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Prediction of flammability of gases by using *F*-number analysis

Shigeo Kondo [a,*], Youkichi Urano [a], Kazuaki Tokuhashi [b], Akifumi Takahashi [b], Katsumi Tanaka [b]

[a] *Research Institute of Innovative Technology for the Earth, National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, Ibaraki 305-0046, Japan*

[b] *National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, Ibaraki 305-0046, Japan*

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Abstract

A novel method of predicting flammability limits has been proposed. This method utilizes a new flammability index called *F*-number. For this purpose, an empirical expression of *F*-number has been derived to account for the flammability characteristics of various organic substances. The analysis has been done by fitting to the observed values of *F*-number for a wide variety of organic gases and vapors. As a result, it has been found that *F*-number is an excellent tool to analyze the flammability characteristics of various substances. It has also been shown that the values of upper and lower flammability limits can be derived from *F*-number together with the stoichiometric concentration corrected for the effect of selective diffusion.

Keywords: *F*-number; Flammability limits; Flammable gases; Stoichiometric concentration; Selective diffusion

1. Introduction

The flammability limit is a well-established index for representing the flammability characteristics of gases and vapors. There is a large volume of flammability limits data obtained by using various methods [1–3]. However, it is not necessarily easy to understand the true flammability characteristics of individual gases solely from the flammability limits data. For example, it is recognized that the flammability characteristics of methane, ethane, and propane are very similar to each other, whereas their values of flammability limits are quite different, e.g. the flammable range of methane is said to be 5.0–15.0, that of ethane 3.0–12.4, and that of propane 2.1–9.5.

* Corresponding author. Tel.: +81-298-61-4770; fax: +81-298-61-4487.
E-mail address: kondo@nimc.go.jp (S. Kondo).

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In a previous paper [4], we have presented an index called *F*-number to address the flammability characteristics in terms of one unique number for each substance. The definition of *F*-number is as follows:

$$F = 1 - \left(\frac{L}{U}\right)^{0.5} \tag{1}$$

Here *L* is the lower flammability limit and *U* the upper flammability limit. It is noted that *F*-number takes values ranging from zero to unity depending on the degree of flammability of substances. Therefore, it can conveniently be used to classify the hazardous properties of various flammable gases and vapors. For example, flammable gases with *F*-number values of 0.0–0.2 are classified as vaguely flammable, those of 0.2–0.4 weakly flammable, those of 0.4–0.6 normally flammable, those of 0.6–0.8 strongly flammable, and those of 0.8–1.0 super flammable.

In the present paper, it is shown that *F*-number can be expressed by an analytical equation in terms of molecular parameters. The value of *F*-number for unknown compounds can be predicted by using this equation. On the other hand, it has been found that the geometric mean of upper and lower flammability limits can be obtained from the stoichiometric concentration corrected for the effect of selective diffusion. Then, the upper and lower flammability limits of unknown compounds can be obtained from the predicted value of *F*-number together with the geometric mean of both limits.

2. Results and discussion

2.1. Analytical expression of F-number

The flammable property comes from the chemical reactivity against oxygen gas. The most important factors that determine the flammability of a substance are the heat of combustion on one hand and the gross activation energy for the combustion reaction on the other. These factors are functions of the chemical structure of the molecule. In other words, they are functions of the kinds and numbers of chemical bonds and chemical groups in the molecule. Therefore, it is expected that *F*-number can also be expressed by an analytical form in terms of various bonds and groups which constitute the molecule. The analytical form of *F*-number may depend on the way we recognize the molecular structure.

As an example, the saturated hydrocarbon molecules such as methane, ethane, and propane have carbon skeletons covered with hydrogen atoms. There are other molecules in which some of hydrogen atoms in the saturated hydrocarbons are replaced by some other atoms or by some chemical groups. There are also many molecules that have double bonds and/or triple bonds in the carbon skeleton. It is also not rare that we encounter such molecules as having ring structures. All these structural factors have to be taken into account to build-up an analytical expression of *F*-number. The problem is how to take into account all these factors.

