Correlations

An Expression for Ratio of Critical Temperature to Critical Pressure with the Heat Capacity for Low to Medium Molecular Weight Compounds

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In this paper, a new correlation for prediction of the ratio of critical temperature to critical pressure has been developed in terms of heat capacity at 298.15 K, which is readily available for many compounds. The correlation has been applied for more than 100 low to medium size compounds. The results of these estimations validate the generalization of this correlation. The comparison between predicted and available experimental data shows an absolute relative error of 4.69 %. The results show that the accuracy of the proposed correlation is similar to the methods of Constantinou and Gani,[7] Ambrose,[2,3] and Joback[5] for various types of compounds.

Introduction

In the application of thermodynamic equations of state, one must have knowledge of critical temperature and critical pressure. The critical constants are key parameters in the prediction of thermodynamic and transfer properties via the principle of the corresponding state. They are also of importance in equation of state calculations and in the design of processes for supercritical fluid extraction. They are often used in composition-dependent mixing rules for the parameters to describe mixtures. Critical temperature and pressure are widely used in estimation of pure component constants. Many of the estimation methods are based on the group contribution concept and require knowledge of the boiling point and structure of the substance. Examples of such methods include those of Lydersen,[1] Ambrose,[2,3] Fedors,[4] Joback,[5] Somayajulu,[6] and Constantinou and Gani.[7]

One of the first successful group contribution methods to estimate critical properties was developed by Lydersen.[1] Joback[5] suggested a modification of Lydersen's[1] method. This method depends on the group contribution method. Joback[5] reevaluated Lydersen's[1] scheme, added several functional groups, and determined the new values of the group contributions. His proposed relations are

$$T_C = T_B\left[0.584 + 0.965\sum\Delta_T - \left(\sum\Delta_T\right)^2\right]^{-1} \tag{1}$$

$$P_C = \left(0.113 + 0.0032n_A - \sum\Delta_P\right)^{-2} \tag{2}$$

The units employed for T_C and P_C are, respectively, Kelvin and bar. n_A is the number of atoms in the molecule. The Δ quantities are evaluated by summing contributions for various atoms or groups of atoms.

Ambrose[2,3] suggested another estimated method including a group contribution technique using the following correlations

$$T_C = T_B\left[1 + \left(1.242 + \sum\Delta_T\right)^{-1}\right] \tag{3}$$

$$P_C = M\left[0.339 + \sum\Delta_P\right]^{-2} \tag{4}$$

where T_C and P_C are, respectively, in Kelvin and bar. In employment of correlations, the normal boiling point T_B (at 1 atm) and molecular weight M are needed. The Joback[5] and Ambrose[2,3] methods perform well for low-to-medium molecular weight compounds. Their validity for high molecular weight and/or structurally complex compounds is not yet clear.[8] The estimation of the critical properties with the methods of Lydersen,[1] Ambrose[2,3] (see Reid et al.[9]), and Joback and Reid[10] (and others, e.g., Klincewicz and Reid;[11] Somayajulu[6]) requires accurate values for the normal boiling point, which is usually not available for high molecular weight compounds. The recent group contribution method by Constantinou and Gani[7] is more general in the sense that the critical temperature (and pressure) is estimated only from the structure of the compound.

Constantinou and Gani[7] developed an advanced group contribution method based on the UNIFAC groups. It is more accurate than the methods of Klincewicz and Reid[11] and Lydersen.[1] They suggested the following correlations

$$\exp(T_C/181.128) = \sum_i N_i t_{c1i} + \sum_j M_j t_{c2j} \tag{5}$$

$$(P_C - 1.3705)^{-0.5} - 0.100220 = \sum_i N_i p_{c1i} + \sum_j M_j p_{c2j} \tag{6}$$

where T_C and P_C are, respectively, in Kelvin and bar. In these equations, N_i and M_j are number of occurrences of the type-*i* first-order group and the type-*j* second-order group in a compound, respectively. t_{c1i}, t_{c2j} and p_{c1i}, p_{c2j} are contributions of the type-*i* and type-*j* for estimation of the critical temperature and critical pressure, respectively. In the group contribution method proposed by Constantinou and Gani[7]—except from the classical UNIFAC main and subgroups which are called first-order groups—second-order groups have been incorporated for the differences of the physical properties among the isomers to be captured. Unlike the methods proposed by Joback and Reid[10] and Ambrose[2,3] (see Reid et al.[9]), Constantinou and Gani[7] gave some emphasis on the proper extrapolation of the critical

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Table 1. Absolute Deviation between Experimental and Predicted Critical Temperature (K) and Critical Pressure (bar) by Various Group Contribution Methods

		Constantinou and Gani		Ambrose		Joback	
compound	ref	ΔT_C	ΔP_C	ΔT_C	ΔP_C	ΔT_C	ΔP_C
nC_{48}	12	0.00	[a]	24	[a]	349	[a]

[a] Lack of experimental data.

properties at high molecular weight; thus, their method may be more useful for high molecular weight compounds (see in Table 1). This point is not confirmed yet by literature evidence based on thorough evaluation/comparison of the above estimation methods for heavy/complex compounds.[8]

Elhassan et al.[13] developed a correlation for *n*-alkanes which is based on the fact that the quantities of T_C/P_C are proportional to the molecular weight for each homologous series. The proposed relation is

$$\ln(T_C/P_C) = -3.70171 + 1.38315 \ln(M + 25.3538) \quad (7)$$

Kontogeorgis et al.[8] suggested that the ratio T_C:P_C can be expressed in terms of the van der Waals surface area that is estimated using the group increments given by Bondi[14] and are readily available in all UNIFAC tables (e.g., Fredeslund et al.[15]) for any compounds. The method is suitable for medium to high molecular weight compounds. The proposed relation is

$$T_C/P_C = 9.0673 + 0.43309(Q_w^{1.3} + Q_w^{1.95}) \quad (8)$$

where T_C is in K; P_C is in bar; and Q_w is the van der Waals surface area.

Due to deficiencies and problems of available group contribution estimation methods for the critical properties, we suggest a correlation that tackles the problem of estimating the critical properties in a different and simpler way. We observed that, unlike the critical properties alone, the ratio T_C:P_C follows a regular trend with the ratio of heat capacity at 298.15 K to the universal gas constant for low-to-medium molecular weight compounds.

The rest of the paper is organized as follows. The correlation of T_C:P_C with the heat capacity of real gas at 298.15 K is presented, and an application of proposed correlation and comparison with other methods is given. We end with discussion of our results and the conclusions.

New Correlation

According to the above correlations, the critical temperature and pressure are dependent on the molecular structure of components. To propose a more general and simple correlation, a term that corresponds to the molecular structure can be used. The heat capacity could be related to the structure of the compounds.[16−21] Joback[5] suggested a group contribution method for the polynomial coefficient of heat capacity of ideal gases as follows

$$C_p(T) = \left(\sum_j n_j\Delta_a - 37.93\right) + \left(\sum_j n_j\Delta_b + 0.210\right)T + \left(\sum_j n_j\Delta_c - 3.91\cdot10^{-4}\right)T^2 + \left(\sum_j n_j\Delta_d + 2.06\cdot10^{-7}\right)T^3 \quad (9)$$

where n_j is the number of groups of the *j*th type and the Δ contributions are for the *j*th atomic or molecules group. The temperature T is in Kelvin, and C_P is in $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. Yoneda[9] modified a group contribution technique for ideal heat capacity that was originally proposed by Anderson et al.[9,16] In this method, one begins with a base molecule and sequentially modifies the structure by substituting other groups to arrive at the final structure. Each substitution has a group contribution value, and values are summed to arrive at the final value of the heat capacity.

Table 2. Variety of Number of Data Points Used in This Study

compound type	no. of data points
hydrocarbons	79
oxygenated hydrocarbons	61
nitrogenated hydrocarbons	11
hydrocarbon sulfide and mercaptanes	7
halogenated hydrocarbons	8
inorganic	12
total	178

$$C_p(T) = \sum_j n_j\Delta_a + \left(\sum_j n_j\Delta_b\right)\left(\frac{T}{1000}\right) + \left(\sum_j n_j\Delta_c\right)\left(\frac{T}{1000}\right)^2 \quad (10)$$

Δ is the contribution, and n_j is the number of times the contribution is required. T is in Kelvin, and C_P is in $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$.

A group contribution method for estimating the ideal gas heat capacity just for hydrocarbons is employed by Thinh et al.[17,18] as the following equation

$$C_p(T) = \sum n_j\left[A + B_1\exp\left(\frac{-C_1}{T^{n_1}}\right) - B_2\exp\left(\frac{-C_2}{T^{n_2}}\right)\right] \quad (11)$$

where T is in Kelvin; C_P is in $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$; and A, B_1, B_2, C_1, C_2, n_1, and n_2 are constants for all hydrocarbon groups. This equation is a modified form suggested earlier by Yuan and Mok.[19] It is sometimes inconvenient to use because it can not be integrated analytically, and numerical techniques must be employed. For the estimation of ideal gas heat capacity, an accurate group contribution method was developed by Benson[20,21] and his colleagues. Contributions are given only for atoms with valences greater than unity. For each group, the key atom is given but followed by a notation specifying other atoms bonded to the key atom. The heat capacity is obtained by summing the necessary group contributions at the system temperature.

