} + B_{Gi}/T - C_{Gi} \ln T - D_{Gi} T) \quad (3)$$

where N_i is the number of group i in the molecule.

However, when the logarithm of the experimental vapor pressure data of n -alkanes, n -alkanols, n -alkanoic acids, and n -alkanones is plotted against the number of carbon atoms in Fig. 1, and the curves show that the contributions of the methylene groups (CH_2) to each organic series differ markedly. When the logarithm of the product of vapor pressure and molecular weight (M) of the compound is used, a similar plot as in Fig. 1 is constructed. Curves with essentially the same trends of the contribution of CH_2 are obtained (Fig. 2). Thus, Eq. (3) is modified to include the effect of molecular weight:

$$\ln (PM) = \sum_i N_i (A_{G_{Mi}} + B_{G_{Mi}}/T - C_{G_{Mi}} \ln T - D_{G_{Mi}} T) \quad (4)$$

where $A_{G_{Mi}}$, $B_{G_{Mi}}$, $C_{G_{Mi}}$, and $D_{G_{Mi}}$ are group constants.

Thus, Eq. (4) is used as the basic relation in the development of the group-contribution model for the vapor pressure. However, the molecular structures (side-chain, alicyclic rings, and double-bonds) are the functional groups ($-\text{OH}$, $-\text{COOH}$, etc.) may have a significant effect on the group contribution to the vapor pressure. Thus, certain types of correction to Eq. (4) are necessary and are denoted as Q . The group-contribution model for the vapor pressure in this study would be

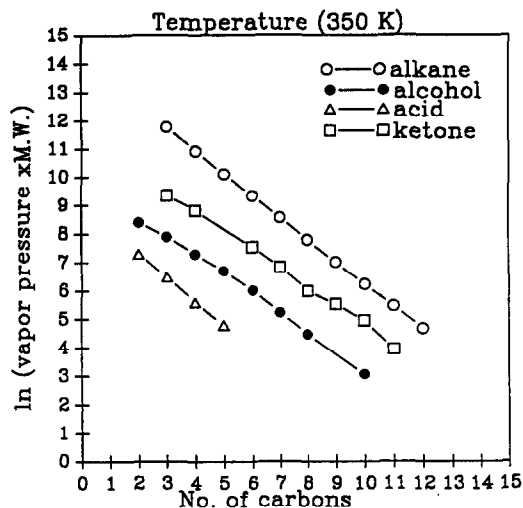
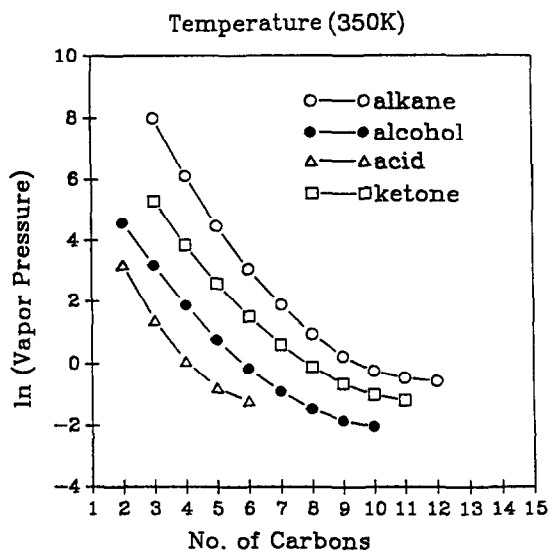


Fig. 1. Vapor pressures of normal organic compounds.

Fig. 2. Vapor pressures multiplied by molecular weights of normal organic compounds.

$$\ln(PM) = \left[\sum_i N_i (a_i + b_i/T - c_i \ln T - d_i T) \right] + Q \quad (5)$$

where P = vapor pressure (kPa); $T = T(K)/100$; $T(K)$ = temperature in Kelvin; M = molecular weight; a_i , b_i , c_i , d_i = predictive group constants of group i ; and Q = specific compound correction. Q is expressed as

$$Q = \sum_{i=1}^2 \xi_i q_i \quad (6)$$

For $i = 1$: structure term

$$\xi_1 = s_0 + s_1 N_{cs} + s_2 N_{bs} + s_3 N_{es} \text{ alkylbenzenes} \quad (6a)$$

$$\xi_1 = 1 \text{ others}$$

for non-ring compounds:

$$q_1 = \alpha_{1n} + \beta_{1n}/T - \gamma_{1n} \ln T - \delta_{1n} T \quad (6b)$$

for ring compounds:

$$q_1 = \alpha_{1r} + \beta_{1r}/T - \gamma_{1r} \ln T - \delta_{1r} T \quad (6c)$$

For $i = 2$: functional group term:

$$\xi_2 = f_0 + f_1 N_{cm} + f_2 N_{cm}^2 + f_3 N_{cm}^3 + f_4 N_{cm}^4 \quad (6d)$$

$$q_2 = \alpha_2 + \beta_2/T - \gamma_2 \ln T - \delta_2/T \quad (6e)$$

Table 1
Examples for counting the N_{cs} , N_{bs} and N_{es} values

Compound	N_{cs}	N_{bs}	N_{es}
Isobutyl benzene	4	1	0
1,2-Diisopropyl benzene	6	2	1
1,2,3-Trimethyl benzene	3	0	2
1,2,4,5-Tetramethyl benzene	4	0	2
1,2,3,4-Tetramethyl benzene	4	0	3

where ξ_1 = structural correction factor; ξ_2 = functional-group correction factor; q_1 = structural correction; q_2 = functional-group correction; α_i , β_i , γ_i , and δ_i = correction constants for correction type i ; and subscripts n and r = non-ring and ring compounds, respectively.