There are two main components that determine the chemical structures of organic molecules: one is the actual form of carbon skeleton and the other is the substitution for hydrogen atoms. The effects of various changes in the carbon skeleton may essentially

contribute additively to determine the value of *F*-number. Therefore, the terms corresponding to the individual changes in the carbon skeleton should be added together to give the final expression of *F*-number. Similarly, the effects of various substitutions for hydrogen atoms may work additively to determine *F*-number. On the other hand, the effect of changes in the carbon skeleton and that of substitution for hydrogen atoms may work synergetically. Therefore, the total effect may be taken into account by making a product form of the two main components. In the following, the details of the individual factors are discussed.

2.1.1. Length of carbon skeleton

It is well known that the bond dissociation energy of saturated hydrocarbons varies with the length of carbon skeleton. In general, the bond dissociation energy decreases as the length of carbon skeleton increases. The decrease is the largest for the first step, i.e. from methane to ethane, and becomes smaller for subsequent steps. Therefore, at the first approximation it may only matter whether the molecule is of mono-carbon skeleton or not.

2.1.2. Unsaturated bonds

In general, existence of unsaturated bonds such as double bonds and triple bonds in a molecule increases the flammability of the molecule. For example, ethylene is more flammable than ethane and acetylene is more flammable than ethylene, for the number of unsaturation is one for ethylene and two for acetylene. In this case, the degree of unsaturation relative to the size of the skeleton (the total number of skeletal carbon atoms) is more important rather than the actual number of unsaturation. For example, the increase of flammability from ethane to ethylene is larger than that from propane to propylene. Similarly, the increase of flammability from ethylene to acetylene is larger than that from propylene to methyl acetylene.

2.1.3. Ring structures

There are two kinds of ring structures, aliphatic rings and aromatic rings. Their effects on the flammability characteristics are indeed different. In this case also, the ratio rather than the absolute number of the rings in the molecule is more important.

2.1.4. Substitution for hydrogen atoms

Substitution of halogen atoms such as fluorine, chlorine, and bromine atoms for hydrogen atoms in hydrocarbon molecules makes halogenated hydrocarbons. The actual effect of substitution may depend on how many hydrogen atoms are replaced by what kind of halogen atoms. The effect may also depend on the total number of hydrogen atoms in the original hydrocarbon molecule, i.e. again ratio rather than the absolute number of substitution is important. In addition to halogen atoms, substitutions of such groups as OH, NO_2, NH_2, CN, and COOH are considered in the present analysis.

Taking into account all these factors, the following equation is obtained as the analytical expression of *F*-number:

$$\begin{aligned} F = {} & p_1(1 + p_2 C_1 + p_3 R_{\mathrm{OE}} + p_4 R_{\mathrm{CO}} + p_5 R_{\mathrm{COO}} + p_6 R_{\mathrm{NH}} + p_7 R_{\mathrm{RNG}} + p_8 R_{\mathrm{ARM}} \\ & + p_9 R_{\mathrm{US}})(1 + p_{10} R_{\mathrm{F}} + p_{11} R_{\mathrm{Cl}} + p_{12} R_{\mathrm{Br}} + p_{13} R_{\mathrm{OH}} + p_{14} R_{\mathrm{NO_2}} + p_{15} R_{\mathrm{NH_2}} \\ & + p_{16} R_{\mathrm{CN}} + p_{17} R_{\mathrm{COOH}}) \end{aligned} \tag{2}$$

This equation does not explicitly contain the numbers of carbon and hydrogen atoms, but they are actually used to calculate the values of R_F, R_{Cl},. . . , R_{COOH}. In this equation, p_1–p_{17} denote coefficients to be determined from the analysis of the observed data. C_1 takes the value of one or zero according to whether the molecule is a compound of mono-carbon skeleton or not. However, the methane derivatives that contain CO, COO, CN, or COOH group are treated exceptionally; C_1 takes the value of zero for these compounds. R_{OE}, R_{CO}, R_{COO}, and R_{NH} denote numbers of ether, carbonyl, ester, and imine groups, respectively, divided by the total number of skeletal carbons. R_{RNG} and R_{ARM} denote numbers of aliphatic and aromatic rings, respectively, divided by the total number of skeletal carbons. R_{US} denotes the total number of unsaturation in the carbon skeleton including aliphatic and aromatic rings divided by the total number of skeletal carbons. R_F, R_{Cl},. . . , and R_{COOH} denote numbers of F, Cl,. . . , and COOH, respectively, divided by the total number of hydrogen atoms in the corresponding pure hydrocarbon molecule.