Using the aforementioned subjects, the heat capacity (C_P) is dependent on the molecular structure of each compound. Also, since the T_C:P_C ratio is dependent on the molecular structure, one can relate the T_C:P_C ratio to the heat capacity. An appropriate correlation for the ratio of the critical temperature to the critical pressure can be introduced in the form of

$$T_C/P_C = \varepsilon C_P/R \quad (12)$$

In this correlation, T_C is the critical temperature in Kelvin; P_C is the critical pressure in atm; R is the universal gas constant; C_P is the heat capacity of real gases at 298.15 K; and ε is the equation coefficient in $\text{K}\cdot\text{atm}^{-1}$. Note that the ratio of the heat capacity to the universal gas constant is dimensionless.

In this study, to obtain the equation coefficient (ε), an extensive database of critical temperature and pressure data together with heat capacities of real gases for low-to-medium molecular weight compounds is used.[22,23] Table 2 represents the variety of number of compounds used in this study. Values of RT_C/P_CC_P have been determined for the data training set which consist of 178 compounds (see Table 3). The data training set includes hydrocarbons (i.e., alkane, alkene, alkyne, and cyclo compounds), halogenated hydrocarbons, oxygenated hydrocarbons (i.e., ether, ketone, ester, alcohol, aldehyde, and carboxylic acid), nitrogenated hydrocarbons, hydrocarbon sulfide, mercaptanes, and inorganic compounds. As one can see in this table,

Table 3. Value of RT_C/P_CC_P and the Ratio T_C/P_C for 178 Components (Training Data Set) Based on Experimental Data, Estimated by Correlation (Equation 13) and Various Group Contribution Methods, Together with Values for Relative Errors, RE = $((T_C/P_C)_{exp} - (T_C/P_C)_{calc})/((T_C/P_C)_{exp})$

			(RT_C/P_CC_P)	$(T_C/P_C)/K \cdot atm^{-1}$						100 RE				
compd no.	chemical special	chemical formula	$K \cdot atm^{-1}$	Exp.	predicted by eq 13	Joback[5]	Cons. & Gani[7]	Ambrose[2,3]	Kontogeorgis et al.[8]	predicted by eq 13	Joback[5]	Cons. & Gani[7]	Ambrose[2,3]	Kontogeorgis et al.[8]
1	Methane	CH_4	0.9802	4.2067	4.3959					4.4977				
2	Ethane	C_2H_6	1.0121	6.3787	6.6443	6.0042	6.3461	6.5584	11.288	4.1633	6.3193	0.5109	2.8185	76.977
3	Propane	C_3H_8	1.0072	8.9010	9.2725	8.5763	7.7471	8.9226	12.544	4.1732	3.8352	12.963	0.2427	40.928
4	*n*-Butane	C_4H_{10}	0.9658	11.425	12.157	11.021	10.781	11.613	14.055	6.4105	3.5353	5.6432	1.6454	23.017
5	*n*-Pentane	C_5H_{12}	0.9829	14.164	14.530	13.891	13.678	14.442	15.816	2.5865	1.9890	3.4274	1.9662	11.666
6	*n*-Octane	C_8H_{18}	1.0368	23.329	22.021	22.750	22.974	23.305	22.555	5.6049	2.4805	1.5216	0.1040	3.3160
7	*n*-Nonane	C_9H_{20}	1.0349	26.081	24.785	24.964	26.346	26.508	25.276	4.9672	4.5326	1.0172	1.6365	3.0873
8	*n*-Decane	$C_{10}H_{22}$	1.0719	29.946	27.847	28.390	29.689	28.224	28.229	7.0081	5.5519	0.8590	5.7516	5.7330
9	1-undecene	$C_{11}H_{22}$	1.0559	31.369	30.005	31.692	31.591	31.151	29.740	4.3482	1.0270	0.7052	0.6945	5.1900
10	*n*-Undecane	$C_{11}H_{24}$	1.0733	33.203	31.596	33.391	33.551[a]	33.103	31.413	4.8379	0.5715	1.0494	0.3007	5.3902
11	*n*-Dodecane	$C_{12}H_{26}$	1.0874	36.632	35.486	36.139	37.386	36.455	34.827	3.1285	1.3827	2.0558	0.4833	4.9300
12	*n*-Tridecane	$C_{13}H_{28}$	1.1243	40.710	39.494	42.013	41.918	39.901	38.468	2.9855	3.1416	2.9657	1.9871	5.5090
13	*n*-Pentadecane	$C_{15}H_{32}$	1.1707	48.801	49.964	50.345	49.792	47.055	46.427	2.3845	3.1635	2.0311	3.5763	4.8645
14	2-Methylpropane	C_4H_{10}	0.9841	11.424	11.950	11.002	9.9074[a]	11.510	14.043	4.6072	3.8815	13.275	0.7576	22.930
15	2-Methylbutane	C_5H_{12}	0.9699	13.843	14.405	14.074	13.194	13.835	15.803	4.0612	1.6615	4.6881	0.0550	14.153
16	2,3-Dimethylbutane	C_6H_{14}	0.9715	16.185	16.565	16.018	15.449[a]	16.619	17.791	2.3482	1.0310	4.5449	2.6864	9.9200
17	2-Methylpentane	C_6H_{14}	0.9819	16.691	16.871	16.273	16.097[a]	16.698	17.807	1.0829	2.6054	3.5600	0.0396	6.6839
18	2,2-dimethylbutane	C_6H_{14}	0.9322	16.073	17.092	14.947	15.414	15.916	18.120	6.3413	7.0051	4.0984	0.9712	12.737
19	2,3-Dimethylpentane	C_7H_{16}	0.9829	18.905	18.913	19.343	19.170[a]	18.755	20.035	0.0435	2.2933	1.4046	0.7927	5.9780
20	2,4-Dimethylpentane	C_7H_{16}	0.9235	19.213	20.382	18.592	18.854	19.167	20.030	6.0879	3.2340	1.8690	0.2414	4.2510
21	2-methylhexane	C_7H_{16}	0.9813	19.669	19.666	18.621	19.291	19.683	20.047	0.0143	5.3312	1.9240	0.0679	1.9219
22	3-methylhexane	C_7H_{16}	0.9679	19.293	19.562	18.714	19.291	19.781	20.047	1.3966	3.0021	0.0120	2.5301	3.9089
23	3-ethylpentane	C_7H_{16}	0.9366	18.945	19.838	18.798	19.291	19.870	20.047	4.7148	0.7779	1.8259	4.8811	5.8190
24	2,2,3-trimethylbutane	C_7H_{16}	0.9165	18.237	19.530	17.437	18.066	18.934	20.383	7.0923	4.3830	0.9370	3.8231	11.765
25	2-methylheptane	C_8H_{18}	1.0019	22.857	22.330	22.267	22.535	22.783	22.530	2.3023	2.5810	1.4110	0.3235	1.4305
26	4-methylheptane	C_8H_{18}	0.9830	22.401	22.305	22.271	22.535	22.787	22.530	0.4255	0.5819	0.5969	1.7219	0.5770
27	3-ethylhexane	C_8H_{18}	0.9498	21.944	22.620	22.318	22.535	22.835	22.530	3.0810	1.7047	2.6926	4.0618	2.6723
28	2,2-dimethylhexane	C_8H_{18}	0.9594	22.013	22.461	21.733	21.733	21.886	24.052	2.0352	1.2709	1.2709	0.5775	9.2608
29	2,3-dimethylhexane	C_8H_{18}	0.9674	21.700	21.952	22.136	22.126	22.667	22.511	1.1650	2.0085	1.9652	4.4580	3.7372
30	2,4-dimethylhexane	C_8H_{18}	0.9347	21.902	22.950	21.784	22.126	22.307	22.511	4.7859	0.5374	1.0263	1.8509	2.7820
31	2,5-dimethylhexane	C_8H_{18}	0.9900	22.375	22.120	22.257	22.126	22.288	22.511	1.1391	0.5292	1.1105	0.3870	0.6080
32	3,3-dimethylhexane	C_8H_{18}	0.9237	21.483	22.774	22.027	21.733	22.182	24.052	6.0108	2.5325	1.1670	3.2530	11.958
33	3-ethyl-2-methylpentane	C_8H_{18}	0.9091	21.273	22.917	22.139	22.126	22.670	22.511	7.7321	4.0719	4.0142	6.5709	5.8219
34	2,2,3-trimethylpentane	C_8H_{18}	0.9242	20.905	22.138	21.957	21.316	22.068	22.899	5.9003	5.0321	1.9677	5.5622	9.5361
35	2,3,4-trimethylpentane	C_8H_{18}	0.9001	21.013	22.862	22.003	21.694	22.549	22.492	8.8017	4.7113	3.2400	7.3136	7.0393
36	2,3,3-Trimethylpentane	C_8H_{18}	0.9251	20.679	21.876	21.663	20.882[a]	20.710	22.904	5.7893	4.6008	0.9784	0.1508	10.760
37	2,2,4-Trimethylpentane	C_8H_{18}	0.9562	21.530	22.036	21.297	21.366[a]	21.507	22.904	2.3523	1.1043	0.7604	0.1053	6.3800
38	2-Methyloctane	C_9H_{20}	0.9963	25.741	25.470	25.616	25.868[a]	25.977	25.248	1.0526	0.4856	0.4950	0.9149	1.9141
39	2,2-Dimethylheptane	C_9H_{20}	0.9674	24.906	25.370	25.053	25.038[a]	25.047	25.671	1.8659	0.5885	0.5291	0.5665	3.0694
40	2,2,5-Trimethylhexane	C_9H_{20}	0.9769	24.772	24.952	24.994	23.398[a]	26.601	25.650	0.7291	0.8929	5.5483	7.3824	3.5410
41	2,2,3,4-Tetramethylpentane	C_9H_{20}	0.9395	23.731	24.847	25.046	24.525[a]	25.083	25.628	4.7032	5.5423	3.3465	5.6964	7.9955
42	2,3,3,4-Tetramethylpentane	C_9H_{20}	0.8659	23.033	26.313	25.757	24.525[a]	25.791	25.628	14.240	11.827	6.4781	11.973	11.268
43	3,3,5-Trimethylheptane	$C_{10}H_{22}$	0.9383	26.617	28.357	28.632	28.207	28.216	28.633	6.5391	7.5723	5.9724	6.0085	7.5746
44	Ethylene	C_2H_4	1.1009	5.6875	5.3939	5.3854				5.1624	5.6831			
45	1-Butene	C_4H_8	1.0248	10.532	10.684	10.262	10.675[a]	10.544	13.432	1.4467	2.6685	1.3541	0.1170	27.529
46	*cis*-2-Butene	C_4H_8	1.0813	10.409	10.052	10.595	10.500[a]	10.939	13.429	3.4261	1.7824	0.8756	5.0905	29.010
47	*trans*-2-Butene	C_4H_8	1.0134	10.644	10.901	10.325	10.490[a]	10.804	13.429	2.4221	2.9969	1.4468	1.5031	26.157
48	1-Pentene	C_5H_{10}	1.0178	13.228	13.239	13.096	13.298	13.420	15.096	0.0861	1.0243	0.5310	1.4478	14.116
49	1-Heptene	C_7H_{14}	1.0468	19.305	18.184	18.886	19.410[a]	19.333	19.159	5.8020	2.2483	0.5469	0.1480	0.7530
50	1-Octene	C_8H_{16}	1.0558	22.340	20.720	21.747	22.375[a]	22.205	21.551	7.2499	2.7644	0.1559	0.6063	3.5314
51	1-Nonene	C_9H_{18}	1.0801	25.798	23.410	25.374	25.044	25.785	24.180	9.2547	1.6922	2.9230	0.0493	6.2730
52	1-Decene	$C_{10}H_{20}$	1.0488	28.261	26.702	28.510	29.198[a]	28.644	27.042	5.5140	0.8837	3.3187	1.3576	4.3122
53	2-Methylpropene	C_4H_8	1.0051	10.639	10.980	10.392	10.825	10.637	13.780	3.2067	2.3999	1.7529	0.0184	29.520
54	2-Methyl-2-butene	C_5H_{10}	1.1176	14.119	12.904	13.218	13.847	13.632	15.485	8.6023	6.3779	1.9242	3.4442	9.6700
55	1,2-Butadiene	C_4H_6	1.0998	10.504	9.9784	9.9733	9.9857[a]	10.201	13.285	5.0041	5.0523	4.9343	2.8846	26.472

