A Unique Equation to Estimate Flash Points of Selected Pure Liquids Application to the Correction of Probably Erroneous Flash Point Values

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A simple empirical equation is presented for the estimation of closed-cup flash points for pure organic liquids. Data needed for the estimation of a flash point (FP) are the normal boiling point (T_{eb}), the standard enthalpy of vaporization at 298.15 K [$\Delta_{vap}H°(298.15\ \text{K})$] of the compound, and the number of carbon atoms (n) in the molecule. The bounds for this equation are: $-100 \leqslant \text{FP}(°\text{C}) \leqslant +200$; $250 \leqslant T_{eb}(\text{K}) \leqslant 650$; $20 \leqslant \Delta_{vap}H°(298.15\ \text{K})/(\text{kJ mol}^{-1}) \leqslant 110$; $1 \leqslant n \leqslant 21$. Compared to other methods (empirical equations, structural group contribution methods, and neural network quantitative structure–property relationships), this simple equation is shown to predict accurately the flash points for a variety of compounds, whatever their chemical groups (monofunctional compounds and polyfunctional compounds) and whatever their structure (linear, branched, cyclic). The same equation is shown to be valid for hydrocarbons, organic nitrogen compounds, organic oxygen compounds, organic sulfur compounds, organic halogen compounds, and organic silicone compounds. It seems that the flash points of organic deuterium compounds, organic tin compounds, organic nickel compounds, organic phosphorus compounds, organic boron compounds, and organic germanium compounds can also be predicted accurately by this equation. A mean absolute deviation of about 3 °C, a standard deviation of about 2 °C, and a maximum absolute deviation of 10 °C are obtained when predictions are compared to experimental data for more than 600 compounds. For all these compounds, the absolute deviation is equal or lower than the reproductibility expected at a 95% confidence level for closed-cup flash point measurement. This estimation technique has its limitations concerning the polyhalogenated compounds for which the equation should be used with caution. The mean absolute deviation and maximum absolute deviation observed and the fact that the equation provides unbiaised predictions lead to the conclusion that several flash points have been reported erroneously, whatever the reason, in one or several reference compilations. In the following lists, the currently accepted flash points for bold compounds err, or probably err, on the hazardous side by at least 10 °C and for the nonbolded compounds, the currently accepted flash points err, or probably err, on the nonhazardous side by at least 10 °C: bicyclohexyl, **sec-butylamine**, **tert-butylamine**, 2-cyclohexen-1-one, ethanethiol, **1,3-cyclohexadiene**, **1,4-pentadiene**, **methyl formate**, **acetonitrile**, cinnamaldehyde, 1-pentanol, diethylene glycol, diethyl fumarate, diethyl phthalate, **trimethylamine**, **dimethylamine**, 1,6-hexanediol, **propylamine**, **methanethiol**, **ethylamine**, **bromoethane**, **1-bromopropane**, **tert-butylbenzene**, **1-chloro-2-methylpropane**, diacetone alcohol, diethanolamine, **2-ethylbutanal**, and **formic acid**. For some other compounds, no other data than the currently accepted flash points are available. Therefore, it cannot be assessed that these flash point data are erroneous but it can be stated that they are probably erroneous. At least, they need experimental re-examination. They are probably erroneous by at least 15 °C: **1,3-cyclopentadiene**, **di-tert-butyl sulfide**, **dimethyl ether**, **dipropyl ether**, **4-heptanone**, bis(2-chloroethyl)ether, 1-decanol, **1-phenyl-1-butanone**, **furan**, **ethylcyclopentane**, 1-heptanethiol, 2,5-hexanediol, **3-hexanone**, **hexanoic acid methyl ester**, 4-methyl-1,3-pentadiene, **propanoyl chloride**, **tetramethylsilane**, thiacyclopentane, **1-chloro-2-methyl-1-propene**, **trans-1,3-pentadiene**, **2,3-dimethylheptane**, triethylenetetramine, **methylal**, **N-ethylisopropylamine**, **3-methyl-2-pentene**, and **2,3-dimethyl-1-butene**. © *2005 American Institute of Physics.*
[DOI: 10.1063/1.1835321]

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1. Introduction

Flash points (FPs) are of great significance to assess fire hazards of liquids and to minimize fire risk during normal storage and handling. The FP is the lowest temperature at which a liquid produces enough vapor to ignite in air at atmospheric pressure when an ignition source (external flame for instance) is applied under specified test conditions. Several methods have been proposed to estimate flash points for many organic compounds. These methods can be divided into four categories: empirical equations,[1–18] neural networks quantitative structure–property relationships,[19,20] structural contribution group methods,[21–23] and other methods.[24]

Several test methods for the reliable measurement of closed-cup flash points in air at atmospheric pressure exist: ASTM E1232—standard test method for temperature limit of flammability of chemicals; ASTM D56—standard test method for flash point by Tag closed cup tester; ASTM D93—standard test methods for flash point by Pensky-Martens closed cup tester; and ASTM D3278—standard test methods for flash points of liquids by small scale closed cup apparatus, among others. Strictly speaking, ASTM E1232 does not define flash point but lower temperature limit (LTL) of flammability. The ignition source for ASTM D56, ASTM D93, and ASTM D3278 is a hydrocarbon gas flame and the ignition source for ASTM E1232 is an electrical arc or a fuse wire. For most of the compounds, the LTL of a compound measured using the method of ASTM E1232 would be the same as the flash point measured using the flash point test

methods ASTM D56, ASTM D93, and ASTM D3278. Some of these methods and related apparatus are described by Lance et al.[25] Repeatability and reproductibility are important data needed to quantify experimental scatter. Those data, and in particular reproductibility as it deals with interlaboratory measurements, are also needed to compare estimated data and experimental data. Montemayor et al.[26] report recent repeatability and reproductibility results for ASTM D56 and ASTM D93. For ASTM D56, with a FP in the region between 38 and 85 °C, the repeatability at a 95% confidence level is found to be about 1 °C for FP below 60 °C and about 1.5 °C for FP at or above 60 °C. The reproductibility (22 labs) at a 95% confidence level is found to be about 4 °C for a FP below 60 °C and to be between 5 and 6 °C for a FP above 60 °C (up to 85 °C). For ASTM D93, with a FP in the region between 60 and 291 °C, both the repeatability and reproductibility at a 95% confidence level are found to be dependent on the FP value: about $0.033\times FP$ (°C) for the repeatability and about $0.075\times FP$ (°C) for the reproductibility (22 labs). These data represent a reproductibility of 4.5 °C for a FP of 60 °C quite coherent with the one observed for the ASTM D56, namely 5 °C. At 100 °C a reproductibility of about 7–8 °C is expected. It is generally reported in the literature whether the flash point has been measured in a closed-cup apparatus or in an open-cup apparatus but it is not always specified which test method was used. It is however possible to consider a reproductibility of 4–5 °C in the 30–60 °C FP temperature range, of 5–6 °C in the 60–85 °C FP temperature range, of 7–9 °C in the 85–120 °C temperature range, of 9–11 °C in the 120–150 °C FP temperature range, of 11–13 °C in the 150–175 °C FP temperature range, and of 13–15 °C in the 175–200 °C FP temperature range. Clearly, reproductibility is worse as the FP temperature increases in the 30–200 °C temperature range. This is quite logical due to experimental difficulties encountered well above the ambient. Although not discussed,[26] reproductibility should also be worse well below 0 °C and at 5–6 °C in the 0–30 °C FP temperature range.

2. Empirical Equations and Semiempirical Equations

Concerning empirical equations, two approaches are possible: either a unique equation for all the compounds, whatever their chemical structure, or several equations, each dealing with a class of compounds.

2.1. One Equation Per Chemical Family

Up to now, the second approach has been shown to be more accurate. Several compounds can have the same boiling point and completely different flash points and this seemed to prevent the establishment of a unique equation predicting the flash point as a function of the normal boiling point. The same experimental evidence holds for the vapor pressure at a given temperature. Therefore, several equations have to be established, each dealing with a class of com-

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pounds. In these equations, flash points are expressed in terms of the normal boiling point of the liquid or in terms of the vapor pressure of the liquid at a given temperature. Satyanarayana and Rao[10] proposed empirical equations in which the flash point is expressed in terms of the normal boiling point. The predictions of the proposed equations are found to be reliable for many compounds, but this does not mean that the agreement between estimation and experiment is correct for all the compounds considered. This point is not mentioned in the paper of Satyanarayara and Rao.[10] In fact, no indication is given in this paper concerning the mean absolute deviation (MAD), the standard deviation and the maximum absolute error from experiment. It should be observed that the search for possible erroneous flash points was beyond the scope of the study of Satyanarayara and Rao.[10]

Flash points also have been expressed as a function of vapor pressures by Fujii and Hermann.[11] In this paper, several expressions were needed. For a class of compounds, linearity seems to be the most appropriate correlation to explain the relationship between the inverse of flash points and the logarithm of vapor pressures at 298.15 K for pure organic compounds. The estimations obtained with these equations were found to be poor.

Although very interesting at first glance, this stategy has, in fact, numerous drawbacks in terms of prediction (or estimation) of flash points. First, there is a need for about 50 such equations to treat the ''simple'' chemical families (including normal alkanes, branched alkanes, cyclic alkanes, aromatic hydrocarbons, aldehydes, and ketones) and several others have to be established for the less-common chemical families. Second, such an equation can hardly be established for families for which experimental data are scarce and third, it is nearly impossible to estimate a flash point for multifunctional (or polyfunctional) compounds.

2.2. A Unique Equation for All Chemical Families

The use of a unique equation for the estimation of the flash points for chemically different compounds is of much interest. Some attempts have been made in that way. Patil[12] suggests the use of a unique equation for the estimation of the flash point of organic compounds:

$$FP(K) = 4.656 + 0.844 T_{eb} - 0.234 \times 10^{-3} T_{eb}^2, \quad (1)$$

where T_{eb}/K is the normal boiling point temperature. Satyanarayana and Rao[10] and Hshieh[13] found that this equation does not represent the experimental data correctly. Hshieh[13] proposed a unique empirical correlation for the estimation of general organic compounds and organic silicon compounds:

$$FP(°C) = -54.5377 + 0.588\,3 T_{eb} + 0.000\,22 T_{eb}^2, \quad (2)$$

where $T_{eb}/°C$ is the normal boiling temperature. This equation is shown to predict the flash points for a wide variety of organic compounds (including organic silicon compounds) with a standard error of 11.66 °C and a probable maximum absolute deviation of at least 30 °C (although this latter point is not discussed by Hiesh[13]). Equation (2) is therefore not

sufficiently accurate to be of interest for the reliable prediction of flash points. This statement will be discussed later in this paper (refer to Sec. 8.2).

Metcalfe and Metcalfe,[14] following Satyanarayana and Kakati,[15] proposed a unique empirical equation

$$FP(°C) = -84.794 + 0.6208 T_{eb} + 37.8127 \times d, \quad (3)$$

with FP in °C, T_{eb}, the normal boiling temperature in °C, and d, the liquid density expressed in g cm^{-3}. However, Hshieh[13] showed previously that there is no statistical correlation between liquid density and flash points so that the introduction of this liquid density term is questionable. The equation performs relatively poorly. The authors report a standard deviation of 10.3 °C and a maximum deviation of 30.3 °C for the 249 organic compounds considered. The standard deviation and the maximum deviation are too high to expect reliable predictions from the use of this equation. Metcalfe and Metcalfe,[14] after exclusion from their data sets of 48 hydroxyl compounds, obtained a new equation which performs slightly better for the 201 remaining compounds than the previous one but still insufficiently for predictive purposes (standard deviation is 8.6 °C and maximum deviation is 26.2 °C). Moreover, the logic followed here should lead, in fact, to the establishment of different equations for different chemical families, and one can believe from the results reported above that the establishment of a unique equation is impossible. Therefore, two other approaches have been developed for the estimation of flash points, namely neural networks quantitative structure–property relationships and structural group contribution methods.

3. Neural Networks Quantitative Structure–Property Relationships

Tetteh *et al.*[19] use radial basis function neural network models for the simultaneous estimation of flash point and boiling point. With this method, they obtained a MAD of about 12 °C for 400 general organic compounds (Si compounds not included) but as well, although not discussed in the paper, the maximum absolute error reaches about 40 °C as shown in Table 1. The mean absolute deviation and the maximum absolute error are too high to allow a reliable estimation of a flash point; more exactly the flash point predicted can be either very accurate or far off. The literature describing neural network modeling to predict physiocochemical properties of organic compounds was reviewed by Taskinen and Yliruusi.[20]

4. Structural Group Contribution Methods

The structural group contribution methods have been used extensively for years to predict physicochemical properties, in particular, the enthalpy of formation. Two methods have been proposed concerning flash points: the method of Suzuki *et al.*[21] and the method of Albahri.[22] These methods were only devoted to the estimation of the flash points of hydrocarbons.

TABLE 1. Comparison between estimated and experimental flash points (FP) as given in Tetteh *et al.*[a] FP are estimated according to neural network models. The present study shows that these compounds do not exhibit anomalous experimental flash points

Compound name	Estimated FP (°C)	Experimental FP (°C)
diethylamine	4.4	−23
fluorobenzene	9.1	−15
2,2-dimethylbutane	−23.8	−48
2-methylaniline	48	85
2,3-dimethylaniline	59.9	97
Nitroethane	0.5	28
Methanol	−11.6	11
Ethanol	1.2	13
n-pentane	−28.2	−49

[a]See Tetteh *et al.*[19]

For about 500 compounds, a mean absolute deviation of 5.3 °C was obtained with the method of Albahri.[22] This is quite good, but the maximum absolute error obtained is too high: 35.7 °C. A limitation of this method is the considerable work needed to determine the structural group contributions for compounds other than hydrocarbons.