Eq. (6a) is mainly used to account for the effect of the alkyl substituents on the vapor pressures of the substituted benzenes. N_{cs} is the number of carbon atoms on the alkyl-substituent, N_{bs} is the number of branched alkyl-substituents, and N_{es} is the number of neighboring alkyl-substituents. s_0 , s_1 , s_2 , and s_3 are constants. The N_{cs} , N_{bs} , and N_{es} values are shown in Table 1. The effect of the functional groups (–OH, –COOH, etc.) on the vapor pressure is corrected according to the number of carbon atoms in the molecule as in Eq. (6d). f_0 , f_1 , f_2 , and f_3 are constants of the functional group correction factor. N_{cm} is the number of carbon atoms in a molecule.

The predictive constants, a_i , b_i , c_i , and d_i , of the group contributions are given in Table 2. Owing to the strong effect of the cyclane ring size on vapor pressures, the values of the group contributions are shown with various ring sizes. The correction values for the specific compounds in Eq. (6) are shown in Table 3. It should be noted that the T values used in the working equations are the temperature in Kelvin divided by 100.

3. Generation of the group constants

The next step in the group-contribution method involves the determination of the group constants, a_i , b_i , c_i , and d_i , for various groups and the correction constants, Q , for some specific compounds. The database contains reliable experimental data for 342 organic compounds with 5359 data points. These organic compounds are classified in 42 molecular groups. Except for the ether group (O) and amine groups (NH₂ and NH), the group assignment in this study is to identify first the carbon atom and then its attached non-carbon atoms and/or functional groups. Thus, the CH₃ group represents a primary methyl group and CH₂OH a primary alkanol group. The following symbols characterize each of its particular carbon bonds: C_d, a double bonded carbon atom; C_{d2}, two double bonded carbon atoms; C_t, a triple bonded carbon atom; C_r, a cycloparaffinic carbon atom; C_a, an aromatic carbon atom; and C_{rd}, a double bonded cycloparaffinic carbon atom.

Table 2
The groups and their contribution values to vapor pressure

Group	a_i	b_i	c_i	d_i
<i>Alkanes</i>				
CH ₄	18.3662	−14.4079	6.3518	−2.3592
CH ₃	11.7714	−12.5737	2.2841	−0.2608
CH ₂	3.2193	−9.0445	1.3134	−0.0660
CH	−4.4782	−5.1317	1.9526	−0.2331
C	−37.4783	34.4263	−17.2189	2.3381
<i>Alkenes</i>				
C _d H ₂	11.2767	−11.1067	1.5073	−0.0519
C _d H	5.6569	−12.5108	3.8423	−0.5502
C _d	−7.6051	−2.6066	−0.6709	0.0722
C _{d2}	13.3695	−25.8650	13.2055	−2.6484
<i>Alkynes</i>				
C _t H	−2.3899	5.9453	−13.5683	2.8676
C _t	31.9325	−50.1135	28.6956	−4.9136
<i>Aromatics</i>				
C _a H	12.9190	−20.0023	6.9269	−0.8458
C _a	−10.7912	4.9887	−5.3565	0.8294
<i>Alcohols</i>				
CH ₃ OH	32.2058	−60.8324	6.7966	−0.6097
CH ₂ OH	11.2577	−39.9951	−7.2416	1.9198
CHOH	50.8829	−99.9544	29.3664	−3.0041
COH	91.0039	−159.6483	67.8890	−8.4641
<i>Aldehydes</i>				
HCHO	−21.2585	27.9625	−54.8211	12.9193
CHO	16.9447	−33.5580	2.0406	0.2633
<i>Acids</i>				
HCOOH	41.6876	−72.9309	17.0700	−2.3461
COOH	−22.3639	6.7934	−27.2066	3.6193
<i>Ketones</i>				
CO	11.4451	−33.7548	4.7095	−0.2817
C _r O	15.7318	−35.7242	0.6442	1.3149
<i>Esters</i>				
HCOO	30.6109	−52.9005	13.9862	−1.6838
COO	26.7818	−55.0233	16.2873	−1.8386
<i>Ethers</i>				
O	6.2950	−15.6498	3.5276	−0.4449
<i>Amines</i>				
NH ₂	14.5523	−28.1233	−0.0641	0.5749
NH	8.3018	−24.0019	1.1789	0.5033
<i>Nitriles</i>				
HCN	82.3928	−121.5608	49.9955	−7.0105
CN	23.3144	−50.7044	6.9185	−0.5110

Table 2 (Continued)