2.2. F-number analysis

The data of flammability limits have been taken from the literature [2], and converted to *F*-number values using Eq. (1). The least-squares analysis has been carried out using Eq. (2). A total of 238 data have been used in the analysis.

Table 1 shows the result of the analysis. The values of lower and upper flammability limits are listed in the third and fourth columns, respectively. The numbers in the fifth column are the *F*-number values calculated from the flammability limits data. The calculated values of *F*-number is listed in the sixth column and the differences between them in the seventh column. On the whole, agreement between the observed and calculated values of *F*-number is quite good. However, there are some for which agreement between the observed and calculated values is not good. For example, discrepancy is noted for acetylene, ethylene, and ethylene oxide. For these compounds, the flammable range is much wider than the predicted value by the present scheme. They are known for their property of dissociative explosion. Due to this property, the flammable ranges of these compounds seems to have been extended toward 100% concentration. For other compounds for which agreement between the observed and calculated values is not good, the reasons for the discrepancies are not clear. However, considering that the experimental data used here have been measured with a variety of methods under various conditions in different laboratories, this kind of situation is quite understandable. It is well known that the values of flammability limits strongly depend on the apparatus used and the conditions under which the values are determined [1,2,5–7]. In fact, in many cases where agreement between the observed and calculated values is not good, the observed values themselves do not seem to be very reliable. Including everything, the average deviation of the calculated values of *F*-number from the respective observed ones is 0.047, which is 9.2% as the relative value.

Table 2 shows the values of parameters p_1–p_{17} resulting from the analysis. The value of parameter p_2 has been found to be negative, which means that the compounds of mono-carbon skeleton are less flammable than other compounds. The sign is important for parameters p_3–p_9 as well; if the sign is positive the effect is to increase the flammable property, and vice versa. The parameters p_3, p_4, p_5, and p_6 denote, respectively, the effects of insertion of ether, carbonyl, ester, and imine groups to the carbon skeleton. Insertion of ether and