Katritzky *et al.*[23] performed a quantitative structure property relationship analysis of flash points of organic compounds. They propose 20 equations able to predict flash points. The better of these equations is:

$$FP(K) = (0.72 \pm 0.014)T_{eb} + (76.99 \pm 11.97)RNCG$$
$$+ (2.05 \pm 0.33)HDCA - (8.40 \pm 7.63) \qquad (3')$$

and exhibits a standard deviation of 11 °C and a maximum absolute deviation of 46 °C. In this equation, T_{eb}/K is the normal boiling point, RNCG is defined as the ratio of maximum (by absolute value) atomic partial negative surface charge and the sum of similar negative charges in the molecule and HDCA represents the sum of solvent-accessible surface area of the H-bonding donor atoms. More details can be found in Katritzky *et al.*[23]

5. Other Methods

The flash point of a compound can also be estimated accurately if the lower flammability limit (LFL) and the vapor pressure curve of the compound are known.[24] However, LFL are unknown for many compounds although those compounds are known to be combustible and, when known, LFL are generally available only at 25 °C or at an unspecified temperature (equal to the FP temperature or above). This can be a problem because LFL are temperature dependent (even if this dependency is generally rather weak).

Another method is called the "half-stoichiometric rule." It is actually a rule of thumb estimate for the LFL and, if the vapor pressure curve of the compound is known, this rule allows the determination of the FP. However, the half stoichiometric rule is very rough and can be far off for some compounds.

6. Scopes of the Study

All the above studies were not devoted to the discussion of the reliability of the experimental flash points reported in the literature and it can be stated that about all the above methods failed probably because erroneous data have been included in the data sets used for the establishments of these methods. This point is briefly discussed by Kline *et al.*[27] However, anomalous flash points have been observed for some compounds (for instance a flash point value above the normal boiling point of the compound). In some cases, typographical errors and in some cases unit conversion errors (mostly from °F to °C) or both are the cause of this. Jones,[28,29] Jones and Godefroy,[30] Godefroy and Jones,[31] following Griffiths and Barnard,[32] used the "half-stoichiometric rule" and found that a difference between calculated and measured flash points values of more than a few degrees is the exception rather than the rule. By using the half-stoichiometric rule, it was found that flash points for six compounds, benzoic acid, formic acid, dimethylether, ethylamine, dimethylamine, and glycerol, need reexamination because the predicted flash points are by about 15 °C or more lower than the experimentally measured flash points. The search for likely erroneous flash points is of importance for safety reasons, in particular when the "true" flash point is well below the commonly reported flash point. The "half-stoichiometric rule" has been validated experimentally by Jones with formic acid whose flash point (43±5 °C) was found experimentally about equal with the one predicted according to the half-stoichiometric rule (46–47 °C), that is more than 20 °C lower than the experimental reported flash point for formic acid (69 °C), which is more probably the flash point of a water/formic acid solution. However, it appears that not all compounds conform closely to the half-stoichiometric rule; for instance, aniline and chlorobenzene for which the vapor pressure at the flash point is not half of stoichiometric but 0.72 and 0.76 of stoichiometric, respectively. This ratio to the stoichiometric concentration can actually range from 0.2 up to 1. The strict use of the half-stoichiometric rule can therefore lead to the wrong conclusion that the flash point of some compounds is probably erroneous. Therefore, the predictions of the half-stoichiometric rule cannot be assessed unambiguously even if it is a valuable tool for a lot of compounds.

The goals of this work are:

(1) to propose a unique empiric equation able to estimate accurately, quickly, and without computational resources the flash point of a carbon-containing compound whatever its chemical structure is;

(2) to validate this equation with a lot of carbon-containing compounds other than the ones just considered for Eq. (4a);

(3) to detect compounds for which the reported flash points are probably erroneous and to build a reliable database; and

(4) to estimate flash points for compounds for which no

flash point data are available in the literature, in the chemical manufacturers materials safety data sheets (MSDS), or on the internet, although these compounds are known to be combustible.

7. Flash Point Data

There are several sources for flash point data. These include:

(1) International Chemical Safety Cards (ICSCs)[33] on the internet;
(2) *CRC Handbook of Chemical Physics and Physical Chemistry*[34] or other handbooks,[35,36]
(3) US Bureau of Mines (now Pittsburgh Research Center) reports and compilations,[37,38]
(4) chemical manufacturer's MSDSs,[39,40]
(5) Physical and Theoretical Chemistry Laboratory (PTCL) Oxford University chemical and other safety information,[41]
(6) National Institute for Occupational Safety and Health (NIOSH) Pocket Guide (NPG) to Chemical Hazards,[42] and
(7) the NFPA publication "Fire Protection Guide to Hazardous Materials." [43]

ICSCs[33] published by UNEP/ILO/WHO/EU in the frame of the International Program on Chemical Safety (IPCS) are considered here as the major source of reliable data because the data are updated when necessary. A U.S. version of the ICSCs published by the NIOSH exists. About 1300 compounds, not all organic, not all combustible, are reported in the ICSCs against less than 150 in the *CRC Handbook of Chemical Physics and Physical Chemistry*.[34] These cards are also available on the Internet. Several hundred flash points are not available in these cards, but in chemical manufacturers' MSDS or other compilations.

8. Results

8.1. Establishment of the Equation

Fifty nine carbon-containing compounds have been selected mostly from the ICSCs[33] for the establishment of the equation. The number of compounds should not be too small and also should not include erroneous data. The six compounds suggested for reexamination by Jones,[28,29] Jones and Godefroy,[30] and Godefroy and Jones[31] have been excluded from this list. The compounds were selected to cover a wide temperature range (from very low temperature flash points up to high temperature flash points) and a wide range of chemical structures (linear, branched, cyclic compounds, from 1 up to 16 carbon atoms in the molecule). Basically, the compounds of interest here are hydrocarbons, organic oxygen compounds, organic nitrogen compounds, organic sulfur compounds, organic halogen compounds, and in general, C–H–N–O–S–X compounds whatever their structures. In this database the following chemical classes are included
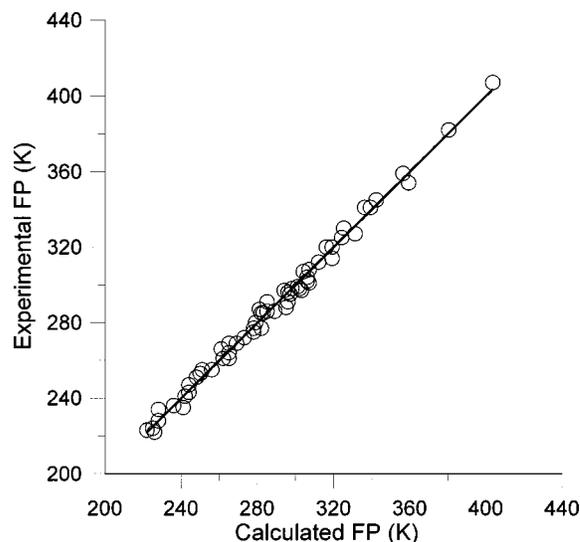
FIG. 1. Comparison between experimental and calculated flash points with Eq. (4a). Full line is both the line experimental FP=calculated FP and the best fit of the 59 points.

with one or more compounds: alkanes (linear, branched, cyclic), aromatics, alcohols (linear, branched, cyclic), ethers, thiols, sulfides, ketones, esters, carboxylic acids, alkenes, chloroalkanes, aldehydes, amines, and nitro compounds. The establishment of a unique equation against only one parameter such as the normal boiling point would only lead to a rough estimation as several compounds can have the same normal boiling point with completely different flash points. To obtain a unique equation, the flash point has to be expressed as a function of two or three parameters. The three parameters considered here are the normal boiling point (T_{eb}), the standard enthalpy of vaporization at 298.15 K, and the number (n) of carbon atoms in the molecule. Of all the types of equations tested, it appears that the closed cup (CC) FP can best be expressed for the 59 selected compounds by

$$\text{FP(K)} = 1.477 \times T_{eb}^{+0.79686} \times \Delta H^{\circ\,+0.16845}_{vap} \times n^{-0.05948},$$
(4a)

where T_{eb}/K is the normal boiling temperature of the compound, ΔH°_{vap} the standard enthalpy of vaporization at 298.15 K of the compound expressed in kJ mol^{-1}, and n the total number of carbon atoms in the molecule. It was not possible to get a reliable expression without including the n term in the equation. Indeed, the equation obtained without the n term with this power law form does not allow a reliable estimation of the flash point of the molecules containing 1 or 2 carbon atoms (mean absolute deviation 5.3 °C, but absolute maximum deviation of 29 °C for nitromethane and 20 °C for methanol). Figure 1 shows the agreement between estimated and experimental flash points. With this equation the mean absolute deviation is 2.9 °C for the −50–133.9 °C FP temperature range considered, with a maximum absolute error of 7 °C. For FP below 0 °C, the mean absolute deviation is 2.3 °C, for FP comprised between 0 and 30 °C the mean absolute deviation is 3.2 °C, for FP comprised between

TABLE 2. Comparison between calculated and experimental closed-cup (CC) flash points of the 59 compounds selected in the database test set. Mean absolute deviation is 2.9 °C and maximum absolute error is 7 °C (1-propanol) between experimental and estimated FP, with Eq. (4a)

Species	Calculated FP (°C)	Experimental FP (°C)	References[a,b]	CAS Registry Number
acetone	−22	−18	ICSCs CC	67-64-1
butanal	−12	−7	ICSCs	123-72-8
1-butanethiol	5	2	ICSCs CC	109-79-5
butanoic acid	69	72	ICSCs CC	107-92-6
1-butanol	33	29	ICSCs CC	71-36-3
2-butanol	21	24	ICSCs CC	78-92-2
2-butanone	−8	−9	ICSCs CC	78-93-3
butyl acetate	24	22	ICSCs CC	123-86-4
n-butylamine	−8	−12	ICSCs CC	109-73-9
		−8.5 °C BASF MSDS		
butyl formate	12	18	ICSCs CC	592-84-7
1-chlorobutane	−11	−12	ICSCs	109-69-3
chloroethane	−51	−50	ICSCs CC	75-00-3
cyclohexane	−17	−18	ICSCs CC	110-82-7
		(flammable solid)		
cyclohexanol	63	68	ICSCs CC	108-93-0
cyclopentane	−37	−37	ICSCs CC	287-92-3
cyclopentanone	28	26	ICSCs	120-92-3
n-decane	51	50.9±0.8 °C	[44] CC	124-18-5
		52.8±1.0 °C	[44] CC	
1-decene	46	47	[41] CC	872-05-9
di-n-butylamine	43	47	ICSCs	111-92-2
		39 °C BASF MSDS		
		42.5 [56] CC		
dibutylether	29	25	[38] CC	142-96-1
diethylether	−45	−45	ICSCs CC	60-29-7
dimethyl sulfide	−32	−38	[38] CC	75-18-3
dipentylether	52	57	[41]	693-65-2
ethanal	−45	−39	ICSCs CC	75-07-0
ethanol	12	13	ICSCs CC	64-17-5
		11,3; 12.4	Kong et al.[45]	
ethyl acetate	−8	−4	ICSCs CC	141-78-6
		−6.9 to −6.8	Kong et al.[45]	
ethylbenzene	23	18	ICSCs CC	100-41-4
ethyl formate	−23	−20	ICSCs CC	109-94-4
n-heptane	−4	−4	ICSCs CC	142-82-5
2-heptanone	39	39	ICSCs	110-43-0
n-hexadecane	130	133.9±2.8	[44] CC	544-76-3
n-hexane	−25	−22	ICSCs CC	110-54-3
2-hexanol	46	41	ICSCs	626-93-7
2-hexanone	23	23	ICSCs CC	591-78-6
1-hexene	−29	−26	ICSCs	592-41-6
nitroethane	34	28	ICSCs CC	79-24-3
nitromethane	34	35	ICSCs CC	75-52-5
2-nitropropane	30	24	ICSCs CC	79-46-9
n-nonane	33	31	ICSCs CC	111-84-2
mesityl oxide	25	25	ICSCs CC	141-79-7
methanol	9	12	ICSCs CC	67-56-1
		7–7.7	Kong et al.[45]	
2-methylheptane	9	4.4	ICSCs	592-27-8
methyl isopropyl ketone	0	−1	ICSCs	563-80-4
2-methylpentane	−31	−32	ICSCs CC	107-83-5
n-octane	16	13	ICSCs CC	111-65-9
1-octanol	86	81	ICSCs CC	111-87-5
n-pentane	−48	−49	ICSCs CC	109-66-0
pentanoic acid	83	86	ICSCs CC	109-52-4
3-pentanol	31	34	ICSCs CC	584-02-1
2-pentanone	6	7	ICSCs CC	107-87-9
1-pentene	−47	−51	[41] CC	109-67-1
propanal	−29	−30	ICSCs	123-38-6
propanoic acid	58	54	ICSCs CC	79-09-4
1-propanol	22	15	ICSCs CC	71-23-8
2-propanol	10	11.7	ICSCs CC	67-63-0
propyl acetate	8	14	ICSCs CC	109-60-4
tetradecane	107	109.3±2.7	[44] CC	629-59-4
toluene	5	4	ICSCs CC	108-88-3
undecane	66	67.1±0.7	[44] CC	1120-21-4
		68.7±1.4		

[a]ICSCs: International Chemical Safety Cards,[33] CC: closed cup.
[b]MSDS: material safety data sheets.

TABLE 3. Comparison between the estimations made by using Eq. (2) of Hshieh, and Eq. (4a) presented here for some compounds of Table 2. For the 59 compounds of Table 1, the mean absolute deviations are 9 and 2.9 °C for Eqs. (2) and (4a), respectively, and maximum absolute errors are 28 and 7 °C for Eqs. (2) and (4a), respectively

Species	FP (°C) estimated with Eq. (2)	FP (°C) estimated with Eq. (4)	Literature value (°C)
pentane	−33	−48	−49
mesityl oxide	26	25	25
2-propanol	−4	10	11.7
nitromethane	7	34	35
cyclohexanol	45	63	68
butyl acetate	23	24	22
toluene	13	5	4
butanoic acid	47	69	72
acetone	−21	−22	−18
methanol	−15	9	12
hexadecane	128	130	133.9

30 and 60 °C the mean absolute deviation is 3.5 °C, for FP comprised between 85 and 120 °C the mean absolute deviation is 2.7 °C, and for FP comprised between 120 and 150 °C the absolute deviation is 3.9 °C (but only one compound). The mean absolute deviations reported are equal to or better than the reproductibility data reported in Sec. I. A comparison between calculated flash point and experimental flash point is given in Table 2. When $\Delta_{vap}H°$ cannot be estimated easily, the FP can be expressed by

$$FP(K) = 0.3544 \times T_{eb}^{+1.14711} \times n^{-0.07677}. \quad (4b)$$

With this equation and compounds of Table 2, an average absolute deviation of 4.5 °C and a maximum absolute deviation of 15 °C have been obtained. The use of Eq. (4a) is recommended. Equation (4b) should only be considered for a rough estimation, even if Eq. (4b) performs better than the previously published equations.