Table 3 Continued

			(RT_C/P_CC_P)	$(T_C/P_C)/\mathrm{K{\cdot}atm^{-1}}$						100 RE				
compd no.	chemical special	chemical formula	$\mathrm{K{\cdot}atm^{-1}}$	Exp.	predicted by eq 13	Joback[5]	Cons. & Gani[7]	Ambrose[2,3]	Kontogeorgis et al.[8]	predicted by eq 13	Joback[5]	Cons. & Gani[7]	Ambrose[2,3]	Kontogeorgis et al.[8]
56	1,3-Butadiene	C_4H_6	1.0982	10.018	9.5558	10.014	10.082[a]	10.048	12.847	4.6133	0.0426	0.6386	0.2988	28.234
57	2-Methyl-1,3-butadiene	C_5H_8	1.0325[b]	12.738	12.630	12.595	13.574[a]	12.686	14.794	0.8469	1.1442	6.5697	0.4014	16.148
58	Acetylene	C_2H_2	0.9610	5.0798	5.5280	5.2812				8.8237	3.9651			
59	1-Pentyne	C_5H_8	0.9154	11.692	13.033	11.643	12.056	12.407	14.807	11.469	0.4264	3.1139	6.1132	26.650
60	2-Pentyne	C_5H_8	1.1060	13.081	12.155	12.477	12.364[a]	12.365	14.820	7.0768	4.9074	5.4792	5.4761	13.296
61	1-Hexyne	C_6H_{10}	0.9272[b]	14.369	15.514	12.463	14.651	14.600	16.678	7.9712	15.497	1.9656	1.6130	16.070
62	2-Hexyne	C_6H_{10}	1.0764[b]	15.758	14.738	13.296	15.450	15.745	16.693	6.4715	15.875	1.9526	0.0762	5.9327
63	3-Hexyne	C_6H_{10}	1.0917[b]	15.570	14.395	14.823	14.897[a]	15.628	16.693	7.5421	5.1052	4.3217	0.3700	7.2100
64	Vinylacetylene	C_4H_4	1.0682[b]	9.4073	9.2418	9.1993	8.8659[a]	11.180	12.616	1.7593	2.2907	5.7543	18.846	34.110
65	Methylcyclopentane	C_6H_{12}	1.0853	14.281	13.388	13.541	14.054[a]	10.955	15.540	6.2519	5.5416	1.5899	23.291	8.8140
66	Ethylcyclopentane	C_7H_{14}	1.0601	16.972	15.977	17.824	17.695[a]	17.985	17.510	5.8593	5.0242	4.2583	5.9669	3.1710
67	*cis*-1,3-Dimethylcyclopentane	C_7H_{14}	1.0017	16.416	16.319	17.086	16.417[a]	17.888	17.490	0.5883	4.0831	0.0067	8.9659	6.5445
68	*trans*-1,3-Dimethylcyclopentane	C_7H_{14}	1.0053	16.476	16.320	17.048	16.417	17.845	17.490	0.9448	3.4756	0.3553	8.3137	6.1587
69	Cyclooctane	C_8H_{16}	1.0310	18.364	17.609	21.899	19.932	18.631	19.734	4.1067	19.250	8.5394	1.4556	7.4621
70	1,1-Dimethylcyclohexane	C_8H_{16}	1.0957[b]	20.373	18.323	18.259	19.502[a]	19.439	20.075	10.058	11.730	4.2751	4.5830	1.4870
71	Ethylcyclohexane	C_8H_{16}	1.0617[b]	20.303	18.810	21.161	20.626[a]	21.105	19.722	7.3491	4.1077	1.5928	3.9488	2.8606
72	1-Methylcyclopentene	C_6H_{10}	1.1013	13.297	12.385	13.395	14.523[a]	8.2904	13.815	6.8551	0.7398	9.2241	37.653	3.8983
73	Cyclohexene	C_6H_{10}	1.0636	12.934	12.466	13.225	13.978[a]	11.174	14.843	3.6171	2.2331	8.0740	13.609	14.759
74	Propylbenzene	C_9H_{12}	1.0967	20.211	18.173	19.873	21.485[a]	20.261	18.594	10.083	1.7224	6.2994	0.2434	7.9990
75	1,2,3-Trimethylbenzene	C_9H_{12}	1.0341	19.539	18.600	21.293	21.428[a]	22.066	19.221	4.8035	8.9741	9.6683	12.930	1.6252
76	1,2,4-Trimethylbenzene	C_9H_{12}	1.0919	20.237	18.269	20.953	20.577	19.178	18.825	9.7246	3.4622	1.6788	5.2359	6.9785
77	Isopropylbenzene	C_9H_{12}	1.1185	20.108	17.760	24.734	25.645[a]	20.300	18.578	11.672	18.948	27.532	0.9592	7.6110
78	Biphenyl	$C_{12}H_{10}$	1.0441[b]	20.718	19.478	22.970	27.493[a]	24.320	19.396	5.9825	9.9353	32.703	17.385	6.3778
79	Styrene	C_8H_8	1.1475[b]	16.869	14.793	16.339	18.386	17.752	15.417	12.303	3.2870	8.9984	5.2306	8.6070
80	2-Butanol	$C_4H_{10}O$	0.9466	12.932	13.848	12.206	12.057[a]	12.280	17.082	7.0880	6.0225	6.7620	5.0383	32.089
81	2-Propanol	C_3H_8O	0.9961	10.752	11.179	10.325	10.457[a]	10.597	15.162	3.9800	4.1928	2.7414	1.4386	41.015
82	2-Methyl-1-propanol	$C_4H_{10}O$	0.9372	12.904	13.946	12.478	13.204	12.508	17.077	8.0782	3.3032	2.3267	3.0704	32.338
83	2-Methyl-2-propanol	$C_4H_{10}O$	0.9414	12.855	13.842	12.442	11.987	11.479	17.387	7.6844	3.3578	6.7467	10.699	35.255
84	1-Pentanol	$C_5H_{12}O$	0.9777	15.346	15.694	15.023	16.043	15.304	19.260	2.2680	2.0987	4.5432	0.2711	25.505
85	2-Methyl-1-butanol	$C_5H_{12}O$	0.9280	14.792	15.914	14.634	16.010	15.029	19.244	7.5864	1.0937	8.2310	1.6059	30.090
86	2-Methyl-2-butanol	$C_5H_{12}O$	0.9078	14.566	16.009	13.579	15.128	13.762	19.579	9.9114	6.7768	3.8532	5.5236	34.414
87	3-Methyl-1-butanol	$C_5H_{12}O$	0.9432	14.996	15.877	14.700	16.010	15.027	19.244	5.8783	2.0368	6.7645	0.2116	28.327
88	1-Hexanol	$C_6H_{14}O$	0.9716	17.903	18.170	17.317	18.784	17.842	21.663	1.4949	3.4299	4.9237	0.3397	21.000
89	Phenol	C_6H_6O	0.9234	11.608	12.846	11.472		11.464	13.768	10.671	1.1961		1.2330	18.610
90	*m*-Cresol	C_7H_8O	1.0597	15.823	15.002	14.290	14.073	14.235	15.581	5.1836	10.867	11.055	10.035	1.5262
91	*p*-Cresol	C_7H_8O	0.9223	13.863	15.092	14.473	14.246	14.418	15.581	8.8703	4.2670	2.7592	4.0017	12.391
92	2-Ethylphenol	$C_8H_{10}O$	0.8992	16.561	18.162	16.776	19.275	16.867	17.977	9.6706	1.2985	16.390	1.8490	8.5480
93	3-Ethylphenol	$C_8H_{10}O$	0.9694	17.545	17.871	17.264	20.219[a]	17.349	17.977	1.8602	1.5992	15.239	1.1194	2.4589
94	4-Ethylphenol	$C_8H_{10}O$	0.9881	17.918	17.903	17.249	20.219[a]	18.039	17.977	0.0821	3.7328	12.839	0.6710	0.3250
95	3,5-Dimethylphenol	$C_8H_{10}O$	0.9433	17.552	18.336	17.691	22.236[a]	17.444	18.524	4.4678	0.7958	26.690	0.6146	5.5417
96	1-Decanol	$C_{10}H_{22}O$	0.9847	29.253	30.005	28.996	31.398	29.223	33.604	2.5711	0.8764	7.3344	0.1007	14.875
97	Dimethyl ether	C_2H_6O	0.9726	7.6926	8.3335	8.1921	7.4037	7.9337	11.814	8.3320	6.1787	3.7550	3.1351	53.583
98	Methyl *n*-propyl ether	$C_4H_{10}O$	0.9455[b]	12.801	13.736	12.611	12.429	12.761	14.807	7.3083	1.4804	2.9068	0.3060	15.674
99	Methyl isopropyl ether	$C_4H_{10}O$	0.9050[b]	12.099	13.581	12.665	11.317	12.137	14.795	12.250	4.5325	6.4638	0.3195	22.281
100	Methyl isobutyl ether	$C_5H_{12}O$	0.9352[b]	14.767	15.779	14.822	14.315[a]	15.439	16.961	6.8541	0.3758	3.0651	4.5507	14.854
101	Diethyl ether	$C_4H_{10}O$	0.9253	12.991	14.193	12.665	12.756[a]	12.816	14.807	9.2560	2.6050	1.8045	1.3613	13.980
102	Ethyl propyl ether	$C_5H_{12}O$	0.9234[b]	15.040	16.228	14.915	13.964[a]	15.235	16.678	7.9029	0.8506	7.1517	1.3016	10.893
103	Methyl phenyl ether	C_7H_8O	1.1332	15.319	13.717	13.040	15.939[a]	10.037	15.445	10.452	17.709	4.0430	34.480	0.8170
104	1-Propanal	C_3H_6O	1.0710[b]	10.387	10.122	10.302	9.2644[a]	9.0305	12.804	2.5434	0.8148	10.814	13.059	23.267
105	1-Pentanal	$C_5H_{10}O$	0.9551[b]	14.448	15.179	14.840	15.158	14.260	16.170	5.0653	2.6745	4.9131	1.3002	11.916
106	1-Heptanal	$C_7H_{14}O$	0.9547[b]	19.659	20.181	19.376	20.739	19.114	20.512	2.6568	1.4807	5.4918	2.7697	4.3402
107	1-Octanal	$C_8H_{16}O$	0.9342[b]	21.769	22.819	22.231	24.598	22.795	23.041	4.8248	2.1069	12.996	4.7114	5.8440
108	1-Nonanal	$C_9H_{18}O$	0.9341	24.332	25.701	25.480	26.299	25.220	25.805	5.6299	4.5627	8.0841	3.6496	6.0522
109	Methyl ethyl ketone	C_4H_8O	1.0611	13.169	12.698	12.725	13.046	12.989	14.363	3.5733	3.5414	0.9397	1.3659	9.0610
110	2-Pentanone	$C_5H_{10}O$	1.0557	15.323	14.624	15.298	15.659	15.337	16.170	4.5562	0.1688	2.1908	0.0917	5.5230