Group	a_i	b_i	c_i	d_i
<i>Thiols</i>				
CH ₃ SH	26.7086	−40.4972	4.3364	−0.2641
CH ₂ SH	50.9212	−81.1540	28.7811	−3.4574
CHSH	26.1946	−52.7165	15.4828	−1.5672
CSH	19.7497	−48.3419	18.1297	−2.1625
<i>Chlorides</i>				
CH ₃ Cl	40.0173	−54.4986	18.7193	−3.0053
CH ₂ Cl	27.5618	−45.0267	12.3851	−1.4923
CHCl	24.7329	−46.5664	19.2748	−2.9568
CCl	25.5987	−54.2423	29.0348	−4.9523
<i>Cycloparaffins</i>				
<i>3-Membered ring</i>				
C _r H ₂	16.3562	−21.8909	9.0876	−1.4623
C _r H	1.1698	−9.4777	13.2312	−3.2460
<i>4-Membered ring</i>				
C _r H ₂	16.6125	−23.6312	11.9783	−2.2372
C _{rd} H	20.1476	−28.2782	18.8008	−4.1441
<i>5-Membered ring</i>				
C _r H ₂	5.4635	−9.2804	0.7044	−0.0038
C _r H	25.3819	−43.9590	21.4162	−2.6314
C _r	7.5975	−23.0368	18.2736	−2.9451
C _{rd} H	11.1020	−16.4049	5.8475	−0.8299
<i>6-Membered ring</i>				
C _r H ₂	7.2243	−11.9475	2.6978	−0.3025
C _r H	−5.6954	−0.7688	−1.3039	0.2787
C _r	−36.5572	36.0631	−19.6856	2.9408
C _{rd} H	4.3838	−8.6610	−0.4299	0.2775
<i>7-Membered ring</i>				
C _r H ₂	7.6360	−13.0975	3.1908	−0.3519
<i>8-Membered ring</i>				
C _r H ₂	11.8302	−19.5165	6.3215	−0.7243
<i>10-Membered ring</i>				
C _r H ₂	4.9192	−9.8869	1.5870	−0.1242
<i>12-Membered ring</i>				
C _r H ₂	3.9563	−8.6204	1.1261	−0.0721

To obtain these active group constants, the algorithm proposed by Marquardt (1963) for non-linear least-squares regression is used to adjust the constants to fit the model to the experimental data with the following objective function:

$$F = \sum_{i=1}^K \left[\frac{P(\text{exp}) - P(\text{cal})}{P(\text{exp})} \right]_i^2 \quad (7)$$

Table 3a

Values of structural correction constants for ξ_1 in Eq. (6a)

Compound	s_0	s_1	s_2	s_3
<i>Alkylbenzenes</i>				
1-substituent	−0.0005	0.0050	0.0204	
2-substituents	−0.0336	0.0185	0.0110	−0.0218
3-substituents	−0.1060	0.0354		0.0276
Others	−0.1467	0.0534		−0.0521

Table 3b

Structural correction values for nonring q_1 in Eq. (6b)

Compound	α_{1n}	β_{1n}	γ_{1n}	δ_{1n}
Alkanes ($N_{cm} \geq 21$) ^a	−1.5775	4.4318	−0.6435	−0.0323
<i>Double and triple branched alkanes</i>				
With position 3	−0.4179	0.4465	−0.0812	0.0093
Other positions	0.4061	−0.4338	0.0788	−0.0090
1,3-Dialkenes	1.5443	−3.4154	1.0490	−0.1502
<i>Alkylcyclohexanes</i>				
Cis-1,2	−0.9974	−0.0384	−0.0652	0.0139
Cis-1,3	−0.1253	−0.0169	−0.0287	0.0061
Trans-1,4	0.1595	0.0215	0.0365	−0.0078
1,4-Dienes	−0.8066	−1.5936	0.0791	−0.0511

^a N_{cm} = number of carbon atoms in a molecule.

Table 3c

Structural correction values for ring q_1 in Eq. (6c)

Compound	α_{1r}	β_{1r}	γ_{1r}	δ_{1r}
Alkylbenzenes	10.7912	−4.9887	5.3565	−0.8293
Naphthalene	9.0770	−15.8513	−2.8016	1.2162
<i>Substituted naphthalene</i>				
α position	8.8047	−15.3758	−2.7176	1.1798
(α , α') positions ^a	7.8970	−13.7907	−2.4374	1.0581
(α , β) positions	8.4598	−14.7734	−2.6111	1.1335
(β , β') positions	8.9681	−15.6611	−2.7680	1.2016

^a α positions of different benzene rings on naphthalene.

where K is the number of experimental data considered, $P(\text{exp})$ is the experimental vapor pressure and $P(\text{cal})$ is the calculated vapor pressure. This method is applied to the various families of compounds, beginning with the n -alkanes that require only two groups, CH_3 and CH_2 , to create any straight chain of saturated hydrocarbons and two additional groups, CH and

Table 3d

Correction values of ξ_2 and q_2 in Eqs. (6d) and (6e) for the functional group-containing compound