8.2. Comparisons Between the Estimations Obtained with the Equation Proposed Here and Previous Equations

The estimations given by the equation of Hshieh [Eq. (2)] are compared with the estimations obtained with Eq. (4a) for some compounds of Table 2 (see Table 3). The estimations obtained by using Eq. (2) are much better than the ones obtained by using Eq. (1) but still not sufficiently accurate. For Eq. (2), the mean absolute deviation is 9 °C with a maximum absolute error of 28 °C for the 59 compounds of Table 2. The estimations obtained with the equation presented here (see Table 2: mean absolute deviation of 2.9 °C and maximum absolute error of 7 °C) are much better than the ones obtained with Eq. (2). This result was expected because Eq. (4a) was established with the compounds of Table 2 and therefore Eq. (4a) needs to be validated with many other organic compounds.

8.3. Validation of Eq. (4a)

The prediction of Eq. (4a) has been tested against some other compounds, some of them among the most common solvents, referenced in the ICSCs or/and in the *CRC Handbook of Chemical Physics and Physical Chemistry*. Data needed for calculations (normal boiling point, standard enthalpy of vaporization at 298.15 K) can be found in the *NIST Chemistry Webbook*[46] for both normal boiling point and standard enthalpy of vaporization at 298.15 K, or in other compilations.[47,48] Generally the normal boiling point is well known, except for some compounds such as 1-nitropropane, tributylamine, tetradecane, pentadecane, hexadecane, pentyl formate, and hexyl acetate for which an uncertainty of 60, 20, 10, 20, 10, 20, and 20 °C, respectively, is reported. When these data are lacking, the normal boiling point can be calculated according to methods proposed by Marrero and Gani,[49] Coniglio and Nouviaire,[50] and Katritzky *et al.*[51] The standard enthalpy of vaporization at 298.15 K is also generally quite well known,[46–48] when known, but in some cases data obtained before World War II are erroneous. When these data are lacking or known with high uncertainty, the standard enthalpy of vaporization at 298.15 K can be estimated accurately by using the group additivity method for C–H–N–S–O–X compounds[52,53] according to $\Delta_{vap}H° = \Delta_f H°_{(g)} - \Delta_f H°_{(liq)}$. Alternative enthalpy of vaporization estimation methods are the one proposed by Tu and Liu[54] and others presented in Chickos and Acree[48] and/or in Tu and Liu.[54] For some compounds, the enthalpy of vaporization at 298.15 K can be estimated according to the Clausius–Clapeyron equation with vapor pressure data found in the *CRC Handbook of Chemical Physics and Physical Chemistry*[34] or in the book of Boublik *et al.*[55] This tacitly assumes that $\Delta_{vap}H = \Delta_{vap}H°$, which is not true, but the correction is small because the temperature of interest (298.15 K) is generally well below the normal boiling point and the error is small under such circumstances. The same statement holds for the vaporization enthalpy data at 298.15 K reported in the compilation of Chickos and Acree.[48] The compounds considered are generally liquid at standard pressure and 298.15 K. For a compound, which is a gas at standard pressure and 298.15 K, the enthalpy of vaporization value refers to the hypothetical liquid at standard pressure and 298.15 K. For a compound, which is a solid at standard pressure and 298.15 K, the enthalpy of vaporization value refers to the hypothetical liquid at standard pressure and 298.15 K. Compounds, which boil with decomposition, have generally not been considered.

All flash points in Table 2 and Tables 4–11 have been considered as closed-cup flash points, except where otherwise stated. For almost all the compounds, the source for normal boiling points and standard enthalpy of vaporization at 298.15 K is the *NIST Chemistry Webbook*.[46] When the standard enthalpy of vaporization data is lacking in the *NIST*

TABLE 4. Comparison between calculated, with Eq. (4a), and experimental flash points for compounds from the ICSCs or from various references from the literature. Maximum absolute error is 10 °C for adiponitrile (high FP)

Species	Calculated FP (°C)	Experimental FP (°C)	References[a,b,c,f]	CAS Registry Number
acetic acid, 1,1-dimethylethyl ester	12	15.5	ICSCs CC	540-88-5
acetic acid ethenyl ester	−9	−8	NPG[42]	108-05-4
acetic anhydride	47	49	ICSCs CC	108-24-7
acetophenone	76	82	ICSCs OC	98-86-2
acrolein	−19[d]	−26	ICSCs CC	107-02-8
acrylic acid	55	54	ICSCs CC	79-10-7
acrylonitrile	−6	−1	ICSCs CC	107-13-1
adiponitrile	149	159	ICSCs CC	111-69-3
allyl isothiocyanate	45	46	ICSCs CC	57-06-7
2-amino-2-methyl-1-propanol	72	67	ICSCs CC	124-68-5
aniline	71	70	ICSCs CC	62-53-3
benzaldehyde	59	62	ICSCs CC	100-52-7
benzene	−15	−11	ICSCs CC	71-43-2
benzofuran	52	56	ICSCs	271-89-6
benzonitrile	72	75	ICSCs CC	100-47-0
benzoyl chloride	75	72	ICSCs CC	98-88-4
benzyl alcohol	85	93	ICSCs CC	100-51-6
benzyl chloride	61	67	ICSCs CC	100-44-7
biphenyl	107	113	ICSCs CC	92-52-4
bromobenzene	43	51	ICSCs CC	108-86-1
bromoform	75	83	[34] not combustible[33] (see Sec. 8.5.)	75-25-2
1,3-butadiene	−76	−76	ICSCs CC	106-99-0
2,3-butanedione	2	6	ICSCs	431-03-8
2-butoxyethanol	62	61	ICSCs CC	111-76-2
2-butoxyethyl acetate	74	71	ICSCs CC	112-07-2
sec-butyl acetate	13	17	ICSCs CC	105-46-4
tert-butyl alcohol	7	11	ICSCs CC	75-65-0
butyl propionate	34	32	ICSCs	590-01-2
γ-butyrolactone	91	98	ICSCs CC	96-48-0
camphor	74	66	ICSCs CC Note: 'FP'<MP (flammable solid)	76-22-2
carbonochloridic acid, ethyl ester	9	16	ICSCs CC	541-41-3
chlorobenzene	24	27	ICSCs CC	108-90-7
2-chloro-1,3-butadiene	−27	−20	ICSCs OC	126-99-8
2-chloroethanol	55	60	ICSCs CC	107-07-3
3-chloro-2-methyl-1-propene	−14	−12	ICSCs CC	563-47-3
3-chloropropene	−31	−32	ICSCs CC	107-05-1
2-chlorotoluene	42	43	ICSCs CC	95-49-8
4-chlorotoluene	46	49	ICSCs	106-43-4
o-cresol	79	81	ICSCs CC	95-48-7
m-cresol	85	86	ICSCs	108-39-4
p-cresol	88	86	ICSCs CC	106-44-5
cumene	33	31	ICSCs CC	98-82-8
cyclohexanethiol	44	43	ICSCs CC	1569-69-3
cyclohexanone	42	44	ICSCs CC	108-94-1
cyclohexene	−14	−12	NPG	110-83-8
cyclohexyl acetate	55	58	ICSCs CC	622-45-7
cyclohexylamine	28	28	ICSC CC	108-91-8
p-cymene	49	47	ICSCs CC	99-87-6
di-tert-butyl peroxide	4	12	ICSCs CC	110-05-4
1-decanethiol	106	98.3	NPG	143-10-2
o-dichlorobenzene	64	66	ICSCs CC	95-50-1
m-dichlorobenzene	63	63	ICSCs	541-73-1
p-dichlorobenzene	64	66	ICSCs CC	106-46-7
1,2-dichloroethane	6	13	ICSCs CC	107-06-2
1,2-dichloropropane	8	16	ICSCs CC	78-87-5
diethylamine	−27	<−26	ICSCs CC	109-89-7
o-diethylbenzene	51	55	ICSCs CC	135-01-3
diethyl carbonate	27	25	ICSCs CC	105-58-8

TABLE 4. Comparison between calculated, with Eq. (4a), and experimental flash points for compounds from the ICSCs or from various references from the literature. Maximum absolute error is 10 °C for adiponitrile (high FP)—Continued

Species	Calculated FP (°C)	Experimental FP (°C)	References[a,b,c,f]	CAS Registry Number
diethylene glycol dimethyl ether	46	51	ICSCs CC	111-96-6
diethylenetriamine	100	97	ICSCs CC	111-40-0
diethyl sulfate	96	104	ICSCs CC	64-67-5
diisobutylamine	27	29	ICSCs CC	110-96-3
diisobutyl ketone	49	49	ICSCs CC	108-83-8
diisopropylamine	−12	−6	ICSCs OC	108-18-9
			FP CC<FP OC	
diisopropyl ether	−24	−28	ICSCs	108-20-3
diketene	31	33	ICSCs	674-82-8
N,N-dimethylacetamide	57	63	34	127-19-5
N,N-dimethylaniline	67	62	ICSCs	121-69-7
1,2-dimethylbenzene	29	32	ICSCs CC	95-47-6
1,3-dimethylbenzene	25	25	34	108-38-3
1,4-dimethylbenzene	21	25	34	106-42-3
N,N-dimethyl formamide	57	58	ICSCs CC	68-12-2
dimethylnitrosamine	58	61	ICSCs	62-75-9
dimethyl phthalate	146	146	ICSCs	131-11-3
N,N-dimethyl-1,3-propanediamine	29	35	ICSCs CC	109-55-7
dimethylsulfoxide	91	88	34	67-68-5
1,4-dioxane	10	12	ICSCs	123-91-1
1,3-dioxolane	−3	2	34	646-06-0
diphenylamine	152	153	ICSCs CC	122-39-4
diphenyl ether	112	115	ICSCs CC	101-84-8
1,2-ethanediamine	39	34	ICSCs CC	107-15-3
			38 °C BASF MSDS	
1,2-ethanediol	113	111	ICSCs CC	107-21-1
ethanoic acid	47	39	ICSCs CC	64-19-7
2-ethoxyethanol	41	44	ICSCs CC	110-80-5
2-ethoxyethylacetate	51	51	ICSCs CC	111-15-9
ethyl acrylate	6	9	ICSCs CC	140-88-5
ethyl chloroacetate	48	53	ICSCs CC	105-39-5
ethyl cyanide	9	6	ICSCs CC	107-12-0
ethyleneimine	−12	−11	ICSCs CC	151-56-4
2-ethylhexanal	51	46	ICSCs CC	123-05-7
2-ethylhexanol	78	73	ICSCs	104-76-7
5-ethylidene-2-norbornene	28	38	ICSCs OC	16219-75-3
			FP CC<FP OC	
N-ethylmorpholine	29	32	ICSCs	100-74-3
furfural	56	60	ICSCs CC	98-01-1
furfuryl alcohol	67	65	ICSCs CC	98-00-0
2-heptanol	63	71	ICSCs CC	543-49-7
hexanoic acid	100	102	ICSCs OC	142-62-1
1-hexanol	60	63	ICSCs CC	111-27-3
hexylamine	28	29	ICSCs OC	111-26-2
3-hydroxypropanenitrile	122	129	ICSCs OC	109-78-4
isoamyl alcohol	42	45	ICSCs CC	123-51-3
isobutene	−79	−76	ICSCs CC	115-11-7
isobutyl acetate	16	18	ICSCs CC	110-19-0
isobutylamine	−14	−9	ICSCs CC	78-81-9
isopentyl acetate	31	25	ICSCs CC	123-92-2
isoprene	−49	−54	ICSCs CC	78-79-5
isopropyl acetate	−3	2	ICSCs CC	108-21-4
isopropyl glycidyl ether	27	33	ICSCs CC	4016-14-2
(d) limonene	50	48	ICSCs	5989-27-5
mesitylene	43	50	ICSCs CC	108-67-8
methacrylonitrile	0	1	ICSCs CC	126-98-7
2-methoxyethanol	37	39	ICSCs CC	109-86-4
2-methoxyethylacetate	44	45	ICSCs CC	110-49-6
1-methoxy-2-propanol	40	38	ICSCs	107-98-2
methyl acetate	−20	−13	ICSCs CC	79-20-9
N-methylaniline	82	79.5	ICSCs CC	100-61-8

TABLE 4. Comparison between calculated, with Eq. (4a), and experimental flash points for compounds from the ICSCs or from various references from the literature. Maximum absolute error is 10 °C for adiponitrile (high FP)—Continued