Table 1
Result of F-number analysis

	Gas	Chemical formula	L_{obs}	U_{obs}	F_{obs}	F_{calc}	$F_{obs} - F_{calc}$	$\sqrt{(UL)_{obs}}$	C_{st}	$\sqrt{(UL)_{est}}$	L_{est}	U_{est}
1	Methane	CH_4	5.0	15.0	0.423	0.468	−0.045	8.7	9.5	8.8	4.7	16.5
2	Methyl fluoride	CH_3F	6.8	20.3	0.421	0.428	−0.007	11.8	12.3	12.4	7.1	21.6
3	Methyl chloride	CH_3Cl	8.1	17.4	0.318	0.353	−0.035	11.9	10.7	11.6	7.5	18.0
4	Methyl bromide	CH_3Br	10.0	16.0	0.205	0.098	0.107	12.7	10.7	13.9	12.5	15.4
5	Methyl alcohol	CH_3OH	6.0	36.0	0.592	0.502	0.090	14.7	12.3	12.3	6.1	24.6
6	Methylamine	CH_3NH_2	4.9	20.7	0.513	0.428	0.085	10.1	8.5	8.5	4.9	14.8
7	Acetonitrile	CH_3CN	3.0	16.0	0.567	0.499	0.068	6.9	7.1	7.4	3.7	14.7
8	Acetic acid	CH_3COOH	4.0	19.9	0.552	0.458	0.094	8.9	9.5	10.7	5.8	19.8
9	Chlorofluoromethane	CH_2FCl	14.4	26.5	0.263	0.313	−0.050	19.5	14.4	16.8	11.6	24.5
10	Methylene fluoride	CH_2F_2	13.3	29.3	0.326	0.388	−0.062	19.7	17.3	19.0	11.6	31.0
11	Methylene chloride	CH_2Cl_2	14.0	22.0	0.202	0.238	−0.036	17.6	12.3	15.3	11.7	20.1
12	Acetaldehyde	CH_3CHO	4.0	36.0	0.667	0.597	0.070	12.0	7.7	8.2	3.3	20.3
13	Methyl formate	$HCOOCH_3$	4.5	23.0	0.558	0.525	0.033	10.2	9.5	10.7	5.1	22.6
14	Ethane	CH_3CH_3	3.0	12.5	0.510	0.581	−0.071	6.1	5.7	5.6	2.3	13.4
15	Ethyl chloride	C_2H_5Cl	3.8	15.4	0.503	0.486	0.017	7.7	6.1	7.0	3.6	13.6
16	Ethyl bromide	C_2H_5Br	6.8	8.0	0.078	0.275	−0.197	7.4	6.1	8.3	6.0	11.4
17	Ethyl alcohol	C_2H_5OH	3.3	19.0	0.583	0.609	−0.026	7.9	6.5	7.0	2.7	17.8
18	Ethylamine	$C_2H_5NH_2$	3.5	14.0	0.500	0.548	−0.048	7.0	5.3	5.6	2.5	12.4
19	Propionic acid	CH_3CH_2COOH	2.9	12.1	0.510	0.499	0.011	5.9	5.7	6.8	3.4	13.5
20	1,1-Difluoroethane	CH_3CHF_2	4.0	19.6	0.548	0.514	0.034	8.9	7.7	9.0	4.4	18.5
21	Ethylene dichloride	CH_2ClCH_2Cl	6.2	16.0	0.378	0.390	−0.012	10.0	6.5	8.6	5.2	14.1
22	2-Chloroethanol	CH_2ClCH_2OH	4.9	15.9	0.445	0.513	−0.068	8.8	7.1	8.7	4.2	17.9
23	Ethylenediamine	$H_2NCH_2CH_2NH_2$	4.2	14.4	0.460	0.515	−0.055	7.8	5.0	5.6	2.7	11.6
24	1,1,2-Trifluoroethane	CH_2FCHF_2	6.2	22.6	0.476	0.481	−0.005	11.8	9.5	11.8	6.1	22.8
25	1-Chloro-1,1-difluoroethane	$C_2H_3F_2Cl$	6.8	18.2	0.389	0.419	−0.030	11.1	8.5	11.3	6.6	19.4
26	1-Fluoro-1,1-dichloroethane	CH_3CFCl_2	9.0	15.4	0.236	0.357	−0.121	11.8	7.7	10.8	7.0	16.8
27	1,1,1-Trichloroethane	CH_3CCl_3	7.5	12.5	0.225	0.295	−0.070	9.7	7.1	10.5	7.4	14.8
28	Ethylene	$H_2C{:}CH_2$	2.7	36.0	0.726	0.665	0.061	9.9	6.5	6.4	2.1	19.2
29	Vinyl fluoride	$CH_2{:}CHF$	2.6	21.7	0.654	0.608	0.046	7.5	7.7	8.2	3.2	21.0
30	Vinyl chloride	$CH_2{:}CHCl$	3.6	33.0	0.670	0.502	0.168	10.9	7.1	8.1	4.0	16.3
31	Vinyl bromide	$CH_2{:}CHBr$	9.0	15.0	0.225	0.140	0.085	11.6	7.1	9.6	8.2	11.1
32	Acrylonitrile	$CH_2{:}CHCN$	3.0	17.0	0.580	0.571	0.009	7.1	5.3	5.8	2.5	13.6
33	Acrylic acid	$CH_2{:}CHCOOH$	2.4	8.0	0.452	0.524	−0.072	4.4	6.5	7.8	3.7	16.3

Table 1 (*Continued*)