Compounds ^a	f_0	f_1	f_2	f_3	f_4
1° Alcohols	0.6135	−0.3526	0.0225	−0.0005	
2° Alcohols					
−2-ol	2.0980	−1.0220	0.1234	−0.0051	
−3-ol	0.6605	−0.3627	0.0177		
−4-ol	0.6497	−0.3627	0.0177		
3° Alcohols		0.2191	−0.0546		
Aldehydes	1.0035	−0.6175	0.0634	−0.0021	
Acids	−0.3746	0.1991	−0.0210	0.0005	
Ketones	1.4707	−0.6618	0.0597	−0.0018	
Cyclo-ones	−7.1818	2.8475	−0.3090	0.0114	
Formates	1.6210	−1.1558	0.1970	−0.0122	
Esters	0.1967	0.2456	−0.1453	0.0150	−0.0004
Ethers	−0.0388	0.2216	−0.1152	0.0089	
1° Thiols	0.1169	−0.0962	0.0217	−0.0013	
2° Thiols	0.1740	−0.1300	0.0240		
3° Thiols	−2.7560	1.1230	−0.1085		
1° Amines	−0.1603	−0.1960	0.0134		
($N_{cm} \geq 2$)					
2° Amines		−0.2269	0.0086		
($N_{cm} \geq 3$)					
1-Chloroalkanes ($N_{cm} \geq 2$)		0.0279	−0.0131		
q_2	α_2	β_2	γ_2	δ_2	
	3.2193	−9.0445	1.3134	−0.0660	

^a 1°-primary; 2°-secondary; 3°-tertiary.

Table 4

Average deviation in the estimation of vapor pressures

Series	Data points (compounds)	d (%)	Temp. range (K)	Pressure range (kPa)
Alkanes	1046(64)	4.9	90–625	0.00–4682
Alkenes	399(25)	4.6	105–584	0.01–5066
Alkynes	48(4)	5.6	162–398	0.13–6240
Cyclanes	529(29)	3.7	156–563	0.00–5574
Aromatics	691(47)	5.5	233–631	0.02–4875
Alcohols	612(31)	4.5	180–569	0.00–8103
Aldehydes	141(13)	6.5	185–594	0.13–1161
Acids	183(15)	9.7	293–643	0.13–5066
Ketones	538(27)	5.3	259–601	0.13–4700
Esters	366(28)	6.5	199–569	0.13–5066
Ethers	105(8)	8.6	158–467	0.13–5066
Amines	138(10)	5.0	177–615	0.13–6080
Nitriles	98(9)	2.5	202–605	0.13–5066
Thiols	278(16)	2.1	274–472	9.58–270
Chlorides	115(10)	3.2	174–560	0.13–6079
Overall	5287(336)	5.0	90–643	0.00–8103

C, to represent the branched chain compounds. To generate new group constants, the new set of experimental data for the groups is regressed while the previously generated constants for the other groups are held constant.

The final correlation involves data from the Chemical Engineers' Handbook (Perry and Chilton, 1973), Tables on the Thermophysical Properties of Liquids and Gases (Vargaftik, 1975) and other sources: alkanes (Malaspina et al., 1973; Osborn and Douslin, 1974; Osborn and Scott, 1980; Stein, 1981; Salerno et al., 1986; Chirico et al., 1989), alkenes/alkynes (Thomson, 1946; Myers and Fenske, 1955; Jahangiri et al., 1986; Oscarson et al., 1987), cycloparaffins (Lin et al., 1970; Osborn and Douslin, 1974; Meyer and Hotz, 1976; Hugill and McGlashan, 1978), aromatics (Besley and Bottomley, 1974; Osborn and Douslin, 1974; Osborn and Scott, 1980; Kooner and Alexander Van Hook, 1986; Golding and Machin, 1987; Goodwin, 1988), alcohols/ethers (Ambrose and Sprake, 1970; Ambrose et al., 1974; Ambrose et al., 1975; Thomas et al., 1979; Munday et al., 1980; Liley, 1982; Sachek et al., 1984; Mousa, 1987; Ambrose and Ghiassee, 1990), aldehydes (Ambrose and Sprake, 1974; Mills and Fenton, 1987; Mills et al., 1987; Oscarson et al., 1987; Varughese and Sommerfeld, 1989), acids (Ambrose and co-workers, 1977, 1981; Azpiazu, et al., 1984; Ambrose and Ghiassee, 1987), ketones/esters (Ambrose et al., 1974, 1975; Meyer and Hotz, 1976; Oscarson et al., 1987; Ambrose et al., 1988; Askonas and Daubert, 1988), and amines/nitriles/thiols/halides (Day and Felsing, 1950; Osborn and Douslin, 1966; Kratzke and Muller, 1985; Garcia-Sanchez and Trejo, 1987; Lainez et al., 1987; Francesconi, 1988).