Species	Calculated FP (°C)	Experimental FP (°C)	References[a,b,c,f]	CAS Registry Number
2-methylaniline	80	85	ICSCs CC	95-53-4
3-methylaniline	83	86	ICSCs CC	108-44-1
4-methylaniline	82	86	ICSCs CC	106-49-0
methyl benzoate	80	83	ICSCs CC	93-58-3
methylcyclohexane	−4	−4	34	108-87-2
2-methylcyclohexanol	64	58	ICSCs CC	583-59-5
3-methylcyclohexanol	65	62	ICSCs CC	591-23-1
4-methylcyclohexanol	71	70	ICSCs CC	589-91-3
2-methylcyclohexanone	51	48	ACGIH,[e] CC	583-60-8
N-methylformamide	94	98	ICSCs CC	123-39-7
5-methyl-3-heptanone	44	43	ICSCs CC	541-85-5
2-methylhexane	−11	−18	ICSCs CC	591-76-4
5-methyl-2-hexanone	34	36	ICSCs CC	110-12-3
methyl isobutyl ketone	14	14	ICSCs CC	108-10-1
methyl methacrylate	7	10	ICSCs OC	80-62-6
4-methyl-2-pentanol	41	41	ICSCs	108-11-2
2-methyl-1-propanal	−21	−25	ICSCs	78-84-2
2-methyl-propanoic acid	58	56	ICSCs CC	79-31-2
2-methyl-2-propanethiol	−23	−26	ICSCs CC	75-66-1
2-methyl-2-propenal	−23	−15	ICSCs	78-85-3
2-methylpyridine	24	26	ICSCs CC	109-06-8
3-methylpyridine	35	38	ICSCs CC	108-99-6
MTBE	−32	−28	ICSCs CC	1634-04-4
morpholine	34	35	ICSCs CC	110-91-8
naphthalene	78	79	ICSCs	91-20-3
nitrobenzene	88	88	ICSCs CC	98-95-3
1-nitropropane	30	36	ICSCs	108-03-2
o-nitrotoluene	95	95	ICSCs CC	88-72-2
p-nitrotoluene	104	103	ICSCs CC	99-99-0
1,7-octadiene	8	9	ICSCs	3710-30-3
2-octanol	76	76	ICSCs	123-96-6
1-octene	12	21	ICSCs OC FP CC< FP OC	111-66-0
3-oxobutanoic acid ethyl ester	68	70	ICSCs CC	141-97-9
paraldehyde	19	24	ICSCs CC	123-63-7
2,4-pentanedione	33	34	ICSCs CC	123-54-6
3-pentanone	7	13	ICSCs OC	96-22-0
2-pentyl acetate	30	32	ICSCs CC	626-38-0
phenol	75	79	ICSCs CC	108-95-2
phenyl isocyanate	46	51	ICSCs CC	103-71-9
phthalic anhydride	156	152	ICSCs CC	85-44-9
piperidine	11	16	ICSCs	110-89-4
pivalic acid	63	64	ICSCs CC	75-98-9
1,2-propanediamine	33	33	ICSCs OC	78-90-0
1,2-propanediol	103	99	ICSCs CC	57-55-6
2-propene-1-ol	21	21	ICSCs CC	107-18-6
2-propenoic acid, butyl ester	36	37	ICSCs	141-32-2
propionic anhydride	60	63	ICSCs	123-62-6
propylene oxide	−39	−37	ICSCs CC	75-56-9
propylglycol	50	51	ICSCs OC	2807-30-9
2-propyn-1-ol	27	33	ICSCs CC	107-19-7
pyridine	16	20	ICSCs CC	110-86-1
pyrrolidine	1	3	ICSCs	123-75-1
quinoline	102	105	ICSCs	91-22-5
styrene	30	31	ICSCs CC	100-42-5
1,1,1,2-tetrachloroethane	45	47	34 not combustible[33] (see Sec. 8.5.)	630-20-6
1,1,2,2-tetrachloroethane	59	62	34 not combustible[33] (see Sec. 8.5.)	79-34-5

TABLE 4. Comparison between calculated, with Eq. (4a), and experimental flash points for compounds from the ICSCs or from various references from the literature. Maximum absolute error is 10 °C for adiponitrile (high FP)—Continued

Species	Calculated FP (°C)	Experimental FP (°C)	References[a,b,c,f]	CAS Registry Number
tetrachloroethylene	37	45	34	127-18-4
			not combustible[33]	
			(see Sec. 8.5.)	
THF	−20	−14.5	ICSCs CC	109-99-9
		−20.7	Kong et al.[45]	
tetralin	79	77	34	119-64-2
4-thiapentanal	58	58	ICSCs	3268-49-3
thiophene	−5	−1	ICSCs	110-02-1
1,1,1-trichloroethane	−3	−1	34	71-55-6
			not combustible[33]	
			(see Sec. 8.5.)	
1,1,2-trichloroethane	32	32	34	79-00-5
			not combustible[33]	
			(see Sec. 8.5.)	
triethylamine	−18	−17	ICSCs CC	121-44-8
1,2,3-trimethylbenzene	43	44	ICSCs	526-73-8
1,2,4-trimethylbenzene	46	44	ICSCs CC	95-63-6
2,4,4-trimethyl-1-pentene	−5	−5	ICSCs	107-39-1
2,4,4-trimethyl-2-pentene	−1	1.7	ICSCs OC	107-40-4
4-vinyl-1-cyclohexene	17	16	ICSCs CC	100-40-3

[a]ICSCs: International Chemical Saftey Cards[33]
[b]NPG: NIOSH Pocket Guide
[c]Handbook of Chemical Physics and Physical Chemistry[34]
[d]High uncertainty on the normal boiling point for this compound.
[e]American Conference of Governmental Industrial Hygienists.
[f]OC=open cup; CC=closed cup.

Chemistry Webbook,[46] these data were taken in Chickos and Acree[48] or calculated according to Domalski and Hearing.[53] These tables report the compounds for which satisfactory agreement is obtained between estimated FP and experimental FP. Satisfactory agreement means that the absolute difference between estimated and experimental flash point is lower than the reproductibility or at least equal to the reproductibility. Occasionaly, compounds for which the absolute devia-

TABLE 5. Comparison between calculated, with Eq. (4a), and experimental flash points for compounds from Kuchta.[a] Maximum absolute error is 8 °C

Species	Calculated FP (°C)	Experimental FP (°C)[b]	CAS Registry Number
t-butanol	7	11	75-65-0
2-butenal	9	13	4170-30-3
s-butylbenzene	48	52	135-98-8
diethylaniline	85	85	91-66-7
p-diethylbenzene	54	57	105-05-5
2,2-dimethylbutane	−41	−48	75-83-2
ethyl nitrate	10	10	625-58-1
ethyl nitrite	−42	−35	109-95-5
ethyl propyl ether	−25	−20	628-32-0
isobutylbenzene	48	55	538-93-2
isooctane	−7	−12	540-84-1
isopentanol	42	43	123-51-3
α-pinene	36	33	80-56-8
n-propyl nitrate	23	20	627-13-4

[a]See Kuchta.[38]
[b]FP are generally closed-cup values.

tion is only 2 to 3 °C above the reproductibility data given in Sec. I are also included in these tables. It is the case for some compounds in the 30–60 °C FP temperature range (see for instance ethanoic acid in Table 4). For about 600 compounds reported in Table 2 and Tables 4–11, the mean absolute deviation between estimated closed-cup flash point and experimental closed-cup flash point is found to be equal to 3.4 °C (standard deviation is 2.3 °C) and the maximum absolute deviation is generally 8 °C whatever the temperature range, except in the 150–175 °C temperature range for two compounds with high flash points (adiponitrile and octadecane). The absolute deviation for these two compounds is in agreement with the reproductibility data. Table 4 gives the compounds for which satisfactory agreement is obtained between experimental (from ICSCs) and calculated flash points. The flash points reported in Table 4 are generally CC flash points but when no other data are available open cup (OC) flash points are reported. OC flash points are generally up to 10 °C above CC flash points. Some other data are available in other compilations or publications (see Tables 5, 6, 7, and 8).[12–14,22,35–38,56–58] Some other data are not available in the ICSCs or in the Handbook of Chemistry but in the chemical manufacturer's MSDSs. The predictions of Eq. (4a) are compared in Table 9 with data found in the chemical manufacturers' MSDS. Only compounds with purity higher or equal to 98% have been considered. Table 9 also gives the compounds for which satisfactory agreement is obtained between experimental and calculated flash points.

TABLE 6. Comparison between calculated, with Eq. (4a), and experimental flash points for compounds from the compilation of Kanury.[a] All experimental flash points are CC flash points, except 1-heptanol, maximum absolute deviation is 8 °C

Species	Calculated FP (°C)	Experimental FP (°C)	CAS Registry Number
1-butene	−78	−80	106-98-9
butylbenzene	56	49	104-51-8
cyclobutane	−64	−65	287-23-0
cyclopropane	−95	−95	75-19-4
1,1-dimethylcyclohexane	8		590-66-9
trans-1,2-dimethylcyclohexane	11		6876-23-9
cis-1,2-dimethylcyclohexane	16		2207-01-4
trans-1,3-dimethylcyclohexane	11	11	2207-03-6
cis-1,3-dimethylcyclohexane	9	dimethylcyclohexane	638-04-0
cis-1,4-dimethylcyclohexane	12		624-29-3
1-heptanol	73	71	111-70-6

[a]See Kanury.[56]

Equation (2) is also devoted to the predictions of the flash points of organic silicon compounds. This can explain why Eq. (4a) presented here performs better for hydrocarbons, organic oxygen compounds, organic nitrogen compounds, organic halogen compounds, and organic sulfur compounds. However, Hsieh established an equation specifically for organic silicon compounds:

$$FP(°C) = -51.2385 + 0.4994 T_{eb} + 0.000\,47 T_{eb}^2. \quad (5)$$

Therefore, for completeness, Eq. (4a) has to be tested against organic silicon compounds to assess the improved predictive ability of this equation. Comparisons between estimations of Eq. (4a), estimations of Eq. (5), and literature data are given in Table 10. It should be noted that the literature data reported in Table 10 are some of the data used for the establishment of Eq. (5). The mean absolute deviation for the compounds of Table 10 is 5.35 °C and the maximum absolute error is 19 °C with Eq. (5), whereas the mean absolute deviation is 4.65 °C and the maximum absolute error is 11 °C with Eq. (4a). Surprisingly, Eq. (4a), although established without any organic silicon compounds (see Table 2), performs better than Eq. (5), which is established only with organic silicon compounds. Moreover, if one considers the few data reported in the ICSCs for organic silicon compounds, the agreement between experimental and estimation with Eq. (4a) is even better: mean absolute deviation is 3.7 °C and maximum absolute error is 8 °C. These mean absolute deviation and maximum absolute deviation are about equal with the ones observed with the organic compounds reported in Tables 2 and 4–9. This leads to the conclusion that Eq. (4a) is able to estimate accurately the flash point of organic silicon compounds. The predictions of Eq. (4a) have been tested for other organic compounds not initially considered for the establishment of Eq. (4a), namely organic tin compounds, organic nickel compounds, organic phosphorus compounds, organic boron compounds, and organic deuterated compounds. Although the experimental data are rather scarce for these compounds, Table 11 shows that Eq. (4a) performs quite well also for these compounds. For all the compounds in Tables 2 and 4–11 (about 600 compounds), the mean absolute deviation for FP below 0 °C is 3.29 °C, the mean absolute deviation for FP comprised between 0 and 30 °C is 3.27 °C, the mean absolute deviation for FP comprised between 30 and 60 °C is 3.28 °C, the mean absolute deviation for FP comprised between 60 and 85 °C is 3.35 °C, the mean absolute deviation for FP comprised between 85 and 120 °C is 4 °C, the mean absolute deviation for FP comprised between 120 and 150 °C is 3.5 °C, the mean absolute deviation for FP comprised between 150 and 175 °C is 5.7 °C, and the absolute deviation for FP comprised between 175 and 203 °C is 2 °C (only one compound). All these mean absolute deviations are lower than the reproductibility data reported in Sec. I. Absolute deviations are examined as a function of the FP temperature (Fig. 2) and absolute deviations are examined as a function of the correlation parameters: normal T_{eb} (Fig. 3), standard enthalpy of vaporization at 298.15 K (Fig. 4), and n (Fig. 5). Figures 2–5 show that there is no bias in the predictions.

TABLE 7. Comparison between calculated, with Eq. (4a), and closed-cup experimental flash points for compounds from Patil.[12] Maximum absolute error is 8 °C

Species	Calculated FP (°C)	Experimental FP (°C)	CAS Registry Number
benzenemethanethiol	75	70	100-53-8
benzyl methyl sulfide	71	73	766-92-7
dimethyl sulfite	38	30	616-42-2
diethyl sulfite	56	53	623-81-4
2-methyl-1-hexene	−9	−6	6094-02-6
2-hexyne	−13	−11	764-35-2

TABLE 8. Comparison between calculated, with Eq. (4a), and experimental closed-cup flash points for compounds from Tetteh *et al.*[a] Maximum absolute error is 8 °C

Species	Calculated FP (°C)	Experimental FP (°C)	CAS Registry Number
1-amino-2-propanol	75	77.2	78-96-6
4-bromobiphenyl	150	143.9	92-66-0
1-bromooctane	75	78.3	111-83-1
3-butenenitrile	22	21	109-75-1
N-butylacetamide	118	115.8	1119-49-9
butyl isocyanate	24	28.7	111-36-4
2-chlorobutane	−19	−15	78-86-4
chlorocyclohexane	32	32	542-18-7
1-chloro-4-ethylbenzene	61	64	622-98-0
2-chloro-1-propanol	54	51.7	78-89-7
2,3-dichloro-1-propanol	97	93.3	616-23-9
2,3-dimethylaniline	96	97	87-59-2
trans-1,4-dimethylcyclohexane	8	11.1	2207-04-7
2,4-dimethylpyridine	44	37.2	108-47-4
2-(2-ethoxyethoxy)-ethanol	97	94	111-90-0
N-ethylacetamide	103	110	625-50-3
ethyl benzoate	87	88	93-89-0
4-ethylphenol	97	103.9	123-07-9
heptanoic acid	106	112	111-14-8
1,4-hexadiene	−27	−21.1	592-45-0
2,5-hexanedione	77	79	110-13-4
n-hexylbenzene	85	83	1077-16-3
hexyl ethanoate[b]	53	45	142-92-7
iodobenzene	66	74	591-50-4
1-iodo-3-methylbenzene	82	82.2	625-95-6
isobutyl vinyl ether	−13	−9	109-53-5
3-methoxypropylamine	26	32.2	5332-73-0
3-methyl-4-ethylhexane	25	24	3074-77-9
methyl isothiocyanate	31	32.2	556-61-6
2-methyl-2-propen-1-ol	33	33.3	513-42-8
3-methylstyrene	46	51	100-80-1
octanoyl chloride	75	82	111-64-8
pentanenitrile	36	40.6	110-59-8
1-pentanethiol	24	18.3	110-66-7
2-phenylethanol	98	102	60-12-8
1-propanethiol	−14	−20.8	107-03-9
propyl butyrate	31	37	105-66-8
succinonitrile	131	132.2	110-61-2
1-tetradecene	107	110	1120-36-1
triethoxymethane	35	30	108055-42-1

[a]See Tetteh.[19]
[b]High uncertainty on the normal boiling point for this compound.