Table 3 Continued

			(RT_C/P_CC_P)	(T_C/P_C)/K·atm^{-1}						100 RE				
compd no.	chemical special	chemical formula	K·atm^{-1}	Exp.	predicted by eq 13	Joback[5]	Cons. & Gani[7]	Ambrose[2,3]	Kontogeorgis et al.[8]	predicted by eq 13	Joback[5]	Cons. & Gani[7]	Ambrose[2,3]	Kontogeorgis et al.[8]
111	Methyl isopropyl ketone	$C_5H_{10}O$	1.0813	14.591	13.695	14.746	14.411	15.055	16.155	6.1376	1.0594	1.2318	3.1817	10.718
112	Methyl isobutyl ketone	$C_6H_{12}O$	0.9973	17.705	17.556	17.429	17.467	17.904	20.854	0.8402	1.6040	1.3449	1.1221	17.785
113	3-Methyl-2-pantanone	$C_6H_{12}O$	1.0738[b]	17.487	16.226	15.283	17.521	17.998	18.205	7.2091	14.613	0.1992	2.9187	4.1029
114	Ethyl propyl ketone	$C_6H_{12}O$	0.9569	17.782	18.314	17.512	18.939	16.828	18.216	2.9923	1.5192	6.5078	5.3650	2.4427
115	Ethyl isopropyl ketone	$C_6H_{12}O$	0.9874	17.201	17.254	17.491	17.790[a]	18.040	18.205	0.3091	1.6874	3.4273	4.8825	5.8381
116	Diisopropyl ketone	$C_7H_{14}O$	1.0556[b]	19.072	17.842	19.853		20.582		6.4453	4.0966		7.9189	
117	*n*-Butyric acid	$C_4H_8O_2$	1.1041[b]	15.328	14.050	14.415	15.813	15.455	15.255	8.3346	5.9500	3.1683	0.8339	0.4710
118	2-Methylpropanoic acid	$C_4H_8O_2$	1.1376[b]	16.563	14.665	14.257	12.961	16.263	15.305	11.454	13.922	21.747	1.8112	7.5950
119	Methyl formate	$C_2H_4O_2$	1.0421[b]	8.2551	8.3461	8.7635	8.3898[a]	8.0030	12.048	1.1028	6.1589	1.6321	3.0529	45.956
120	Methyl acetate	$C_3H_6O_2$	1.0712	10.943	10.625	11.714	10.660	11.076	13.466	2.9054	6.6640	2.5874	1.2162	23.051
121	Methyl propanoate	$C_4H_8O_2$	0.9915	13.340	13.659	12.884	12.778[a]	13.508	15.135	2.3932	3.4182	4.2128	1.2652	13.455
122	Methyl *n*-butyrate	$C_5H_{10}O_2$	0.9964	16.145	16.152	16.026	15.889	15.609	17.051	0.0459	0.7509	1.5816	3.3151	5.6170
123	Methyl 2methylpropanoate	$C_5H_{10}O_2$	0.9930	15.971	16.044	15.556	15.293	15.637	17.032	0.4584	2.6016	4.2450	2.0949	6.6423
124	Ethyl propionate	$C_5H_{10}O_2$	1.0346	16.563	15.976	16.080	16.442	16.168	17.051	3.5386	3.0457	0.7343	2.3872	2.9459
125	Ethyl *n*-butyrate	$C_6H_{12}O_2$	1.0491[b]	19.679	18.474	18.436	18.716	18.702	19.210	6.1195	6.8318	4.8898	4.9633	2.3810
126	*n*-Propyl formate	$C_4H_8O_2$	1.0201	13.526	13.480	14.242	13.034	13.577	15.135	0.3346	5.0895	3.6402	0.3790	11.895
127	*n*-Propyl acetate	$C_5H_{10}O_2$	1.0105[b]	16.528	16.290	16.187	15.568	16.117	17.051	1.4363	2.1368	5.8083	2.4883	3.1660
128	*n*-Butyl acetate	$C_6H_{12}O_2$	1.0262[b]	18.868	18.134	18.884	18.691	18.879	19.210	3.8902	0.0810	0.9295	0.0585	1.8092
129	Propyl propanoate	$C_6H_{12}O_2$	1.0157	18.948	18.380	18.465	18.668	18.706	19.205	2.9960	2.5500	1.4760	1.2766	1.3552
130	Ethyl 2-methyl propanoate	$C_6H_{12}O_2$	0.9724[b]	18.247	18.481	17.392	18.351	18.104	19.188	1.2831	4.6832	0.5723	0.7838	5.1596
131	2-Methylpropyl ethanoate	$C_6H_{12}O_2$	0.9565[b]	17.983	18.514	18.161	18.351	18.422	19.188	2.9535	0.9879	2.0447	2.4378	6.6991
132	Pentyl methanoate	$C_6H_{12}O_2$	0.9921[b]	18.883	18.728	19.366	18.668	19.080	19.205	0.8201	2.5599	1.1335	1.0444	1.7075
133	3-Methylbutyl methanoate	$C_6H_{12}O_2$	0.9854[b]	18.706	18.681	19.051	18.351	18.779	19.188	0.1289	1.8449	1.8980	0.3882	2.5776
134	Vinyl acetate	$C_4H_6O_2$	1.1219[b]	13.384	12.251	13.077	10.498	12.501	14.450	8.4651	2.3814	21.559	6.5972	7.9670
135	Ethyl 3-methylbutanoate	$C_7H_{14}O_2$	1.0174	21.818	20.994	20.716	21.362	21.048	21.583	3.7768	5.0519	2.0911	3.5309	1.0757
136	Propyl butanoate	$C_7H_{14}O_2$	1.0206	21.863	20.971	20.189	21.669	21.519	21.602	4.0766	7.6556	0.8845	1.5707	1.1935
137	2-Methylpropyl propanoate	$C_7H_{14}O_2$	1.0043	21.966	21.406	20.812	21.362	21.166	21.583	2.5475	5.2534	2.7526	3.6417	1.7440
138	3-Methylbutyl butanoate	$C_9H_{18}O_2$	0.9976	26.911	26.736	27.417	27.876	27.223	25.777	0.6489	1.8771	3.5834	1.1578	4.2143
139	Ethylene oxide	C_2H_4O	1.1366[b]	6.5477	6.0544	7.4061	6.5163	5.3603		7.5341	13.110	0.4790	18.133	
140	Furan	C_4H_4O	1.1387	8.9485	8.2814	9.7340		11.364		7.4545	8.7791			
141	Methyl amine	CH_5N	0.9227	5.8505	6.6854	6.8946		5.9977	10.982	14.271	17.846		2.5161	87.726
142	Trimethyl amine	C_3H_9N	0.9695	10.707	11.417	10.051	10.344	10.492	11.484	6.6352	6.1268	3.3847	2.0080	7.2581
143	Ethylamine	C_2H_7N	0.9449	8.2682	9.1854	8.5622	8.4064	8.1961	12.164	11.093	3.4802	1.6721	0.8719	47.124
144	Butyl amine	$C_4H_{11}N$	0.9518	13.209	14.046	12.673	14.283	12.992	15.292	6.3368	4.0553	8.1313	1.6388	15.771
145	Diethyl amine	$C_4H_{11}N$	0.9845	13.710	14.089	13.082	13.103	12.487	15.323	2.7696	4.8678	4.4287	8.9220	11.761
146	Isobutyl amine	$C_4H_{11}N$	0.9334	13.317	14.400	12.338	12.484	12.764	15.891	8.1345	7.3539	6.2532	4.1538	19.330
147	Triethyl amine	$C_6H_{15}N$	0.9209	17.836	19.037	16.720	17.366	18.495	19.464	6.7352	6.7639	2.6374	3.6947	9.1270
148	*n*-Propylamine	C_3H_9N	0.9220	10.623	11.868	10.457	10.461[a]	10.453	13.604	11.726	1.6017	1.5180	1.5943	28.066
149	Di-*n*-propylamine	$C_6H_{15}N$	0.9413	17.919	18.731	17.682	18.596[a]	18.487	17.264	4.5314	1.3576	3.7782	3.1732	3.6500
150	Isopropylamine	C_3H_9N	0.8987[b]	10.530	12.051	9.8918	10.415[a]	10.426	13.593	14.453	6.0600	1.0841	0.9925	29.077
151	*N*-Methylaniline	C_7H_9N	0.9087[b]	13.696	15.130	16.324	16.396	17.656	15.985	10.469	16.312	19.711	28.916	16.712
152	Methyl mercaptan	CH_4S	1.0896	6.5861	6.3647	7.3608	6.8911	6.8583	11.247	3.3609	11.762	4.6309	4.1329	70.775
153	Ethyl mercaptan	C_2H_6S	1.0490	9.2125	9.2173	9.1608	8.7757[a]	9.1952	12.492	0.0520	0.5715	4.7404	0.1869	35.608
154	Isobutyl mercaptan	$C_4H_{10}S$	0.9764[b]	13.950	14.418	13.456	13.003	12.403	15.733	3.3579	3.7266	6.7892	11.093	12.784
155	sec-Butyl mercaptan	$C_4H_{10}S$	0.9609[b]	13.826	14.510	12.953	15.045	14.318		4.9511	6.8237	8.8195	3.5649	
156	Dimethyl sulfide	C_2H_6S	1.0351	9.2171	9.3395	9.9383	9.2103	9.2111	12.492	1.3278	7.3538	0.0729	0.0642	35.541
157	Methyl ethyl sulfide	C_3H_8S	1.1089[b]	12.677	11.784	11.975	11.412[a]	11.765	13.995	7.0415	5.9383	9.9801	7.1907	10.393
158	Diethyl sulfide	$C_4H_{10}S$	1.0123	14.255	14.231	14.307	15.045	14.316	15.747	0.1635	0.3664	5.5358	0.4283	10.462
159	Chloroethane	C_2H_5Cl	1.1372	8.5430	7.9241	9.7018	9.2334	9.1395	12.232	7.2447	13.565	8.0823	6.9828	43.191
160	Bromoethane	C_2H_5Br	1.0520	8.1157	8.1333	9.0591	8.2207	7.8942	12.503	0.2166	10.552	1.2941	2.7282	54.061
161	1-Chloropropane	C_3H_7Cl	1.0914	11.131	10.608	12.041	11.243	11.014	13.686	4.6912	8.1788	1.0031	1.0540	22.951
162	2-Chloropropane	C_3H_7Cl	1.0473[b]	10.545	10.483	11.484	10.740[a]	11.956	13.674	0.5876	8.9046	1.8492	13.466	27.976
163	1,1-Dichloropropane	$C_3H_6Cl_2$	1.1270	13.382	12.198	13.253	13.516	13.259	14.990	8.8407	0.9873	1.0035	0.9196	12.015
164	1,2-Dichloropropane	$C_3H_6Cl_2$	1.1586	13.701	12.153	14.298	12.883[a]	14.041	14.964	11.294	4.2266	5.9707	2.4819	9.2150
165	1-Chloropentane	$C_5H_{11}Cl$	1.0586	16.842	15.887	17.348	16.316	17.405	17.336	5.6697	3.0006	3.1215	3.3446	2.9338
166	Fluorobenzene	C_6H_5F	1.0996[b]	12.500	11.723	12.981	12.417	12.790	9.9595	6.2098	3.7567	0.6622	2.3252	20.324

Table 3 Continued

compd no.	chemical special	chemical formula	(RT_C/P_CC_P) K·atm^{-1}	(T_C/P_C)/K·atm^{-1} Exp.	predicted by eq 13	Joback[5]	Cons. & Gani[7]	Ambrose[2,3]	Kontogeorgis et al.[8]	100 RE predicted by eq 13	Joback[5]	Cons. & Gani[7]	Ambrose[2,3]	Kontogeorgis et al.[8]
167	Air		1.0153[b]	3.5410	3.4487					2.6066				
168	Oxygen	O_2	0.8840	3.1201	3.4988					12.136				
169	Nitrogen	N_2	1.0765	3.7720	3.4682					8.0538				
170	Ammonia	NH_3	0.8504	3.6374	4.3792					20.393				
171	Nitrous oxide	N_2O	0.9263	4.3087	4.8105					11.645				
172	Cyanogen	C_2N_2	0.9937[b]	6.8258	7.2499					6.2131				
173	Carbon monoxide	CO	1.1010	3.8591	3.4696					10.093				
174	Carbon dioxide	CO_2	0.9311	4.1711	4.6133					10.601				
175	Hydrogen chloride	HCl	1.1224	3.9348	3.4703					11.804				
176	Hydrogen sulfide	H_2S	1.0225	4.2053	4.1877					0.4193				
177	Sulfur dioxide	SO_2	1.1569	2.5529	1.8759					26.518				
178	Sulfur trioxide	SO_3	0.9959	6.0727	6.4226					5.7617				

[a] Estimated by the second-order group contribution method. [b] In column 4, is obtained from ref 22 and other values from ref 23.