4. Results and discussion

By using the proposed method, the vapor pressures have been calculated for 336 organic liquids and 5287 data points with an overall average absolute percentage deviation of 5.0%. Table 4 shows the detailed analysis, including number of data points, number of compounds, average absolute percentage deviation (d), temperature range, and pressure range. The overall average absolute percentage deviation (d_{ov}) is defined as:

$$d_{ov} = \sum_j (dK)_j / \sum_j (K)_j \quad (8)$$

$$d = \sum_{i=1}^K \left| \frac{P(\text{exp}) - P(\text{cal})}{P(\text{exp})} \right|_i \times 100 \quad (9)$$

where j = compound series; i = compound, and K = number of data points of the compound. Only the numbers of groups in a compound and the molecular weight of that compound are needed. No other physical properties are used as input.

The only general group-contribution method of predicting the vapor pressure for all classes of compounds is the modified UNIFAC method of Jensen et al. (1981) and Yair and Fredenslund (1983). This method is however valid for pressures in the range 1–300 kPa and requires that the second virial coefficients and/or normal boiling points are available. The proposed method is applicable for pressures up to 8000 kPa. The only input needed in the proposed method is the molecular weight which is simple to calculate from the Periodic Table.

The group constants and correction values in Tables 2–3 are only applicable to calculation of the vapor pressures of organic liquids with one functional group (–OH, –COOH, etc.) in the molecule. If calculations for compounds with multifunctional groups are desired, larger errors will be expected and the adequate correction values must be developed to improve the results.

5. Conclusions

The group-contribution model, which is a generalization of the classical group-contribution concept, has been successfully applied to the estimation of the organic-liquid vapor pressures. In this work, the vapor pressures of 336 organic compounds with 5287 data points have been examined and the overall average absolute percentage error is 5.0%. The correlation method yields acceptable predictions up to a pressure of 8000 kPa.

The proposed method may be used for both polar and non-polar components. Only molecular weights, easily calculated from the molecular formula, and structural information are needed. The method is fairly simple and does not require any other physical properties as input.

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List of symbols

A, B, C, D	constants in Eq. (2)
$A_{Gi}, B_{Gi}, C_{Gi}, D_{Gi}$	group constants in Eq. (3)
$A_{GMi}, B_{GMi}, C_{GMi}, D_{GMi}$	group constants in Eq. (4)
a_i, b_i, c_i, d_i	predictive group constants in Eq. (5)
f_0, f_1, f_2, f_3	constants of functional-group correction factor
C_a	carbon atom on an aromatic ring
C_d	carbon atom connected with a double bond
C_{d2}	carbon atom connected with two double bonds
C_r	carbon atom on a cycloalkane ring
C_{rd}	carbon atom connected with a double bond on a cyclane
C_t	carbon atom connected with a triple bond
d	average absolute percentage deviation
d_{ov}	overall average absolute percentage deviation
F	objective function
ΔH_v	heat of vaporization
K	number of data points
M	molecular weight
N_{cs}	number of carbon atoms on substituents of benzene

N_{bs}	number of branched alkyl-substituents on benzene
N_{cs}	number of neighboring alkyl-substituents on benzene
N_{cm}	number of carbon atoms in a molecule
P	vapor pressure in kPa
$P(\text{exp})$	experimental vapor pressure in kPa
$P(\text{cal})$	calculated vapor pressure in kPa
Q	specific compound corrections
q_i	specific compound correction of correction type i
R	gas constant
s_0, s_1, s_2, s_3	constants of structure correction factor in Eq. (6a)
$T(\text{K})$	temperature in Kelvin
T	$T(\text{K})/100$
ΔZ_v	change of compressibility factor in Eq. (1)

Greek letters

$\alpha_i, \beta_i, \gamma_i, \delta_i$	correction constants for correction type i
ξ	correction factor in Eq. (6)

Subscripts

bs	branched alkyl-substituents
cm	carbon atom
cs	carbon atoms on substituents
es	neighboring alkyl-substituents
i	summation index
j	summation index
n	non-ring compounds
ov	overall
r	ring compounds
1	structural correction
2	functional group correction

References

- Ambrose, D. and Ghiassee, N.B., 1987. Vapor pressures and critical temperatures and critical pressures of some alkanolic acids: C_1 to C_{10} . *J. Chem. Thermodyn.*, 19: 505–519.
- Ambrose, D. and Ghiassee, N.B., 1990. Vapor pressures, critical temperatures and critical pressures of benzyl alcohol, octan-2-ol and 2-ethylhexan-1-ol. *J. Chem. Thermodyn.*, 22: 307–311.
- Ambrose, D. and Sprake, C.H.S., 1970. Thermodynamic properties of organic oxygen compounds XXV. Vapor pressures and normal boiling temperatures of aliphatic alcohols, *J. Chem. Thermodyn.*, 2: 631–645.
- Ambrose, D. and Sprake, C.H.S., 1974. Thermodynamic properties of organic oxygen compounds. 32. Vapor pressure and second virial coefficient of propanal. *J. Chem. Thermodyn.*, 6: 453–456.
- Ambrose, D., Ellender, J.H. and Sprake, C.H.S., 1974a. Thermodynamic properties of organic oxygen compounds XXXV. Vapor pressures of aliphatic alcohols. *J. Chem. Thermodyn.*, 6: 909–914.