According to these figures, the bounds for the proposed correlation, Eq. (4a), are: $-100 \leq \mathrm{FP}(°\mathrm{C}) \leq +200$; $250 \leq T_{eb}(\mathrm{K}) \leq 650$; $20 \leq \Delta_{vap}H(298.15\,\mathrm{K})/\mathrm{kJ}\,\mathrm{mol}^{-1} \leq 110$; and $1 \leq n \leq 21$. These bounds can be completed by Figs. 6–8, which allow the users to see if the equation is extrapolated or not for their needs. Extrapolation is not recommended. However, as Figs. 2–8 have been established without the compounds of Table 11, it can also be meaningful for the chemical families given in Table 11 to extrapolate Eq. (4a).

An uncertainty of ± 5 K for the normal boiling point T_{eb} leads to an uncertainty of ± 3 °C for the estimated FP with Eq. (4a) in the -100–200 °C FP temperature range. An uncertainty of ± 2 kJ mol^{-1} for the standard enthalpy of vaporization at 298.15 K leads to an uncertainty of ± 2–3 °C for the estimated FP with Eq. (4a) in the -100–200 °C FP temperature range. Therefore, it can be stated that an accurate value of the normal boiling point is needed, whereas only a quite rough value of the standard enthalpy of vaporization at 298.15 K can be convenient for estimation purposes.

There are some compounds for which the agreement between the estimated flash point with Eq. (4a) and experimental flash point is poor. For these compounds, the absolute deviation is much greater than the reproductibility data presented in Sec. I. As the estimations depend on reliable values of the normal boiling point and of the standard enthalpy of vaporization at 298.15 K, it remains possible that the experimental flash point is the good one for some species. Some old standard enthalpies of vaporization at 298.15 K data reported in the *NIST Webbook* have been replaced by estimates obtained by using the group additivity method as presented by Domalski and Hearing.[53] This lead to the conclusion that

TABLE 9. Comparison between calculated, with Eq. (4a), and experimental flash points of compounds as reported in the chemical manufacturers' MSDS and other sources. Maximum absolute error is 9 °C

Species	Calculated FP (°C)	Experimental FP (°C)	References[a,b,c]	CAS Registry Number
acetaldoxime	43	36	[62]	107-29-9
anethole	97	90	[41]	4180-23-8
benzenethiol	53	50	[41]	108-98-5
benzyl cyanide	99	101	[61]	140-29-4
bibenzyl	127	129	[41]	103-29-7
1-bromobutane	7	13	[41]	109-65-9
4-bromo-1-butene	5	9	Chemical Land[21] MSDS	5162-44-7
2-bromo-1,1-dimethoxyethane	45	53	CHEMADA MSDS	7252-83-7
1-bromoheptane	60	60	[41]	629-04-9
1-bromopentane	26	31	[61]	110-53-2
2-bromopentane	15	20	[61]	107-81-3
1,2-butanediol	99	93	[62]	584-03-2
1,3-butanediol	112	121	[62]	107-88-0
1,4-butanediol	131	135	[62]	110-63-4
butanenitrile	21	17	[41]	109-74-0
2-butenenitrile	22	20	[61]	4786-20-3
cis 2-butene	−70	−73.3	BOC GASES MSDS, CC	590-18-1
trans 2-butene	−72	−73	[39]	624-64-6
trans 2-butenoic acid	88	87	Oxford Chemical Limited, CC	107-93-7
3-buten-1-ol	30	33	[41]	627-27-0
3-buten-2-ol	18	20	[62]	598-32-3
3-butoxypropylamine	61	63	[61]	16499-88-0
butyl cyanide	36	40	NTP CHEMICAL MSDS	110-59-8
t-butylcyclohexane	44	42	[61]	3178-22-1
t-butyl formate	−8	−9	[61]	762-75-4
2-t-butylfuran	8	7	[61]	7040-43-9
2-t-butyl-4-methylphenol	100	100	[61]	2409-55-4
t-butyl methyl sulfide	2	−3	[62]	6163-64-0
S-t-butyl thioacetate	26	33	[61]	999-90-6
butyl nitrate	37	36	PFALTZ & BAUER, Inc. MSDS	928-45-0
n-butyl nitrite	−6	−13	[39] CC	544-16-1
t-butyl nitrite	−19	−23	[61]	540-80-7
t-butyl propionate	25	20	[61]	20487-40-5
s-butyl sulfide	47	39	[61]	626-26-6
butyl vinyl ether	−4	−9	[61]	111-34-2
butyric anhydride	84	87	[61]	106-31-0
2-carene	43	38	[61]	554-61-0
carvacrol	104	106	[61]	499-75-2
chlorocyclopentane	14	15	[61]	930-28-9
1-chloroheptane	45	41	[62]	629-06-1
1-chlorohexane	28	26	[41]	544-10-5
2-chloro-2-methylpropane	−33	−27	Akzo Nobel MSDS	507-20-0
1-chlorononane	77	74	[61]	2473-01-0
1-chlorooctane	61	63	[62]	111-85-3
1-chloropentane	10	11	Riedel de Haen MSDS	543-59-9
2-chloropentane	−1	0	[61]	625-29-6
5-chloro-1-pentyne	17	15	[61]	14267-92-6
2-chlorophenol	55	63	[61]	95-57-8
4-chlorophenol	107	115	[41]	106-48-9
1-chloropropane	−32	−31	[61]	540-54-5
2-chloropropane	−42	−35	[41]	75-29-6
3-chloro-1-propanethiol	49	43	[61]	17481-19-5
3-chloro-1-propanol	73	73	[61]	627-30-5
2-chloropropene	−94	FP<−34	[61]	557-98-2

TABLE 9. Comparison between calculated, with Eq. (4a), and experimental flash points of compounds as reported in the chemical manufacturers' MSDS and other sources. Maximum absolute error is 9 °C—Continued

Species	Calculated FP (°C)	Experimental FP (°C)	References[a,b,c]	CAS Registry Number
2-chloropyridine	62	65.6	Arch Chemicals, Inc.	109-09-1
3-chlorotoluene	42	50	[61]	108-41-8
cineole	54	50	[61]	470-82-6
citronellal	74	75	[61]	2385-77-5
β-citronellol	99	98	[61]	106-22-9
cyclobutanone	8	10	[62]	1191-95-3
cyclobutylamine	−5	−4	[62]	2516-34-9
cyclodecane	67	65	[61]	293-96-9
trans,trans,cis-1,5,9-cyclododecatriene	95	87	[62]	706-31-0
cycloheptane	11	6	[61]	291-64-5
cycloheptanol	77	71	[61]	502-41-0
cycloheptanone	58	55	[62]	502-42-1
1,4-cyclohexadiene	−13	−6	[41]	628-41-1
cyclohexanecarbonitrile	67	65	[61]	766-05-2
1,2-cyclohexanedione	83(4b)	84	[61]	765-87-7
cyclohexanemethylamine	38(4b)	43	[61]	3218-02-8
cyclohexene oxide	22	24	BASF MSDS	286-20-4
cyclohexylbenzene	93	98	[41]	827-52-1
1,5-cyclooctadiene	32	32	[62]	111-78-4
cyclooctane	31	28	[62]	292-64-8
cyclooctanone	71	72	[62]	502-49-8
1,3,5,7-cyclooctatetraene	27	22	[41]	629-20-9
cyclopentanethiol	27	25	[62]	1679-07-8
cyclopentanol	50	51	ALKALI METALS MSDS	96-41-3
cyclopentylamine	12	12	[62]	1003-03-8
cyclopropanecarbonitrile	34	32	EASTMAN MSDS	5500-21-0
cyclopropylamine	−26	−25	EASTMAN MSDS	765-30-0
1-cyclopropylethanone	15	13	[62]	765-43-5
		21	[61]	
cis-decahydronaphthalene	60	58	[22]	493-01-6
trans-decahydronaphthalene	55	52	[61]	493-02-7
decanal	81	85	[41]	112-31-2
1-decanamine	92	86	[41]	2016-57-1
5-decene	48	46	CCST, government of Quebec, Canada, CC	7433-56-9
9-decen-1-ol	115	119	[41]	13019-22-2
1-decyne	55	50	SPC-VOLTA MSDS	764-93-2
dibutyl sulfide	65	60	[41] CC	544-40-1
di-tert-butyl disulfide	74	67	CP CHEM MSDS, CC	110-06-5
1,2-dichlorobutane	24	26	[61]	616-21-7
1,3-dichlorobutane	33	30	[61]	1190-22-3
1,1-dichloropropane	2	7	[61]	78-99-9
1,3-dichloropropane	29	32	[61]	142-28-9
2,2-dichloropropane	−12	−5	[61]	594-20-7
diethylcyanamide	68	69	[61]	617-83-4
diethylene glycol dibutyl ether	116	117	[61]	112-73-2
diethylene glycol diethyl ether	69	71	[61]	112-36-7
diethyl glutarate	103	96	[61]	818-38-2
2,3-dihydrofuran	−28	−24	EASTMAN MSDS	1191-99-7
2,3-dihydro-5-methylfuran	−10	−12	[61]	1487-15-6
2,5-dimethoxy-2,5-dihydrofuran	45	51	BASF MSDS	332-77-4
1,1-dimethoxyethane	−15	−17	[62]	534-15-6
1,2-dimethoxyethane	−3	0	[62]	110-71-4
2-dimethylaminoethanol	46	40	ATOFINA MSDS, CC	108-01-0
2,3-dimethylbutane	−34	−29	[39]	79-29-8
2,3-dimethyl-2,3-butanediol	75	77	[61]	76-09-5
3,3-dimethylbutanoic acid	82	88	[61]	1070-83-3

TABLE 9. Comparison between calculated, with Eq. (4a), and experimental flash points of compounds as reported in the chemical manufacturers' MSDS and other sources. Maximum absolute error is 9 °C—Continued

Species	Calculated FP (°C)	Experimental FP (°C)	References[a,b,c]	CAS Registry Number
2,3-dimethyl-2-butene	−21	−20	[41]	563-79-1
3,3-dimethyl-1-butyne	−47	< −34	[41]	917-92-0
N,N-dimethylcyclohexanemethylamine	49	48	[61]	16607-80-0
N,N-dimethylcyclohexylamine	33	39	[62]	98-94-2
dimethyl disulfide	26	24	[39] CC	624-92-0
2,5-dimethyl-2,4-hexadiene	23	29	ACROS ORGANICS MSDS	764-13-6
2,3-dimethylpentane	−12	−6	[61]	565-59-3
2,4-dimethylpentane	−18	−12	[39] CC	108-08-7
3-methyl-1,3-pentadiene	−26	−28	[61]	4549-74-0
2,3-dimethylphenol	93	95	[62]	526-75-0
2,4-dimethylphenol	90	94	[62]	105-67-9
2,5-dimethylphenol	92	95	[62]	95-87-4
1,4-dimethylpiperazine	27	21.5	BASF MSDS	106-58-1
2,2-dimethylpropane	−69	−65	AGA GAS MSDS, CC	463-82-1
2,2-dimethylpropanenitrile	2	4	[61]	630-18-2
dipropylamine	10	7	BASF MSDS	142-84-7
		7.5	[58] CC	
dodecane	81	74	[39] CC	112-40-3
1-dodecanol	134	127	Mallinckrodt Baker, MSDS, CC	112-53-8
1-dodecene	79	77	CP Chem MSDS, CC	112-41-4
eicosane	177	169	[57]	112-95-8
ethane	−140	−135	[39] OC FP CC<FP OC	74-84-0
1,2-ethanedithiol	57	50	CP Chem MSDS, CC	540-63-6
ethenylcyclohexane	15	22	[62]	695-12-5
1-ethoxybutane	−5	−5	[61]	628-81-9
2-ethoxy-2-methyl-propane	−20	−19	[62]	637-92-3
ethylal	−5	−5	Lambiotte MSDS	462-95-3
2-ethyl-1-butanol	54	53	CELANESE MSDS, CC	97-95-0
ethyl butyrate	19	19	[61]	105-54-4
ethylcyclohexane	18	18	[39]	1678-91-7
diethyl disulfide	48	40	[62]	110-81-6
N,N-diethylmethylamine	−24	−23	[61]	616-39-7
ethylene carbonate	148	150	BASF MSDS	96-49-1
2-ethyl-1-butene	−29	< −20	[39] CC	760-21-4
2-ethyl-1-hexanamine	57	50	Chemical Land[21] MSDS	104-75-6
3-ethylhexane	10	5.85	[57]	619-99-8
ethyl isobutyrate	10	13	[61]	97-62-1
1-ethyl-1-methylcyclopentane	10	6	[22]	16747-50-5
2-ethyloxazoline	29	29	[62]	10431-98-8
1-ethylpiperidine	20	18	[62]	766-09-6
ethyl propionate	6	12	[61]	105-37-3
ethyl vinyl ether	−46	−45	[62]	109-92-2
fluorobenzene	−11	−15	Chemical Land[21] MSDS	462-06-6
fluorocyclohexane	3	<5	[62]	372-46-3
1-fluoroheptane	13	13	[61]	661-11-0
heptadecane	145	148	[41]	629-78-7
1,6-heptadiene	−11	−10	[61]	3070-53-9
1,6-heptadiyne	13	9	[61]	2396-63-6
heptanal	42	41	Celanese Chemicals MSDS, CC	111-71-7
heptanenitrile	62	58	[61]	629-08-3

TABLE 9. Comparison between calculated, with Eq. (4a), and experimental flash points of compounds as reported in the chemical manufacturers' MSDS and other sources. Maximum absolute error is 9 °C—Continued