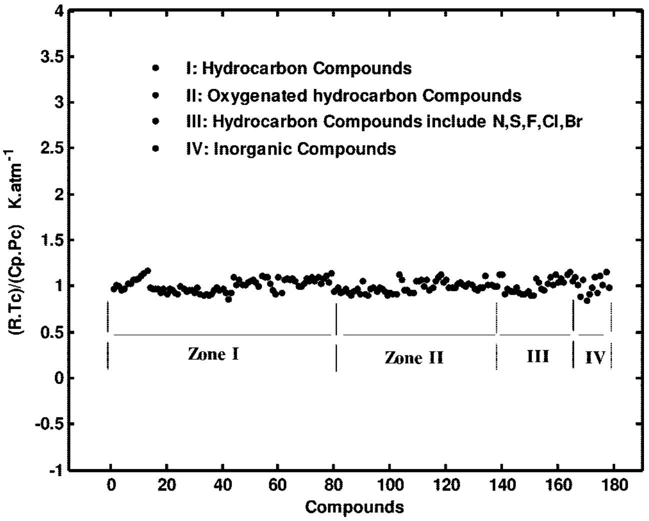

Figure 1. Correlation of RT_C/P_CC_P for 178 compounds

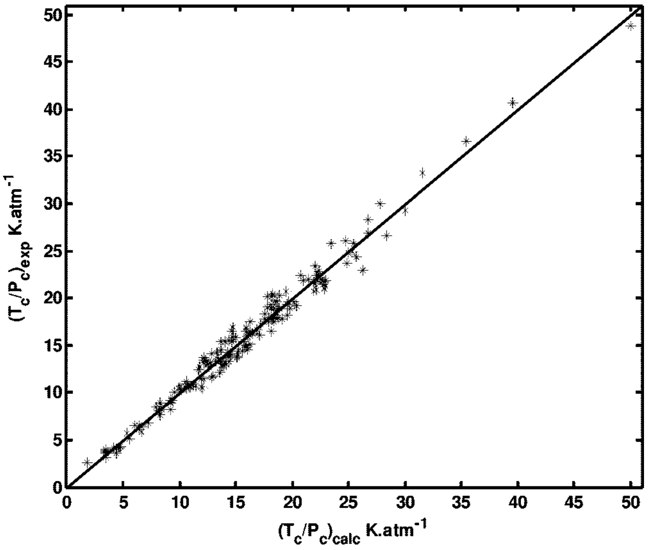

Figure 2. Correlation of experimental T_C/P_C versus T_C/P_C calculated from eq 13 for the training data set.

Table 4. Variety of Number of Test Data Used in This Study

compound type	no. of data points
hydrocarbons	23
oxygenated hydrocarbons	18
nitrogenated hydrocarbons	3
hydrocarbon sulfide and mercaptanes	2
halogenated hydrocarbons	3
total	49

the values of RT_C/P_CC_P for all of the compounds used are nearly close to one. The mean absolute relative error between values of RT_C/P_CC_P and one is less than 5.89 %. Therefore, the equation coefficient (ε) in eq 12 is considered equal to one.

Results and Discussion

Figure 1 shows the value of RT_C/P_CC_P for 178 compounds. It can be seen that the proposed correlation works well for the light and medium organic compounds, but there are considerable errors for some organic and inorganic compounds. Although high molecular weight compounds have a high error, this error is not necessarily for high molecular weight compounds. The value of RT_C/P_CC_P for some of the light compounds deviates from unity similar to the high molecular weight compounds. It

Table 5. Value of RT_C/P_CC_P and Comparison of the Estimated Ratio T_C/P_C by Equation 13 with the Experimental Data and Various Group Contribution Methods, Together with Values for Relative Errors RE = $((T_C/P_C)_{exp} - (T_C/P_C)_{calc})/((T_C/P_C)_{exp})$ for 49 Compounds (Test Data Set)

			(RT_C/P_CC_P)	(T_C/P_C)/K·atm^{-1}						100 RE				
compd no.	chemical special	chemical formula	K·atm^{-1}	exp.	predicted by eq 13	Joback[5]	Cons. & Gani[7]	Ambrose[2,3]	Kontogeorgis et al.[8]	predicted by eq 13	Joback[5]	Cons. & Gani[7]	Ambrose[2,3]	Kontogeorgis et al.[8]
1	*n*-Hexane	C_6H_{14}	0.9914	16.918	16.931	16.552	16.658	17.128	17.823	0.0803	2.1633	1.5368	1.2412	5.3400
2	*n*-Heptane	C_7H_{16}	1.0174	20.123	19.418	19.568	19.749^a	20.186	20.070	3.4994	2.8708	3.1426	0.3112	0.2628
3	2,2-Dimethylpropane	C_5H_{12}	0.9331	13.735	14.810	12.593	12.386	12.243	16.080	7.8334	8.3089	9.8201	10.859	17.075
4	3-Methylpentane	C_6H_{14}	0.9593	16.376	16.937	16.243	16.171	16.619	18.400	3.4261	0.8152	1.2525	1.4808	12.359
5	3-Methylheptane	C_8H_{18}	0.9889	22.389	22.159	22.340	22.535	22.858	22.530	1.0274	0.2162	0.6524	2.0957	0.6325
6	3,4-Dimethylhexane	C_8H_{18}	0.9641	21.419	21.742	21.766	22.126	22.791	22.511	1.5090	1.6174	3.3015	6.4039	5.0967
7	3-Ethyl-3-methylpentane	C_8H_{18}	0.9099	20.843	22.423	22.387	21.733	22.544	24.052	7.5829	7.4081	4.2719	8.1629	15.395
8	2,2,3,3-Tetramethylpentane	C_9H_{20}	0.8787	22.463	25.174	25.106	25.924^a	25.254	26.077	12.070	11.765	15.408	12.427	16.088
9	2,2,5-Trimethylheptane	$C_{10}H_{22}$	0.9697	27.081	27.835	28.303	28.207	27.892	28.633	2.7859	4.5149	4.1576	2.9954	5.7324
10	Propylene	C_3H_6	1.0279	8.0003	8.2040	7.9079	7.1336^a	7.9834	12.020	2.5456	1.1546	10.833	0.2109	50.190
11	1-Hexene	C_6H_{12}	1.0347	16.264	15.714	15.913	16.302^a	16.340	17.006	3.3791	2.2372	0.2313	0.4637	4.5815
12	2-Methyl-1-butene	C_5H_{10}	1.0318	13.656	13.458	13.429	14.172	12.949	15.499	1.4470	1.7121	3.7744	5.1799	13.492
13	1-Dodecene	$C_{12}H_{24}$	1.0284	33.411	33.728	40.874	30.087	34.757	33.020	0.9487	22.338	9.9478	4.0297	1.1600
14	*n*-Tetradecane	$C_{14}H_{30}$	1.1482	44.725	44.412	45.180	45.505	42.995	42.335	0.6992	1.0223	1.7444	3.8672	5.3420
15	Methylacetylene	C_3H_4	0.9940	7.2548	7.7016	7.5041	7.6520	7.7615	11.814	6.1586	3.3669	0.1942	5.4474	62.851
16	Dimethylacetylene	C_4H_6	1.0497	9.8654	9.8285	10.291	10.124	10.398	13.195	0.3736	4.1914	2.6215	5.4029	33.758