- Ambrose, D., Sprake, C.H.S. and Townsend, R., 1974b. Thermodynamic properties of organic oxygen compounds XXXVII. Vapor pressure of methanol, ethanol, pentan-1-ol and octan-1-ol from the normal boiling temperature to the critical temperature. *J. Chem. Thermodyn.*, 7: 185–190.
- Ambrose, D., Ellender, J.H., Lees, E.B., Sprake, C.H.S. and Townsend, R., 1975a. Thermodynamic properties of organic oxygen compounds XXXVIII. Vapor pressures of some aliphatic ketones. *J. Chem. Thermodyn.*, 7: 453–472.
- Ambrose, D., Sprake, C.H.S. and Townsend, R., 1975b. Thermodynamic properties of organic oxygen compounds XXXIII. Vapor pressure of acetone. *J. Chem. Thermodyn.*, 7: 185–190.
- Ambrose, D., Ellender, J.H., Sprake, C.H.S. and Townsend, R., 1977. Thermodynamic properties of organic oxygen compounds XLV. The vapor pressure of acetic acid. *J. Chem. Thermodyn.*, 9: 735–741.
- Ambrose, D., Ellender, J.H., Gundry, H.A., Lee, D.A. and Townsend, R., 1981. Thermodynamic properties of organic oxygen compounds LI. The vapor pressures of some esters and fatty acids. *J. Chem. Thermodyn.*, 13: 795–802.
- Ambrose, D., Giassee, N.B. and Tuckerman, R., 1988. Vapor pressure and critical temperature and critical pressure of 4-methylpentan-2-one. *J. Chem. Thermodyn.*, 20: 767–768.
- Askonas, C.F. and Daubert, T.E., 1988. Vapor pressure determination of eight oxygenated compounds. *J. Chem. Eng. Data*, 33: 225–229.
- Apiazu, Y., Royo, F. and Gutierrez Losa, C., 1984. Vapor pressures of (tetrachloromethane + α,ω -dichloroalkane). *J. Chem. Thermodyn.*, 16: 561–565.
- Besley, L.M. and Bottomley, G.A., 1974. Vapor pressure of toluene from 273.15 to 298.15 K. *J. Chem. Thermodyn.*, 6: 577–580.
- Chirico, R.D., Nguyen, A., Steele, W.V. and Strube, M.M., 1989. Vapor pressure of *n*-alkanes revisited. New high-precision vapor pressure data on *n*-decane, *n*-eicosane, *n*-octacosane. *J. Chem. Eng. Data*, 34: 149–156.
- Day, H.O. and Felsing, W.A., 1950. Some vapor pressures and the critical constants of trimethylamine. *J. Am. Chem. Soc.*, 72: 1698–1699.
- Francesconi, R., 1988. Excess thermodynamic properties for the binary system 1,4-dioxane–acetonitrile at 40°C. *J. Chem. Eng. Data*, 33: 80–83.
- Fredenslund, A., Gemhling, J. and Rasmussen, P., 1977. Vapor–Liquid Equilibria using UNIFAC. Elsevier, Amsterdam.
- Garcia-Sanchez, F. and Trejo, A., 1987. Vapor pressure and critical constants of 1,1-dichloroethane. *J. Chem. Thermodyn.*, 19: 359–361.
- Golding, P.D. and Machin, W.D., 1987. The vapor pressure of benzene. Part 2. Saturated vapor pressures from 279 to 300 K. *J. Chem. Soc., Faraday Trans. 1*, 83: 2719–2726.
- Goodwin, R.D., 1988. Benzene thermophysical properties from 279 to 900 K at pressures to 1000 bar. *J. Phys. Chem. Ref. Data*, 17: 1541–1636.
- Hugill, J.A. and McGlashan, M.L., 1978. The vapor pressure from 451 K to the critical temperature and the critical pressure of cyclohexane. *J. Chem. Thermodyn.*, 10: 95–100.
- Jahangiri, M., Jacobsen, R.T., Stewart, R.B. and McCarty, R.D., 1986. A thermodynamic property formulation for ethylene from the freezing line to 450 K at pressures to 260 MPa. *Int. J. Thermophys.*, 7: 491–501.
- Jensen, T., Fredenslund, A. and Rasmussen, P., 1981. Pure-component vapor pressures using UNIFAC group contribution. *Ind. Eng. Chem., Fundam.*, 20: 239–246.
- Kooner, Z.S. and Alexander Van Hook, W., 1986. Apparatus to measure vapor pressure, differential vapor pressure, liquid molar volume and compressibility of liquids and solutions to the critical point. Vapor pressures, molar volumes and compressibilities of protiobenzene and deuteriobenzene at elevated temperatures. *J. Phys. Chem.*, 90: 4860–4865.
- Kratzke, H. and Muller, S., 1985. Thermodynamic properties of acetonitrile 2. (P , ρ , T) of saturated and compressed liquid acetonitrile. *J. Chem. Thermodyn.*, 17: 151–158.
- Lainez, A., Miller, J.F., Zollweg, J.A. and Streett, W.B., 1987. Volumetric and speed-of-sound measurements for liquid tetrachloromethane under pressure. *J. Chem. Thermodyn.*, 19: 1251–1260.
- Liley, P.E., 1982. Thermodynamic properties of methanol. *Chem. Eng.*, 29: 59–60.