Species	Calculated FP (°C)	Experimental FP (°C)	References[a,b,c]	CAS Registry Number 3-heptanone
1-heptene	−8	−8	ORGANIC TECHNOLOGIES MSDS	592-76-7
cis-2-heptene	−1	−6	[61]	6443-92-1
trans-2-heptene	−5	−1	[61]	14686-13-6
cis-3-heptene	−6	−7	[61]	7642-10-6
trans-3-heptene	−6	−6	[61]	14686-14-7
heptylbenzene	97	95	[41]	1078-71-3
1-heptyne	1	−2	[22]	628-71-7
1-hexadecene	125	132	CP Chem MSDS	629-73-2
hexamethyldisilazane	22	23	[41] CC	999-97-3
hexanal	22	25	KREMS CHEMIE MSDS	66-25-1
2-hexene (cis/trans)	−26	−27	[22]	592-43-8
5-hexen-1-ol	49	47	[61]	821-41-0
1-hexyne	−19	−20	Merck KGaA MSDS	693-02-7
N-(hydroxyethyl)piperazine	131	135	AGROWCHEM MSDS	103-76-4
1-iodobutane	30	33	Deepwater MSDS, CC	542-69-8
2-iodobutane	20	23	Deepwater MSDS, CC	513-48-4
1-iodohexane	62	67	Deepwater MSDS, CC	638-45-9
1-iodopentane	46	43	Merck KGaA MSDS	628-17-1
3-iodo-1-propene	17	18	New Jersey dept. Of Health MSDS	556-56-9
isobutene	−83	−88	[39] CC	75-28-5
isobutyl nitrate	27	21	[39] CC	543-29-3
isobutyl nitrite	−15	−23	NTP CHEMICAL MSDS	542-56-3
2-isopropoxyethanol	43	43	[41]	109-59-1
isopropylcyclohexane	32	35	[22]	696-29-7
2-mercaptoethanol	75	73	[41] CC	60-24-2
3-methyl-1-butene	−61	−57	[39]	563-45-1
isopentane	−55	−57	[22]	78-78-4
isopropylamine	−40	−37	BASF MSDS	75-31-0
2-methoxybutane	−29	−30	[61]	6795-87-5
methylamine	−57	<−30 −62	BASF MSDS [58]	74-89-5
2-methylaminoethanol	73	71	ATOFINA MSDS, CC	109-83-1
2-methyl-1-butanethiol	16	19	[61]	1878-18-8
3-methyl-2-butanethiol	11	19	OXFORD CHEMICAL LIMITED MSDS, CC	2084-18-6
3-methylbutanoic acid	71	74	CELANESE MSDS, CC	503-74-2
2-methyl-1-butanol	41	42.5	BASF MSDS	137-32-6
2-methyl-2-butanol	19	21	[61]	75-85-4
2-methyl-1-butene	−51	<−34	[61]	563-46-2
2-methyl-2-butene	−46	−45	[39]	513-35-9
N-methylbutylamine	−1	1	[61]	110-68-9
methyl butyrate	7	11	[61]	623-42-7
1-methylcyclohexene	4	−3	[41]	591-49-1
methylcyclopentane	−23	−29	[39]	96-37-7
1-methylcyclopentene	−19	−17.2	Scott Specialty Gases MDSD	693-89-0
methyl cyclopropanecarboxylate	17	17	EASTMAN MSDS	2868-37-3

TABLE 9. Comparison between calculated, with Eq. (4a), and experimental flash points of compounds as reported in the chemical manufacturers' MSDS and other sources. Maximum absolute error is 9 °C—Continued

Species	Calculated FP (°C)	Experimental FP (°C)	References[a,b,c]	CAS Registry Number 3-heptanone
methyldiethanolamine	141	137.7	ACCRON MSDS, CC	105-59-9
2-methyl-1,3-dioxolane	3	−2	[62]	497-26-7
methylenecyclohexane	−1	−6	PTCL MSDS	1192-37-6
2-methylfuran	−24	−30	PENN SPECIALTY CHEMICALS, CC	534-22-5
3-methylheptane	10	7	[62]	589-81-1
2-methyl-1-heptene	9	10	[61]	15870-10-7
2-methyl-2-heptene	12	8	[61]	627-97-4
methyl heptanoate	54	52	[62]	106-73-0
3-methylhexane	−9	−3	CCST, government of Quebec, Canada, CC	589-34-4
methyl isobutyrate	−1	3	[61]	547-63-7
N-methylmorpholine	16	14	BASF MSDS	109-02-4
2-methylnaphthalene	94	97	NTP CHEMICAL MSDS	91-57-6
4-methylnonane	45	38	[22]	17301-94-9
methyl 2-octynoate	92	88	[61]	111-12-6
3-methylpentane	−29	−32	CP Chem MSDS, CC	96-14-0
2-methyl-1-pentanol	53	54	Canadian Center for Occupational Health and Safety (CCOHS), CC	105-30-6
3-methyl-1-pentanol	58	58	[61]	589-35-5
3-methyl-2-pentanol	43	40	[61]	565-60-6
4-methyl-1-pentanol	55	51	[61]	626-89-1
2-methyl-3-pentanol	38	46	[61]	565-67-3
2-methyl-3-pentanone	12	13	[61]	565-69-5
3-methyl-2-pentanone	15	12	[61]	565-61-7
2-methyl-1-pentene	−30	−26	[61]	763-29-1
2-methyl-2-pentene	−26	−23	[61]	625-27-4
4-methyl-1-pentene	−37	−31	[39] CC	691-37-2
N-methyl-2-propanamine	−30	−31	[61]	4747-21-1
2-methyl-1-propanol	27	27	[61]	78-83-1
4-methylpyridine	36	37	KOEI CHEMICAL MSDS, CC	108-89-4
1-methylpyrrole	20	15	[61]	96-54-8
1-methylpyrrolidine	−12	−18	KOEI CHEMICAL MSDS, CC	120-94-5
1-methyl-2-pyrrolidinone	85	86	[61]	872-50-4
methyl salicylate	89	96	Mallinckrodt Baker, Inc MSDS	119-36-8
4-methylstyrene	48	45	[61]	622-97-9
2-methyltetrahydrofuran	−13	−11	PENN SPECIALTY CHEMICALS	96-47-9
2-methylthiophene	13	7	[39] CC	554-14-3
3-methylthiophene	15	11	DEGUSSA MSDS	616-44-4
methyl valerate	24	22	[61]	624-24-8
nitrocyclohexane	83	74	[61]	1122-60-7
2-nitrophenol	110	102	[41]	88-75-5
nonadecane	166	168	[41]	629-92-5
1,8-nonadiene	21	26	[61]	4900-30-5
1,8-nonadiyne	49	41	[61]	2396-65-8
n-nonanal	68	71	CELANESE MSDS, CC	124-19-6
1-nonanol	99	97.78	The Good Scents Company MSDS, CC	143-08-8
2-nonanone	70	69	MOORE INGREDIENTS CC	821-55-6

TABLE 9. Comparison between calculated, with Eq. (4a), and experimental flash points of compounds as reported in the chemical manufacturers' MSDS and other sources. Maximum absolute error is 9 °C—Continued

Species	Calculated FP (°C)	Experimental FP (°C)	References[a,b,c]	CAS Registry Number 3-heptanone
5-nonanone	62	60	CCST, government of Quebec, Canada, CC[61]	502-56-7
2,5-norbornadiene	−11	−11		121-46-0
2-norbornene	−9	−15	TICONA GmbH MSDS Note: 'FP'<MP (flammable solid)	498-66-8
octadecane	157	166	EMEDCO MSDS[61]	593-45-3
1,7-octadiyne	30	23		871-84-1
octanal	53	52	KREMS CHEMIE MSDS[61]	124-13-0
octanenitrile	75	73		124-12-9
octanoic acid	117	110	NTP CHEMICAL MSDS[61]	124-07-2
3-octanol	73	65		20296-29-1
2-octanone	57	62	SIGMA-ALDRICH MSDS	111-13-7
3-octanone	50	53	Merck KGaA MSDS	106-68-3
2-octene	15	14	ACROS ORGANICS	111-67-1
octylamine	61	60	BASF MSDS[41]	111-86-4
n-octylbenzene	114	107		2189-60-8
1-octyne	17	16	Merck KGaA MSDS[62]	629-05-0
2-octyne	26	28		2809-67-8
4-octyne	21	18	Merck KGaA MSDS[61]	1942-45-6
pentanal	7	8 12	ICSC OC	110-62-3
1,5-pentanediol	137	136	BASF MSDS[62]	111-29-5
1,5-pentanedithiol	99	95		928-98-3
2-pentanethiol	14	9.3	CP Chem MSDS, CC[62]	2084-19-7
pentanoic acid ethyl ester	34	38	[41]	539-82-2
2-pentanol	33	40	[39]	6032-29-7
trans-2-pentene	−48	−45		646-04-8
(E) 2-pentenenitrile	29	26	DuPont MSDS, CC	26294-98-4
pentylbenzene	68	65	Acros Organics MSDS[62]	538-68-1
1-pentyne	−41	<−34	[62]	627-19-0
2-pentyne	−33	−30	[62]	627-21-4
phthalan	68	63	[61]	496-14-0
pinacolone	5	5	[62]	75-97-8
propane	−104	−104	George Propane MSDS, OC	74-98-6
1,3-propanediamine	52	48	ACROS ORGANICS	109-76-2
1,2-propadiene	−97	−101.1	Scott Specialty Gases MDSD[39]	463-49-0
propene	−107	−108		115-07-1
2-propenyl-cyclopentane	15	12	CCST, government of Quebec, Canada, CC	3524-75-2
n-propylbenzene	38	30	CP Chem MSDS, CC[61]	103-65-1
propylcyclohexane	35	35	[41]	1678-92-8
pyrimidine	36	31		289-95-2
pyrrole	35	33	BASF MSDS	109-97-7
tribenzylamine	205	203	ACROS ORGANICS MSDS	620-40-6

TABLE 9. Comparison between calculated, with Eq. (4a), and experimental flash points of compounds as reported in the chemical manufacturers' MSDS and other sources. Maximum absolute error is 9 °C—Continued

Species	Calculated FP (°C)	Experimental FP (°C)	References[a,b,c]	CAS Registry Number 3-heptanone
tributylamine	73	72	KOEI Chemical MSDS CC	102-82-9
trichloroethylsilane	16	22.2	U.S. EPA, OC	115-21-9
tridecane	95	102	[41]	629-50-5
triethylsilane	5	−3	STOCHEM MSDS	617-86-7
trimethoxymethane	9	15	[62]	149-73-5
3,5,5-trimethyl-1-hexanol	84	79	KYOWA MSDS	3452-97-9
2,4,6-trimethylpyridine	52	57	[61]	108-75-8
tripropylamine	37	36	[41]	102-69-2
2-undecanol	112	107	Merck KGaA MSDS	1653-30-1
2-undecanone	96	89	Moore Ingredients, CC	112-12-9
6-undecanone	88	88	Acros Organics MSDS	927-49-1
undecylbenzene	143	144	[22]	6742-54-7
1-undecyne	71	65	[62]	2243-98-3
δ-valerolactone	101	100	[61]	542-28-9
γ-valerolactone	88	81	[61]	108-29-2
vinyltrimethylsilane	−28	−24	[62]	754-05-2

the experimental flash points for 2-octanone, 2-chloroethanol, biphenyl, quinoline, methyl benzoate, o-cresol, p-cresol, N-methylaniline, isobutyl acetate, and isobutylbenzene, for instance, are correct. The consideration of the reported uncertainties on the normal boiling point leads to the conclusion that the experimental flash points reported for 2-heptanol and dimethylsulfoxide are reasonably correct as well.

TABLE 10. Comparison of the estimations of closed-cup flash points with Eq. (5) and Eq. (4a) for organic silicon compounds. Literature values are from Hshieh[a]

Species	Estimated FP (°C) with Eq. (5)	Estimated FP (°C) with Eq. (4)	FP literature value (°C)	CAS Registry Number
allyltrichlorosilane	14	26	31	107-37-9
chlorotriethylsilane	32	34	30	994-30-9
decamethylcyclopentasiloxane	75	80	77	541-02-6
dichlorodimethylsilane	−14	−8	−16	75-78-5
			−9 ICSC CC	
diethoxydimethylsilane	12	14	11	78-62-6
1,3-diethoxytetramethyldisiloxane	41	45	38	
dimethylphenylsilane	38	39	38	766-77-8
hexamethyldisiloxane	4	3	−3	107-46-0
methyldichlorosilane	−29	−21	−32	20156-50-7
			−22 ICSC CC	
methyltrichlorosilane	−16	1	3	75-79-6
methyltrimethoxysilane	5	5	11	1185-55-3
octamethylcyclotetrasiloxane	51	55	57	556-67-2
			56 ICSC	
tetraethoxysilane	46	49	50	78-10-4
tetraethylsilane	36	34	32	631-36-7
tetramethoxysilane	17	26	21	681-84-5
tetravinylsilane	22	20	18	1112-55-6
triethoxymethylsilane	30	32	24	2031-67-6
trifluorophenylsilane	4	1	−5	368-47-8
trimethylchlorosilane	−20	−23	−18	75-77-4
			−27 ICSC	
tripropylsilane	49	37	43	998-29-8

[a]See Hshieh.[13]

TABLE 11. Comparison between estimated flash points, with Eq. (4a), and experimental flash points for organic tin, organic nickel, organic phosphorus, organic boron, organic germanium, and organic deuterated compounds