17	1-Heptyne	C_7H_{12}	0.9937^b	18.096	17.973	16.449	17.391	17.799	18.792	0.6768	9.1014	3.8958	1.6412	3.8481
18	1-Octyne	C_8H_{14}	1.0040^b	21.019	20.506	22.281	20.573	19.890	21.145	2.4368	5.7387	2.1237	5.3728	0.6000
19	Cyclobutane	C_4H_8	1.0861	9.3381	9.0324	9.3160	9.8103	9.5546	12.348	3.2732	0.2364	5.0573	2.3182	32.236
20	Cyclohexane	C_6H_{12}	1.0622	13.680	13.131	14.530	15.026^a	13.648	15.554	4.0130	5.9215	9.8359	0.2309	13.693
21	Methylcyclohexane	C_7H_{14}	1.0249	16.660	16.199	16.729	17.695^a	16.936	17.510	2.7652	0.4223	6.2133	1.6592	5.1056
22	Cyclopentene	C_5H_8	1.0962	10.680	10.166	10.773	11.531^a	10.641	13.215	4.8117	0.8814	7.9739	0.3652	23.736
23	*o*-Xylene	C_8H_{10}	1.0719	17.077	15.906	17.834	16.332	17.324	16.604	6.8523	4.3007	4.3630	1.4505	2.7645
24	Ethanol	C_2H_6O	1.0861	8.5087	8.2564	9.1288	7.9023^a	8.3536	13.500	2.9649	7.3000	7.1260	1.8218	58.669
25	1-Propanol	C_3H_8O	1.0334	10.622	10.685	10.580	11.130	10.540	15.175	0.6014	0.4041	4.7744	0.7721	42.859
26	1-Butanol	$C_4H_{10}O$	1.0128	13.145	13.223	12.593	13.493	12.825	17.097	0.5935	4.4428	2.6472	2.4346	30.062
27	Cyclohexanol	$C_6H_{12}O$	1.0118	15.496	15.349	14.137	14.692^a	13.197	18.925	0.9426	8.7642	5.1922	14.836	22.124
28	*o*-Cresol	C_7H_8O	0.9123	13.968	15.345	14.138	14.248	14.316	15.581	9.8642	1.2192	2.0072	2.4925	11.551
29	1-Nonanol	$C_9H_{20}O$	0.9559	23.033	23.626	25.757	24.525	25.791	25.628	2.5784	11.827	6.4781	11.973	11.268
30	Methyl *n*-butyl ether	$C_5H_{12}O$	0.9809^b	15.612	15.892	15.426	15.518	15.756	16.678	1.7986	1.2158	0.6003	0.9248	6.8321
31	Methyl *tert*-butyl ether	$C_5H_{12}O$	0.9603^b	14.770	15.409	14.835	14.654^a	15.089	16.961	4.3263	0.4381	0.7867	2.6677	14.830
32	1-Butanal	C_4H_8O	1.0146	12.600	12.705	12.283	12.756^a	11.623	14.363	0.8399	2.6101	1.2392	7.7537	13.993
33	1-Hexanal	$C_6H_{12}O$	0.9686	17.307	17.661		17.078		18.221	2.0456		1.3223		5.2810
34	2-Hexanone	$C_6H_{12}O$	1.0073	17.970	17.635	17.476	18.439	18.441	18.221	1.8627	2.8653	2.6086	2.6187	1.3950
35	3-Pentanone	$C_5H_{10}O$	0.9842	15.361	15.614	15.287	16.546	15.365	16.170	1.6480	0.4886	7.7122	0.0314	5.2630
36	Pentanoic acid	$C_5H_{10}O_2$	1.0742^b	18.194	16.816	17.057	15.609	18.562	17.047	7.5733	6.2501	14.209	2.0227	6.3030
37	Ethyl formate	$C_3H_6O_2$	1.0162	10.937	11.149	11.932	10.645	10.872	13.466	1.9469	8.4562	2.6703	0.5933	23.125
38	Ethyl acetate	$C_4H_8O_2$	1.0074	13.772	13.857	12.786	13.016^a	12.845	15.135	0.6181	7.8140	5.4896	6.7329	9.9010
39	Ethyl pentanoate	$C_7H_{14}O_2$	0.9614	20.770	21.147	20.322	21.669	21.661	21.602	1.8157	2.1537	4.3319	4.2938	4.0066
40	Propyl 2-methylpropanoate	$C_7H_{14}O_2$	1.0250	21.855	20.876	20.751	21.362	21.104	21.583	4.4795	5.0502	2.2576	3.4349	1.2440
41	3-Methylbutyl ethanoate	$C_7H_{14}O_2$	1.0214	21.593	20.702	19.567	21.066	21.448	21.583	4.1241	9.3837	2.4426	0.6731	0.0469
42	Dimethyl amine	C_2H_7N	0.9889^b	8.4219	8.9505	9.1774	7.6932	8.6329	12.183	6.2769	8.3416	8.6518	2.5055	44.670
43	Aniline	C_6H_7N	0.9920	13.238	13.558	14.358	13.297^a	13.998	14.177	2.4241	7.9056	0.4489	5.7377	7.0930
44	Butyl amine	$C_4H_{11}N$	0.9518	13.209	14.046	12.673	14.283	12.992	15.292	6.3368	4.0553	8.1313	1.6388	15.771
45	*n*-Propyl mercaptan	C_3H_8S	1.0291^b	11.743	11.764	11.649	11.409	12.632	13.995	0.1828	0.8187	2.8439	7.5705	19.177
46	Isopentyl mercaptan	$C_5H_{12}S$	1.0082	17.481	17.180	15.906	16.074	20.808	17.724	1.7216	9.0109	8.0477	19.033	1.3901
47	Bromomethane	CH_3Br	1.1570^b	5.9148	5.3331	7.1621	6.3936	5.6813	11.255	9.8338	21.087	8.0954	3.9475	90.296
48	Fluoroethane	C_2H_5F	1.0658	7.5905	7.5165	7.8913		8.1090		0.9748	3.9628		6.8317	
49	2-Chlorobutane	C_4H_9Cl	1.0658	14.314	13.637	14.148	13.327	14.029	15.373	4.7281	1.1577	6.8901	1.9893	7.3996