- Lin, D.C.K., Silberberg, I.H. and McKetta, J.J., 1970. Volumetric behavior, vapor pressures and critical properties of cyclopropane. *J. Chem. Eng. Data*, 15: 483–492.
- Malaspina, L., Gigli, R. and Bardi, G., 1973. Microcalorimetric determination of the enthalpy of sublimation of benzoic acid and anthracene. *J. Chem. Phys.*, 59: 387–394.
- Marquardt, D.W., 1963. An algorithm for least-square estimation of nonlinear parameters. *J. Soc. Ind. Appl. Math.*, 11: 431–436.
- Meyer, E.F. and Hotz, C.A., 1976. Cohesive energies in polar organic liquids. 3. Cyclic ketones. *J. Chem. Eng. Data*, 21: 274–279.
- Mills, P.L. and Fenton, R.L., 1987. Vapor pressures, liquid densities, liquid heat capacities, and ideal gas thermodynamic properties for 3-methylhexanal and 3,4-dimethylpentanal. *J. Chem. Eng. Data*, 32: 266–273.
- Mills, P.L., Fenton, R.L. and Schaefer, G.F., 1987. Physical and thermodynamic properties for novel C₁₄ unsaturated aldehydes and C₁₆ saturated amines. *J. Chem. Eng. Data*, 32: 251–265.
- Mousa, A.H.N., 1987. Critical properties, heat of vaporization and vapor pressure of ethanol from 20 kPa to the critical point. *J. Chem. Eng. Jpn.*, 20: 635–637.
- Munday, E.B., Mullins, J.C. and Edle, D.D., 1980. Vapor pressure data for toluene, 1-pentanol, 1-butanol, water and 1-propanol and for the water and 1-propanol system from 273.15 K to 323.25 K. *J. Chem. Eng. Data*, 25: 191–194.
- Myers, H.S. and Fenske, M.R., 1955. Measurement and correlation of vapor pressure data for high boiling hydrocarbons. *Ind. Eng. Chem.*, 47: 1652–1658.
- Osborn, A.G. and Douslin, D.R., 1966. Vapor pressure relations of 36 sulfur compounds present in petroleum. *J. Chem. Eng. Data*, 11: 502–509.
- Osborn, A.G. and Douslin, D.R., 1974. Vapor-pressure relations for 15 hydrocarbons. *J. Chem. Eng. Data*, 19: 114–117.
- Osborn, A.G. and Scott, D.W., 1980. Vapor pressures of 17 miscellaneous organic compounds. *J. Chem. Thermodyn.*, 12: 429–438.
- Oscarson, J.L., Lundell, S.O. and Cunningham, J.R., 1987. Phase equilibria for ten binary systems. *AIChE Symp. Ser.*, 83: 1–17.
- Perry, R.H. and Chilton, C.H., 1973. *Chemical Engineers' Handbook*, 5th edn. McGraw-Hill, New York.
- Reid, R.C., Prausnitz, J.M. and Poling, B.E., 1987. *The Properties of Gases and Liquids*, 4th edn. McGraw-Hill, New York, Chapter 7.
- Sachek, A.I., Markovnik, V.S., Peshchenko, A.D., Shvaro, O.V. and Andreevskii, D.N., 1984. Vapor pressure of secondary C₅–C₈ alcohols of normal structure. *Sov. Chem. Ind.*, 16: 705–715.
- Salerno, S., Cascella, M., May, D., Watson, P. and Tassios, D., 1986. Prediction of vapor pressures and saturated volumes with a simple cubic equation of state: Part I: A reliable Database. *Fluid Phase Equilibria*, 27: 15–34.
- Stein, S.E., 1981. Application of additive estimation methods to vaporization properties of liquids *n*-alkane. *J. Chem. Soc., Faraday Trans. 1*, 77: 1457–1467.
- Thomas, L.H., Meatyard, R., Smith, H. and Davies, G.H., 1979. Vapor pressures and molar entropies of vaporization of monohydric alcohols. *J. Chem. Eng. Data*, 24: 159–161.
- Thomson, G.W.M., 1946. The Antoine equation for vapor pressure data. *Chem. Rev.*, 38: 1–39.
- Vargaftik, N.B., 1975. *Tables on the Thermophysical Properties of Liquids and Gases*, 2nd edn. Wiley, New York.
- Varughese, B. and Sommerfeld, J.T., 1989. Vapor pressure of pivalaldehyde. *J. Chem. Eng. Data*, 34: 25–26.
- Yair, O.B. and Fredenslund, A., 1983. Extension of the UNIFAC group-contribution method for the prediction of pure-component vapor pressures. *Ind. Eng. Chem., Process Des. Dev.*, 22: 433–436.

Appendix A: Use of the method

The proposed method can be used to calculate the vapor pressures of any organic compound with the necessary groups that are available.