Species	Calculated FP (°C)	Experimental FP (°C)	References	Comments	CAS Registry Number
benzene-d6	−19	−11	[41] CC		1076-43-3
cyclohexane-d12	−17	−18	[41] CC		1735-17-7
nickel tetracarbonyl	−37	<−20	[39] CC		13463-39-3
tetraethylgermane	42	35	[61]		597-63-7
tetraethyllead	65	72	[61]		78-00-2
tetraethyltin	58	53	OSHA MSDS		597-64-8
tetramethyltin	−13	−12	OSHA MSDS		594-27-4
trimethyl borate	−11	−8	[39]	FP<27 °C ICSCs	121-43-7
trimethylphosphite	26	27	[12]		121-45-9
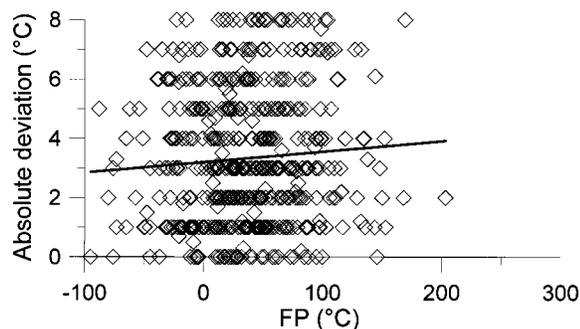
FIG. 2. Absolute deviation as a function of the flash point value. The linear regression (full line) indicates that Eq. (4a) behaves almost identically in the −100 °C/200 °C FP temperature range. Absolute deviation=$|FP_{exp}-FP_{calc}|$.
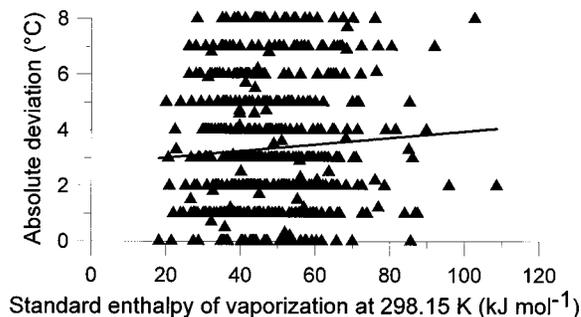
FIG. 4. Absolute deviation as a function of the correlation parameter $\Delta_{vap}H°(298.15\,K)$. The linear regression (full line) indicates that Eq. (4a) behaves almost identically in the 20–110 kJ mol^{-1} standard enthalpy of vaporization at the 298.15 K range. Absolute deviation=$|FP_{exp}-FP_{calc}|$.
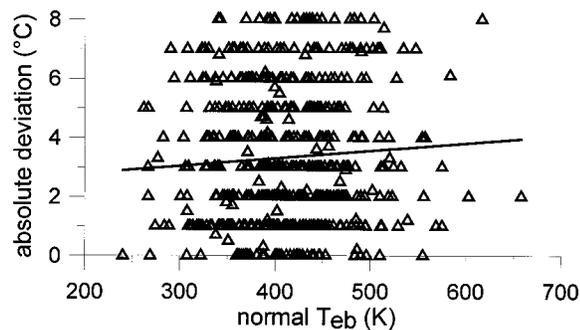
FIG. 3. Absolute deviation as a function of the correlation parameter T_{eb}. The linear regression (full line) indicates that Eq. (4a) behaves almost identically in the 250–650 K T_{eb} temperature range. Absolute deviation =$|FP_{exp}-FP_{calc}|$.
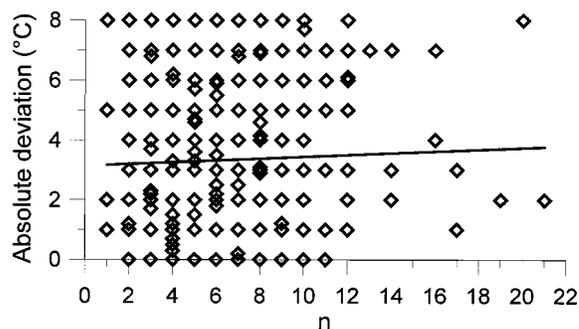
FIG. 5. Absolute deviation as a function of the correlation parameter n. The linear regression (full line) indicates that Eq. (4a) behaves almost identically whatever the number of carbon atoms in the molecule. Absolute deviation =$|FP_{exp}-FP_{calc}|$.
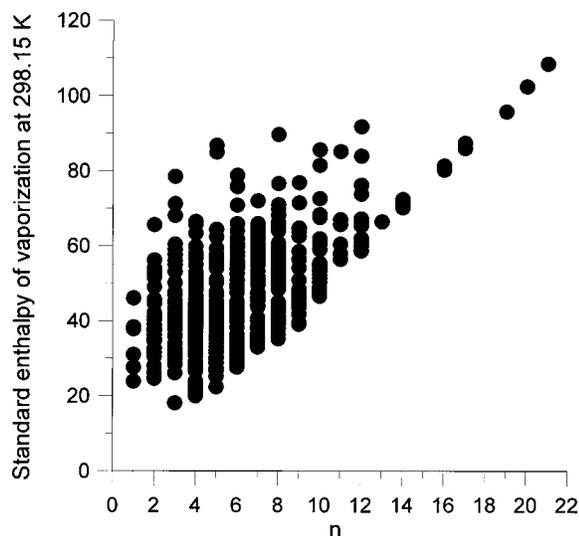
FIG. 6. Standard enthalpy of vaporization at 298.15 K as a function of the number of carbon atoms in the molecule.
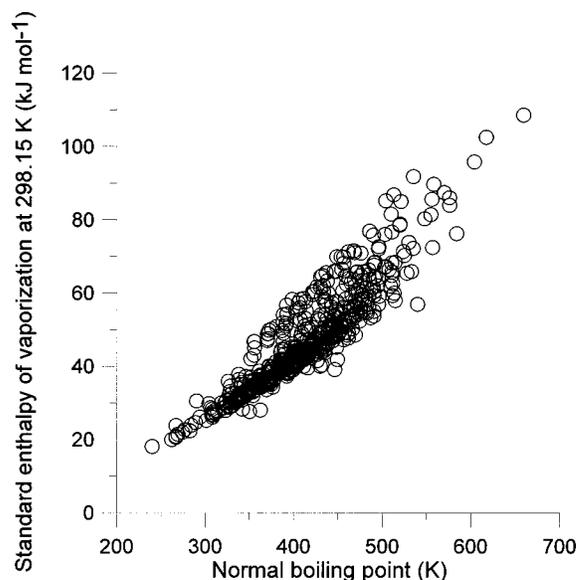
FIG. 8. Standard enthalpy of vaporization at 298.15 K as a function of the normal boiling point.

8.4. Erroneous and Probably Erroneous Flash Point Data

For the other compounds, the reported flash points do not agree with the calculated ones (see Table 12) even after re-examination of the accuracy of the parameters included in Eq. (4a). This table only reports the compounds with a well-defined flash point, i.e., those reported as highly flammable, flammable, or combustible liquids. The compounds reported as ''not combustible'' in some database and as combustible in some others (as for instance trichlorethylene and some halogenated compounds) are generally not considered in Table 12 because it is beyond the scope of the present Eq. (4a) to predict ignitability or not. A way to prevent the use of this equation for noncombustible or weakly combustible compounds is to consider the ''net heat of oxidation'' tech-

nique described by Britton[59] and Britton and Frurip.[60] This will be discussed further in Sec. 8.5. In Table 12, four compounds: dimethylether, dimethylamine, ethylamine, and formic acid, have been reported as probably erroneous by Jones by using the half-stoichiometric rule. The estimations of the ''true'' flash point following the half-stoichiometric rule or by using Eq. (4a) are almost the same (see Table 13). Explanations for the existence of erroneous flash point data in the literature are numerous: typographical errors, conversion errors from °F to °C, and flash point measured with aqueous solution instead of pure liquid. This holds for all the organic compounds of Table 12 but another explanation also holds for the organic halogenated compounds of Table 12. This will be discussed further in Sec. 8.5. Then, the compounds of Table 12 can be shared in several categories.
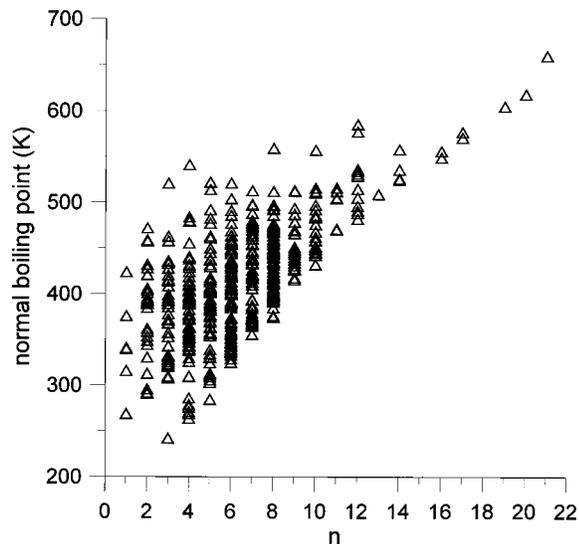
Some predictions, although not coherent either with IC-SCs or with handbook data, are consistent with chemical manufacturers' MSDS: tert-butylamine, ethanethiol, methyl formate, acetonitrile, 1-pentanol, diethylene glycol, diethyl phthalate, trimethylamine, dimethylamine, 1,6-hexanediol, propylamine, etc. Therefore the flash points for these compounds have to be corrected in the ICSCs and in the other compilations.

Some CC predictions are also consistent with OC experimental data because CC flash points are lower than OC flash point: dibutyl sulfide, methylal, 1-octene, and methoxybenzene. For these species the CC estimations are consistent with the OC data found because CC flash points are lower than OC flash points. Nevertheless, a difference of 10 °C or more between CC and OC flash points is doubtful.

For some other compounds, the flash point is known to be lower or higher than a given temperature. Very often, this temperature has been reported erroneously as the flash point in the various compilations. It is the case here for methanethiol, ethylamine, and bromoethane. Estimations with Eq.

FIG. 7. Normal boiling points as a function of the number of carbon atoms in the molecule.

TABLE 12. Erroneous flash points and probably erroneous flash points. In the comments column are given compounds belonging to the same chemical family for which Eq. (4a) performs reasonably well

Species	Calculated FP (°C)	Experimental or literature FP (°C)	References	Comments	CAS Registry Number
acetonitrile	2	12.8	ICSCs CC	6 °C[39] OC 2 °C Mallinckrodt Baker, Inc.; 5 °C[61]	75-05-8
benzyl bromide	67	79	ICSCs CC	Bromobenzene	100-39-0
bicyclohexyl	92	74	39	92 °C[41,61]	92-51-3
bromoethane	−31	−20	ICSCs CC	−23 °C[61]	74-96-4
1-bromopropane	−12	21	41	Theoretical FP=−7 °C according to the LFL and vapor pressure of 1-bromopropane	106-94-5
t-butyl acetoacetate	71	60	61		1694-31-1
sec-butylamine	−21	−9	ICSCs CC	−19[61]	13952-84-6
butylcyclohexane	52	41	12	isopropylcyclohexane	1678-93-9
2-butanethiol	−5	−23 21	CP Chem[61]	1-butanethiol. CP Chem data is estimated	513-53-1
t-butylamine	−35	−9	34	−38 °C BASF MSDS	75-64-9
t-butylbenzene	44	60	38	34 °C[41]	98-06-6
2-t-butyl-6-methylphenol	94	107	61	2-tert-butyl-4-methylphenol	2219-82-1
bis(2-chloroethyl)ether	70	55	ICSCs CC		111-44-4
1-chloro-2-methylpropane	−18	21	61	−10 °C ICSCs	513-36-0
1-chloro-2-methyl-1-propene	−17	−1	61	3-chloro-2-methyl-1-propene	513-37-1
cinnamaldehyde	107	71	61	111 °C[39]	14371-10-9
1,3-cyclohexadiene	−16	26	ICSCs CC	−18 °C[61]	592-57-4
2-cyclohexen-1-one	55	34	19	56 °C[61]	930-68-7
1,3-cyclopentadiene	−43	25	ICSCs OC	1,4-cyclohexadiene	542-92-7
diacetone alcohol	57	47	34	62 °C ATOFINA MSDS, CC	123-42-2
dibutyl disulfide	102	113	CP CHEM MSDS, OC	FP CC<FP OC	629-45-8
di-t-butyl sulfide	32	48	19		107-47-1
1-decanol	112	82	61	2-undecanol	112-30-1
1,1-dichloroethane	−16	−6	ICSCs CC	see Sec. 8.5.	75-34-3
1,1-dichloroethylene	−40	−25	ICSCs CC	see Sec. 8.5.	75-35-4
cis-1,2-dichloroethylene	−15	6	ICSCs CC	see Sec. 8.5.	156-59-2
trans-1,2-dichloroethylene	−17	2-4	ICSCs CC	see Sec. 8.5.	156-60-5
diethanolamine	167	137	NPG	169 °C[41] CC	111-42-2
1,1-diethoxyethane	−3	−21	62	1,1-dimethoxyethane	105-57-7
diethylene glycol	146	124	ICSCs CC	138 °C EQUISTAR MSDS, CC 143 °C DELTREX CHEMICALS MSDS	111-46-6
diethyl fumarate	108	91	61	104 °C ACROS ORGANICS MSDS	623-91-6
diethyl phthalate	156	117	ICSCs CC	161 °C Mallinckrodt Baker, MSDS, CC	84-66-2
dimethylamine	−54	−18	34	Erroneous data according to the half-stoichiometric rule −55 °C BASF MSDS −57 °C CC[58]	124-40-3
2,3-dimethyl-1-butene	−35	−18	ACROS ORGANICS MSDS		563-78-0
dimethyl carbonate	7	18	61	Diethyl carbonate	616-38-6
dimethyl ether	−84	−41	56 CC	Erroneous data according to the half-stoichiometric rule	115-10-6
2,3-dimethylheptane	24	90	61	2,3-dimethylpentane	3074-71-3
dipropyl ether	−7	21	ICSCs CC	Diethyl ether Dibutyl ether Dipentyl ether diisopropyl ether	111-43-3

TABLE 12. Erroneous flash points and probably erroneous flash points. In the comments column are given compounds belonging to the same chemical family for which Eq. (4a) performs reasonably well—Continued