^{a} Estimated by the second-order group contribution method. ^{b} In column 4: obtained from ref 22 and other values from ref 23.

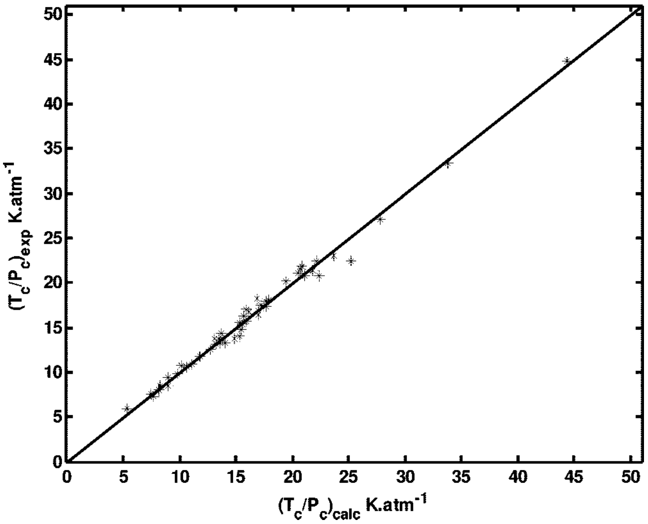

Figure 3. Correlation of experimental T_C/P_C versus of T_C/P_C calculated from eq 13 for the test data set.

can be described that the characterizations and properties of the compounds are extremely dependent on the structure of the compounds. For example, the compounds which have double or triple bonds will deviate more from unity because these bonds affect the properties of compounds. In addition, some of the groups such as O, N, and Cl will influence the electronegativity of compounds and so change the compounds' properties. Therefore, not only deviation from unity for some compounds is dependent on the molecular weight but also it is affected by the molecular structure. Consequently, to improve the accuracy of the previous correlation (eq 12), a cubic polynomial function is considered as follows

$$\frac{T_C}{P_C} = a\left(\frac{C_P}{R}\right)^3 + b\left(\frac{C_P}{R}\right)^2 + c\left(\frac{C_P}{R}\right) + d \qquad (13)$$

By optimizing the relative error between experimental data and predicted values, it is found that the optimal constants of this equation are: $a = 0.0006314$, $b = -0.03017$, $c = 1.384$, $d = -1.038$. The linear regression, R-value, and RMSE between the desired and the predicted values from the correlation (13) are 0.9818 and 0.9852, respectively. The predicted values for T_C/P_C given by this new correlation, together with the values for various group contribution methods and relative errors (RE) for 178 components, are given in Table 3.

Figure 2 shows the closeness of the correlation between the predicted results from eq 13 and the experimental training data set. A perfect fit (experimental equal to predicted data) is indicated by the solid line. The close proximity of the best linear fit to the perfect fit, as observed in Figure 2, shows a good correlation among predictions and experimental data.

Also, the performance of the proposed correlation was tested using another set of 49 experimental data (Table 5) that were not previously used for training of the correlation. Table 4 provides information on the type and number of different compounds that comprised the test data set used in this study. The results indicate that the mean relative error (MRE) of the proposed correlation is less than 3.33 % for the test data set.

Figure 3 indicates there is good correlation between predicted and experimental test data of the T_C:P_C ratio. In this figure, the correlation outputs are plotted versus the experimental data as stars. A perfect fit (experimental equal to predicted data) is indicated by the solid line. The slope and the y-intercept of the best linear regression relating experimental to predicted data are, respectively, 0.9661 and 0.4614 which nearly overlaps the perfect linear fit. The correlation coefficient (R-value) between the predictions and the experimental test data is 0.9896. This shows a very good correlation among the training and test data.

The results obtained using the proposed simple new correlation (eq 13) were compared with the experimental T_C:P_C test data and the values predicted using the methods of Joback,[5] Ambrose,[2,3] Constantinou and Gani,[7] and also Kontogeorgis[8] in Table 5. Also, in this table, results for the 49 compounds including the values of RT_C/P_CC_P and relative errors (RE) are shown. The mean relative error between values of RT_C/P_CC_P and one is less than 4.24 %. Also, the mean relative errors (MRE) between all the predictive methods and experimental data for this data set are: proposed correlation 3.33 %; Ambrose[2,3] method 4.15 %; Constantinou and Gani[7] method 4.78 %; Joback[5] method 4.99 %; and Kontogeorgis[8] method 16.37 %. The results show a good agreement between the proposed correlation and the experimental data. Also, the MRE of the proposed correlation is less than the previous methods for the test data set.

One of the advantages of the proposed correlation is in its ability to predict the T_C:P_C ratio for organic and inorganic compounds. It should be noted (as can be seen at the end of Table 3) that the proposed correlation is the only applicable method to predict the T_C:P_C ratio for inorganic compounds. The other methods are unable to predict the T_C:P_C ratio for inorganic compounds since there are not enough group contributions for these compounds. This limitation could be considered as a weakness for the other methods.

According to Table 3, one of the disadvantages of the Constantinou and Gani[7] and Kontogeorgis[8] methods appears when these are used to evaluate the T_C:P_C ratio for isomers of compounds such as octane. Critical temperature and pressure estimation by these methods is independent of any properties of the compounds such as boiling point temperature, molecular weight, or atom numbers in the molecule, so the estimation of T_C and P_C is only dependent on group contributions. Since isomers of one compound have the same group contributions, then the methods developed based on group contribution are not able to accurately predict values for T_C and P_C.

Tables 3 and 5 show the Kontogeorgis[8] method strongly depends on the molecular weight of the compounds. The evaluated T_C:P_C ratio by the Kontogeorgis[8] method would be more accurate for high molecular weight compounds. So, it could be better to use this method only for medium-to-high molecular weight compounds.

Although these methods have some disadvantages, it should mentioned that the Constantinou and Gani[7] method requires no compound properties to be measured but only the structural formula of a compound. This shows the generality of this method. A major benefit of using the Ambrose,[2,3] Constantinou and Gani,[7] and Joback[5] methods is the ability of these methods to predict both critical temperature and critical pressure while the proposed correlation can be used to estimate one of the two critical properties whenever only the other one is available.

It is considerable that these methods are relatively complex because they need to be familiar with the molecular structure which in some cases is really time consuming, but the proposed correlation is simple and just needs the heat capacity to predict the T_C:P_C ratio. In addition, the calculation of critical temperature and pressure by these methods may be impossible because the group contributions of some compounds such as methane, ethylene, and acetylene are not available.