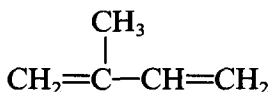
Table A1

The various groups and their contribution constants

Group	No.	a_i	b_i	c_i	d_i
CH ₃	1	11.7714	-12.5737	2.2841	-0.2608
C _d H ₂	2	11.2767	-11.1067	1.5073	-0.0519
C _d H	1	5.6569	-12.5108	3.8423	-0.5502
C _d	1	-7.6052	-2.6065	-0.6709	0.0722
Σ		32.3765	-49.9044	8.4701	-0.8426
Q ^a		1.5443	-3.4154	1.0490	-0.1502
Total		33.9208	-53.3198	9.5191	-0.9928

^a Structural correction for 1,3-diene.*Example 1*

Estimation of the vapor pressure of 2-methyl-1,3-butadiene (molecular weight = 68.119 kDa). The experimental vapor pressure is 60.747 kPa at 20°C (Vargaftik, 1975). The molecular structure is



The various groups and their contributions to the constants A , B , C and D are given in Table A1.

$$\ln(PM)(\text{kPa}) = (A + B/T - C \ln T - DT) \quad T = T(\text{K})/100$$

$$= [33.9208 - 53.3198/(T/100) - 9.5191 \ln(T/100) + 0.9928(T/100)]$$

At $T = 293.15$ K, $P(\text{exp}) = 60.747$ kPa and $P(\text{cal}) = 65.574$ kPa.

$$\% \text{ error} = [(65.574 - 60.747)/60.747]100 = 7.95\%.$$

Example 2

Estimation of the vapor pressure of 1,2-diisopropylbenzene (molecular weight = 162.276 kDa). The experimental vapor pressure is 5.333 kPa at 114.0°C (Perry and Chilton, 1973). The molecular structure is

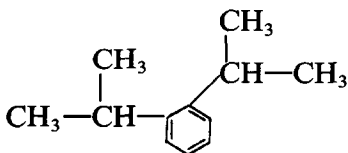


Table A2

The various groups and their contribution constants

Group	No.	a_i	b_i	c_i	d_i
CH ₃	4	11.7714	−12.5737	2.2841	−0.2608
CH	2	−4.4782	−5.1317	1.9526	−0.2331
C _a H	4	12.9190	−20.0023	6.9269	−0.8458
C _a	2	−10.7912	4.9887	−5.3565	0.8294
Σ		68.2228	−130.5900	30.0362	−3.2338
Q ^a		0.8417	−0.3891	0.4178	−0.0660
Total		69.0645	−130.9791	30.4540	−3.2998

^a Structural correction for branched alkylbenzenes; $n_{cs} = 6$, $N_{bs} = 2$, $N_{es} = 1$, $\xi_1 = 0.078$, $Q = \xi_1 \times q_1$.

The various groups and their contributions to the constants A , B , C and D are given in Table A2.

$$\ln(PM)(\text{kPa}) = (A + B/T - C \ln T - DT) \quad T = T(\text{K})/100$$

$$= \{69.0645 - 130.9791/(T/100) - 30.4540 \ln(T/100) + 3.2998(T/100)\}$$

At $T = 387.15$ K, $P(\text{exp}) = 5.333$ and $P(\text{cal}) = 5.447$ kPa

$$\% \text{ error} = [(5.447 - 5.333)/5.333]100 = 2.14\%.$$

Example 3

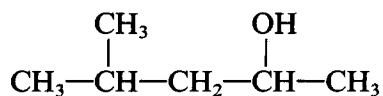
Estimation of the vapor pressure of 4-methyl-2-pentanol (molecular weight = 102.18 kDa). The experimental vapor pressure is 0.0973 kPa at 6.3°C (Thomas et al., 1979). The molecular structure is

Table A3

The various groups and their contribution constants

Group	No.	a_i	b_i	c_i	d_i
CH ₃	3	11.7714	−12.5737	2.2841	−0.2608
CH ₂	1	3.2193	−9.0445	1.3134	−0.0660
CH	1	−4.4782	−5.1317	1.9526	−0.2331
CHOH	1	50.8829	−99.9544	29.3664	−3.0041
Σ		84.9382	−151.8517	39.4847	−4.0856
Q ^a		−2.2471	6.3131	−0.9167	0.0461
Total		82.6911	−145.5386	38.5680	−4.0395

^a Functional group correction for secondary alcohols; $N_{cm} = 6$, $\xi_2 = -0.698$, $Q = \xi_2 \times q_2$ of secondary alcohols.



The various groups and their contributions to the constants A , B , C and D are given in Table A3.

$$\begin{aligned} \ln(PM)(\text{kPa}) &= (A + B/T - C \ln T - DT) & T &= T(\text{K})/100 \\ &= [82.6911 - 145.5386/(T/100) - 38.5680 \ln(T/100) + 4.0395(T/100)] \end{aligned}$$

At $T = 279.45 \text{ K}$, $P(\text{exp}) = 0.0973 \text{ kPa}$ and $P(\text{cal}) = 0.0942 \text{ kPa}$.

$$\% \text{ error} = [(0.0942 - 0.0973)/0.0973]100 = 3.17\%.$$