Species	Calculated FP (°C)	Experimental or literature FP (°C)	References	Comments	CAS Registry Number
ethanethiol	−34	−48	ICSCs	−38.9 °C OXYCHEM MSDS, CC	75-08-1
ethylamine	−46	−17	ICSCs CC	Erroneous data according to the half-stoichiometric rule FP< −17 °C[33] FP= −46 °C[34]	75-04-7
2-ethylbutanal	11	21	[56] CC	8 °C Celanese Chemical MSDS, CC	97-96-1
ethylcyclopentane	−1	15	[61]	methylcyclopentane	1640-89-7
N-ethylisopropylamine	−19	16	[61]		19961-27-4
formic acid	47	69	ICSCs [56] CC	Also erroneous data according to the half-stoichiometric rule 48 °C BASF MSDS 43±5 °C[31]	64-18-6
furan	−46	−35	ICSCs CC	1,4-dioxane 1,3-dioxolane tetrahydrofuran	110-00-9
1-heptanethiol	59	41	[19]	1-pentanethiol	1639-09-4
4-heptanone	35	49	[19]	3-heptanone	123-19-3
1,6-hexanediol	143	101	ICSCs	147 °C Merck KGaA MSDS	629-11-8
2,5-hexanediol	120	101	ICSCs		2935-44-6
3-hexanone	20	35	[41]	2-hexanone	589-38-8
hexanoic acid, methyl ester	40	72	[41]		106-70-7
methanethiol	−49	−18	ICSCs	FP< −18 °C in ATOFINA MSDS and in Matheson[39] OC. −53 °C[57]	74-93-1
methoxybenzene	41	52	ICSCs OC	FP CC<FP OC	100-66-3
1-methoxybutane	−20	−10	[61]	2-methoxybutane	628-28-4
methylal	−32	−18	ICSCs OC	FP CC<FP OC	109-87-5
methylenecyclopentane	−29	−19	[61]	methylenecyclohexane	1528-30-9
methyl formate	−32	−19	ICSCs	−32 °C NTP Chemical MSDS −26 °C mitsubishi gas chemical company MSDS	107-31-3
1-methylnaphthalene	94	82	ICSCs	2-methylnaphthalene	90-12-0
4-methyl-1,3-pentadiene	−19	−34	[19]	3-methyl-1,3-pentadiene	926-56-7
3-methyl-2-pentene	−25	−6	[61]	2-methyl-2-pentene	922-61-2
1-octanethiol	77	69	CP CHEM MSDS, OC	1-pentanethiol cyclohexanethiol	111-88-6
trans-1,3-pentadiene	−43	−28	[61]		2004-70-8
1,4-pentadiene	−56	4	[41]	−20 °C[62]	591-93-5
1-pentanol	47	33	ICSCs CC	49 °C BASF MSDS	71-41-0
n-pentyl acetate	38	25	ICSCs CC	2-pentyl acetate	628-63-7
1-phenyl-1-butanone	70	88	[61]		495-40-9
propanoyl chloride	−8	12	[19]	octanoyl chloride	79-03-8
propylamine	−27	−12	[34]	FP< −37 °C (ICSCs) −30 BASF MSDS	107-10-8
tetrahydropyran	−7	−20	[19]		142-68-7
tetramethylsilane	−51	−27	[39] CC		75-76-3
thiacyclopentane	21	12	ICSCs		110-01-0
1-tridecene	93	80	[22]	1-tetradecene	2437-56-1
triethylenetetramine	149	135	ICSCs CC		112-24-3
trimethylamine	−72	−7	[34]	−65 °C BASF MSDS −71 °C CC[58]	75-50-3

TABLE 13. Agreement between the ''half-stoichiometric rule'' and Eq. (4a) for the search of erroneous flash points in the literature

Compound name	FP estimated with the half-stoichiometric rule (°C)	FP estimated with Eq. (4) (°C)
dimethylether	−83	−84
dimethylamine	−56	−53
ethylamine	−50	−46
formic acid	47	47
glycerol	184	186

(4a) appear to be consistent with the recommendations that the flash point is below or above a certain temperature. For ethylamine, the initial recommendation that FP is below −17 °C is reported in the ICSCs such as FP is equal to −17 °C. Equation (4a) predicts a CC flash point of −46 °C, which is equal to the flash point for ethylamine reported in the *Handbook of Chemical Physics and Physical Chemistry*.[34]

For all the remaining compounds of Table 12 it cannot be assessed that the experimental flash point is erroneous but that it is probably erroneous due to the lack of contradictory experimental values. The statement that these literature flash points are probably erroneous can be assessed by considering the database given here (Table 2 and Tables 4−11) and Figs. 2−8. For all these species there is a need for experimental reexamination. Caution has to be taken when the reported experimental flash point is well above the estimated one.

8.5. Limitations of this Estimation Technique

The simple technique provided in this paper does have its limitations. The estimation equation indicates that all the compounds have a flash point, including compounds which are not combustible or weakly combustible, in particular polyhalogenated compounds: chloroform, carbon tetrachloride, tetrachloroethylene, dichloromethane, trichloroethylene, bromoform, trichlorofluoromethane, and 1,1,2,2-tetrachloroethane for instance. All these compounds do not exhibit flash point with ASTM D56, ASTM D93, and ASTM D 3278 methods, even if some of them are combustible in other experimental conditions. There are, however, ''flash point'' values for bromoform, trichloroethylene, tetrachloroethylene, and 1,1,2,2-tetrachloroethane in the *CRC Handbook of Chemical Physics and Physical Chemistry*[34] and Eq. (4a) gives correct values of the flash points. A limiting case is 1,1,1-trichloroethane for which vapor/air mixtures are difficult to ignite but may be developed under certain conditions, i.e., the substance burns only in excess oxygen or if a strong source of ignition is present.[33] Flash points values are given for 1,1,1-trichloroethane (FP=−1 °C) and 1,1,2-trichloroethane (FP=32 °C) in the *CRC Handbook of Chemical Physics* and *Physical Chemistry*[34] and Eq. (4a) also estimates correctly the flash points of these two compounds, although they are very different. A recent study of Kong *et al.*[45] shows that the flash point value of halogenated compounds is very dependent on the ignition energy. This is probably the reason why in some databases some compounds exhibit flash point and in some other databases the same compounds are declared as not combustible. Strictly speaking, the flash points reported in the *CRC Handbook of Chemical Physics and Physical Chemistry*[34] are not flash points as defined in ASTM D56, ASTM D93, and ASTM D3278 but LTL of flammability, i.e., flash points obtained with more energetic ignition sources than the hydrocarbon gas flames used in ASTM D56, ASTM D93, and ASTM D3278. From a chemical kinetics point of view, it is well known that some halogenated compounds/air mixtures are difficult to ignite with hydrocarbon gas flames because halogenated compounds act as sinks for radicals and thus inhibit ignition. Therefore some halogenated compounds are used as fire suppressants (in particular CF_3Br). Equation (4a) seems to estimate correctly the LTL of the some halogenated compounds. On the contrary, when a flash point exists for a halogenated compound (with the ASTM D56, ASTM D93, and ASTM D3278 methods), it can be possible that Eq. (4a) estimates the LTL and not the flash point. This is probably the case for 1,1-dichloroethane, cis and trans 1,2-

TABLE 14. Limitations of Eq. (4a)

Species	$|\Delta_{comb}H°(298.15\ K)|$ (kJ/mol fuel)	S	$|\Delta_{comb}H°/S|$ (kJ/mol O_2)	CAS Registry Number
trichlorofluoromethane	104.8	1	104.8	75-69-4
carbon tetrachloride	297.5	1	297.5	56-23-5
tetrachloroethylene	368.6	2	184.3	127-18-4
chloroform	411.2	1.25	329	67-66-3
carbon tetrabromide	443.7	1	443.7	558-13-4
dichloromethane	539.8	1.5	359.9	75-09-2
bromoform	569.8	1.25	455.8	75-25-2
1,1,2,2-tetrachloroethane	873.2	2.5	349.3	79-34-5
trichloroethylene	888.8	2.25	395	79-01-6
1,1,1-trichloroethane	1005.3	2.75	365.6	71-55-6
1,1-dichloroethylene	1031	2.5	412.4	75-35-4
1,1-dichloroethane	1143	3	381	75-34-3
1,2-dichloroethane	1145.2	3	381.7	107-06-2
chloroethane	1279.3	3.25	393.6	75-00-3

TABLE 15. Estimated FP, by using Eq. (4a), for compounds for which no data are available in the literature or in MSDS

Species	T_{eb} (K)	$\Delta_{vap}H°$(298.15 K) (kJ mol^{-1})	Calculated FP (°C)	CAS Registry Number
allyl cyclohexane	400.23	44	17	2114-42-3
bicyclo[4,1,0]heptane	383	38.1	5	286-08-8
cis-bicyclo[3,3,0]octane	410.28	43.1	24	1755-05-1
cyclobutanecarbonitrile	422.7	44.37	42	4426-11-3
cyclononanone	493.6	53.15	81	3350-30-9
decanenitrile	516.9	66.84	107	1975-78-6
decylcyclohexane	560	78.7	132	1795-16-0
1,1-dimethylcyclopropane	295	25	−59	1630-94-0
3,3-dimethylhexane	385.1	37.6	3	563-16-6
2,5-dimethyl-3-hexene	374.9	38	−2	15910-22-2
2,2-dimethylpentane	352.3	32.56	−20	590-35-2
trans-1,2-divinylcyclobutane	385.7	42.26	9	6553-48-6
2-ethylacrolein	366	36.81	−1	922-63-4
ethylcyclobutane	343.8	31.42	−24	4806-61-5
1-ethylcyclohexene	409	43.22	24	1453-24-3
1-ethylcyclopentene	379	38.5	3	2146-38-5
ethylidene cyclohexane	410	42	23	1003-64-1
1-methoxypropane	312	27.9	−41	557-17-5
2-methoxypropane	303.9	26.78	−48	598-53-8
4-methylbiphenyl	541	69.58	117	644-08-6
2-methyl-1-buten-3-yne	305	27	−50	78-80-8
3-methylcyclopentene	339	31	−27	1120-62-3
4-methylcyclopentene	348.7	32	−20	1759-81-5
2-methyldecane	462.4	54.29	61	6975-98-0
2-methyloctane	416.1	44.99	28	3221-61-2
3-methyloctane	417	45.07	28	2216-33-3
1-nonene	419	45.52	30	124-11-8
nonylbenzene	552	77.25	127	1081-77-2
1-nonyne	423	50.26	37	3452-09-3
1-octen-3-yne	407	43.25	23	17679-92-4
2-oxo-propanal	345	38	−4	78-98-8
pentacosane	675.1	128	223	629-99-2
spiropentane	312.1	27.7	−45	157-40-4
tetracosane	664.5	122.9	215	646-31-1
1-tetradecanol	562.2	101.62	154	112-72-1
2,2,3,3-tetramethylbutane	379.6	42.94	6	594-82-1
3,5,7,9-tetraoxaundecane	413.7	53.65	40	4431-82-7
2,2,3-trimethylbutane	354.1	32.19	−19	464-06-2
2,2,3-trimethylpentane	383.1	36.98	1	564-02-3

dichloroethylene, and 1,1-dichloroethylene for which Eq. (4a) predicts flash points (in fact probably LTL) up to 20 °C lower than the experimental flash point (see Table 12). The fact that the equation estimates the LTL instead of the flash point only concerns the halogenated compounds with two or more halogen atoms in the molecule because the flash points of monohalogenated compounds are generally correctly estimated. A way to prevent the "false" use of this equation is to consider the "net heat of oxidation" technique described by Britton[59] and Britton and Frurip.[60] Briefly the net heat (enthalpy) of oxidation (expressed in kJ per mole of oxygen and noted $\Delta_{comb}H°/S$) is defined as the net enthalpy of combustion (in kJ per mole of fuel and noted $\Delta_{comb}H°$) divided by the stoichiometric ratio of oxygen to fuel (noted S) as written in the stoichiometric equation. Table 14 gives the net enthalpy of combustion at 298.15 K for some compounds. In this table, only four compounds (1,1-dichloroethylene, 1,1-dichloroethane, 1,2-dichloroethane, and chloroethane) ex-

hibit flash points with ASTM D56, ASTM D93, and ASTM D3278 methods and 1,1,1-trichloroethane can be considered as a limit case. From this table it appears that the resulting limitation on the permissible net enthalpy of combustion is −1000 kJ (mol fuel)$^{-1}$ and the resulting limitation on the permissible net enthalpy of oxidation is −380 kJ mol^{-1} oxygen for the use of Eq. (4a) for halogenated compounds. For compounds with two or more halogen atoms, the estimate given by Eq. (4a) can be up to 20 °C lower than the flash point measured in ASTM D56, ASTM D93, and ASTM D3278 flash point testers (see the discussion just above). Another alternative is to consider that generally if the sum of the number of C–C bonds and C–H bonds in the molecule exceeds the number of C–X bonds, one can expect the compound to be flammable. Marginal flammability is expected if the number of C–X bonds equals the sum of the number of C–C and C–H bonds. The agreement between estimates and values reported in the literature is observed when the ratio of

the sum of the number of C–C and C–H bonds to the number of C–X bonds is at least equal to 4. This holds for the monohalogenated compounds: chloroethane, 1-chloropropane, 2-chloropropane, 1-chlorobutane, 2-chlorobutane, 1-chloropentane, 2-chloropentane, 1-chlorohexane, 1-chloroheptane, 1-chlorooctane, 1-chlorononane, 1-bromobutane, 1-bromopentane, 1-bromoheptane, 1-fluoroheptane, and for the dihalogenated compounds: 1,1-, 1,2-, 1,3-, and 2,2-dichloropropane, 1,1- and 1,2-dichlorobutane, o-, m-, and p-dichlorobenzene.

8.6. FP Estimation for Compounds for Which No Experimental FP Data are Available

Table 15 gives estimated FP for compounds for which no experimental FP data are available, as far as we know. About 30 compounds are reported in Table 15 but hundreds of other compounds could have been reported in this table.

9. Conclusions

A unique empirical equation has been established to estimate the closed cup flash point. This equation is shown to be valid for numerous organic compounds (hydrocarbons, organic oxygen compounds, and organic nitrogen compounds), including the most common solvents and multifunctional compounds. This equation is also valid for organic sulfur compounds, organic halogen compounds (see text), organic silicon compounds, and seems to be valid for organic tin compounds, organic nickel compounds, organic phosphorous compounds, organic boron compounds, organic germanium compounds, and organic deuterated compounds.

This equation can be used to check the reliability of a single experimental value, to decide the more reliable flash point among several contradictory values, and to estimate a flash point when no data are available. Caution has to be taken in that this equation does not predict whether the compound under consideration is combustible or not. This limitation of the equation is discussed for halogenated compounds and recommendations are given for the correct use of the equation for these compounds.

Comparisons between estimated flash point values with this equation and experimental flash point values show that less than 5% of flash points examined are erroneous or probably erroneous and err on the dangerous side. Future works should address:

(1) additional validation of the equation presented here,
(2) extensive search for possible erroneous data, and
(3) experimental validation.

The chemistry is not considered in this study, other than the inclusion of the number of carbon in it. Flash point data can also be analyzed through the use of validated detailed kinetic models. However, detailed kinetic models have been established and validated for less than 1/20th of the species presented here in the tables.

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