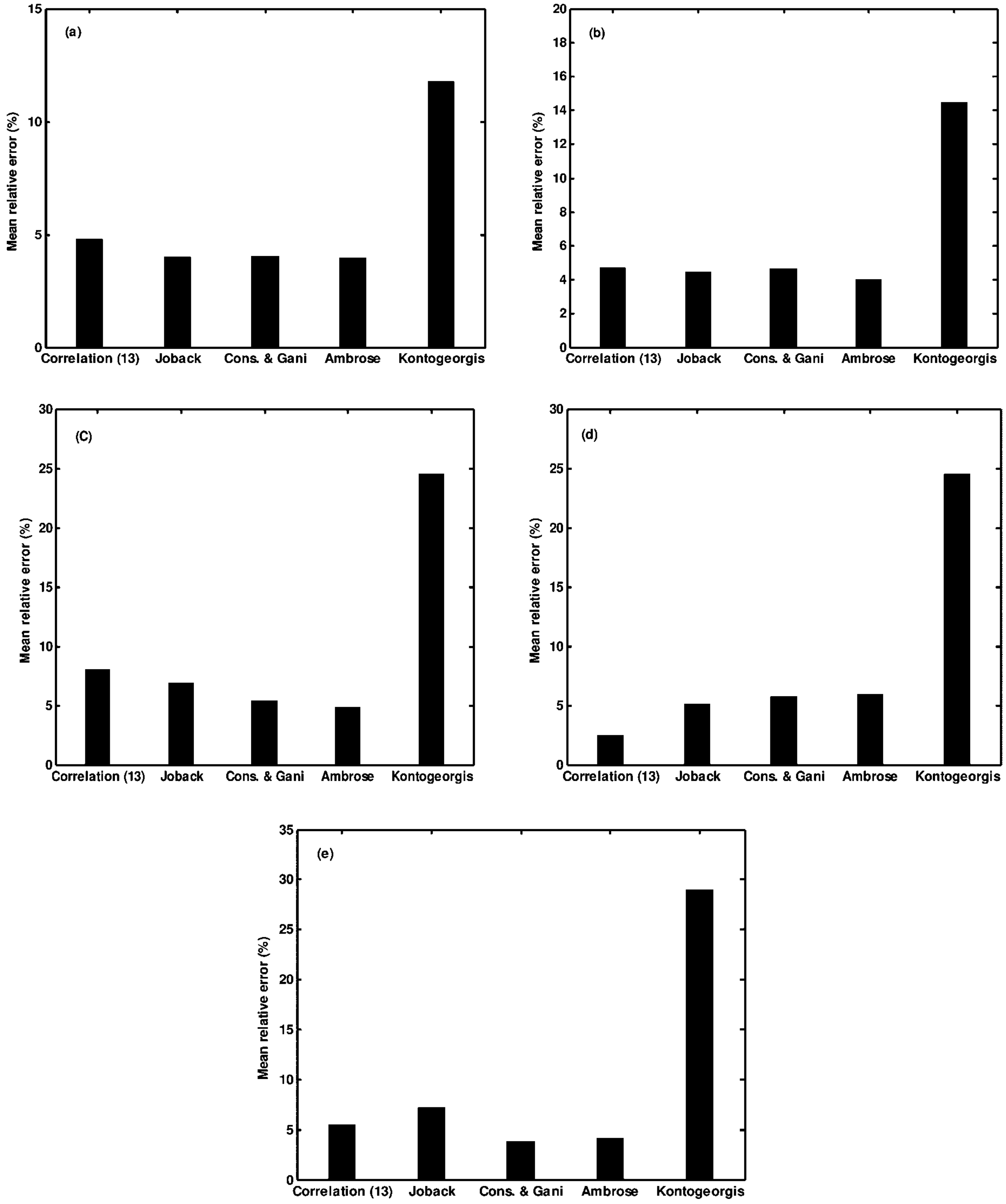

Figure 4. Mean relative errors of proposed correlation and various methods used in prediction of T_C/P_C for all types of compounds. (a) Hydrocarbons. (b) Oxygenated hydrocarbons. (c) Nitrogenated hydrocarbons. (d) Hydrocarbon sulfide and mercaptanes. (e) Halogenated hydrocarbons.

Figure 4 shows the mean relative errors corresponding to the proposed correlation and Joback,[5] Constantinou and Gani,[7] Ambrose,[2,3] and Kontogeorgis[8] methods for hydrocarbons, oxygenated hydrocarbons, nitrogenated hydrocarbons, hydrocarbon sulfide and mercaptanes, and halogenated hydrocarbons. This figure illustrates that the Kontogeorgis[8] method is the least accurate method in prediction of the T_C:P_C ratio for various types of compounds used with errors of 11.79 % for hydrocarbons, 13.30 % for oxygenated hydrocarbons, 24.51 % for nitrogenated hydrocarbons, 24.52 % for hydrocarbon sulfide and mercaptanes, and 29.04 % for halogenated hydrocarbons. According to Figure 4a, b, and c, almost all methods except the Kontogeorgis[8] method result in similar errors when they are used for hydrocarbons, oxygenated and nitrogenated hydrocarbons. Furthermore, it should be noted that the proposed correlation requires just one basic property (i.e., heat capacity), whereas in the Joback[5] method, normal boiling point and number of atoms in the molecule, and in the Ambrose[2,3] method, molecular weight and normal boiling point, in addition to group contributions are also required.

Figure 4d presents that the proposed correlation is the best accurate method in prediction of the T_C:P_C ratio for hydrocarbon sulfide and mercaptanes with an error of 2.46 %, while the Ambrose[2,3] method has an error of 5.91 %, Joback[5] method 5.15 %, and Constantinou and Gani[7] method 5.71 %. As can be seen in Figure 4e, it seems that the Constantinou and Gani[7] and

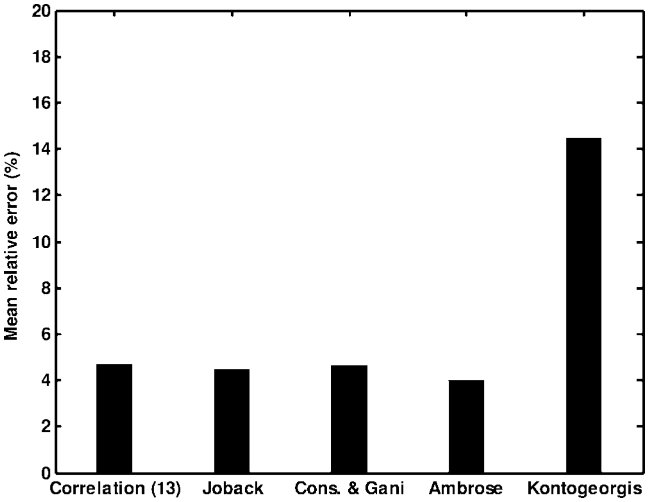

Figure 5. Overall performance of proposed correlation and various methods in the prediction of T_C/P_C for all types of compounds

Ambrose[2,3] methods are the best for halogenated hydrocarbons with errors of 3.80 % and 4.19 %, respectively. The proposed correlation is the next most accurate approach with an error of 5.48 %.

Figure 5 shows the overall performance of proposed correlation and various methods in prediction of the T_C:P_C ratio for all types of compounds. The correlation of Ambrose[2,3] yields the best result, with a typical error less than 3.99 %. The overall performance of the Joback[5] method is rather good with an error of around 4.45 %. The proposed correlation is equally good with respect to Constantinou and Gani,[7] with an error of 4.69 %, but the proposed correlation is more general. The Kontogeorgis[8] method is the least accurate method with an error less than 14.50 %. It seems that the accuracy of the proposed correlation is similar to the methods of Constantinou and Gani,[7] Ambrose,[2,3] and Joback,[5] for various types of compounds.

However, the important point is that the proposed correlation is simple and general to predict critical temperature to critical pressure ratio for low to medium molecular weight compounds.

Conclusions

It was shown in this study that, unlike the critical properties alone, a simple correlation of the T_C:P_C ratio with the heat capacity at 298.15 K can be developed for low to medium molecular weight compounds. The proposed correlation can be used to estimate one of the two critical properties whenever only the other one is available.

It is important to note that the proposed correlation just requires one basic property (i.e., heat capacity), whereas the other methods need two basic properties in addition to group contributions.

The proposed correlation is simple and general to predict critical temperature to critical pressure ratio for low to medium molecular weight compounds. This proposed correlation is applicable to predict the T_C:P_C ratio for organic and inorganic compounds, while the other methods just predict this ratio for organic compounds.

Appendix

Nomenclature

C_P	Heat capacity
M	Molecular weight
M_j	Number of occurrences of the type-*j* second-order group in a compound
n_A	Number of atoms in the molecule
n_j	Number of groups of the *j*th type
N_i	Number of occurrences of the type-*i* first-order group in a compound
p_{c1i}	Contribution of the type-*i* first-order group for estimation of the critical pressure
p_{c2j}	Contribution of the type-*j* second-order group for estimation of the critical pressure
P_C	Critical pressure
Q_w	van der Waals surface area
R	Universal gas constant
t_{c1i}	Contribution of the type-*i* first-order group for estimation of the critical temperature
t_{c2j}	Contribution of the type-*j* second-order group for estimation of the critical temperature
T_B	Normal boiling point at 1 atm
T_C	Critical temperature
SG	Specific gravity of liquid hydrocarbons at 60 °F relative to water at the same temperature
Δ	Contributions for the *j*th atomic or molecules group
Δ_P	Group contribution for P_C
Δ_T	Group contribution for T_C

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