	Gas	Chemical formula	L_{obs}	U_{obs}	F_{obs}	F_{calc}	$F_{obs} - F_{calc}$	$\sqrt{(UL)_{obs}}$	C_{st}	$\sqrt{(UL)_{est}}$	L_{est}	U_{est}
34	Vinylidene fluoride	CH_2:CF_2	5.5	21.3	0.492	0.551	−0.059	10.8	9.5	10.9	4.9	24.3
35	Vinylidene chloride	CH_2:CCl_2	6.5	15.5	0.352	0.338	0.014	10.0	7.7	10.1	6.7	15.3
36	1,2-Dechloroethylene	ClCH:CHCl	5.6	12.8	0.339	0.338	0.001	8.5	7.7	10.1	6.7	15.3
37	Trichloroethylene	ClHC:CCl_2	8.0	10.5	0.127	0.174	−0.047	9.2	8.5	12.5	10.3	15.1
38	Tetrafluoroethylene	F_2C:CF_2	10.0	50.0	0.553	0.436	0.117	22.4	17.3	22.9	12.9	40.6
39	Trifluorochloroethylene	CF_2:CFCl	8.4	16.0	0.275	0.330	−0.055	11.6	14.4	20.1	13.5	30.0
40	Acetylene	CH:CH	2.5	100.0	0.842	0.750	0.092	15.8	7.7	7.5	1.9	30.0
41	Methyl ether	$(CH_3)_2O$	3.4	27.0	0.645	0.620	0.025	9.6	6.5	7.0	2.6	18.3
42	Acetone	CH_3COCH_3	2.5	13.0	0.561	0.589	−0.028	5.7	5.0	5.6	2.3	13.6
43	Propanal	CH_3CH_2CHO	2.6	17.0	0.609	0.589	0.020	6.7	5.0	5.6	2.3	13.6
44	Methyl acetate	CH_3COOCH_3	3.1	16.0	0.560	0.553	0.007	7.0	5.7	6.8	3.0	15.1
45	Ethyl formate	$HCO_2C_2H_5$	2.8	16.0	0.582	0.553	0.029	6.7	5.7	6.8	3.0	15.1
46	Dimethylamine	$(CH_3)_2NH$	2.8	14.4	0.559	0.577	−0.018	6.4	5.3	5.6	2.4	13.3
47	Acetic anhydride	$(CH_3CO)_2O$	2.7	10.3	0.488	0.561	−0.073	5.3	5.0	6.6	2.9	15.1
48	Methyl chloroacetate	$CH_2ClCOOCH_3$	7.5	18.5	0.363	0.462	−0.099	11.8	6.1	8.2	4.4	15.3
49	Acrolein	CH_2:CHCHO	2.8	31.0	0.699	0.673	0.026	9.3	5.7	6.3	2.1	19.3
50	Ethylenimine	C_2H_4NH	3.6	46.0	0.720	0.664	0.056	12.9	6.1	6.4	2.1	19.0
51	Ethylene oxide	C_2H_4O	3.0	100.0	0.827	0.707	0.120	17.3	7.7	8.2	2.4	27.9
52	Maleic anhydride	$(CHCO)_2O$	1.4	7.1	0.556	0.732	−0.176	3.2	6.5	8.6	2.3	32.0
53	Propane	$CH_3CH_2CH_3$	2.1	9.5	0.530	0.581	−0.051	4.5	4.0	4.3	1.8	10.2
54	Propyl chloride	C_3H_7Cl	2.6	11.1	0.516	0.510	0.006	5.4	4.2	5.2	2.5	10.5
55	*Iso*-propyl chloride	$(CH_3)_2CHCl$	2.8	10.7	0.488	0.510	−0.022	5.5	4.2	5.2	2.5	10.5
56	Propyl alcohol	$CH_3CH_2CH_2OH$	2.2	13.7	0.599	0.602	−0.003	5.5	4.5	5.0	2.0	12.7
57	*Iso*-propyl alcohol	$(CH_3)_2CHOH$	2.0	12.7	0.603	0.602	0.001	5.0	4.5	5.0	2.0	12.7
58	2-Nitropropane	$CH_3CH(NO_2)CH_3$	2.6	11.0	0.514	0.619	−0.105	5.4	5.3	6.7	2.6	17.7
59	Propylamine	$CH_3(CH_2)_2NH_2$	2.0	10.4	0.561	0.556	0.005	4.6	3.8	4.3	1.9	9.8
60	Butyric acid	$CH_3(CH_2)_2COOH$	2.0	10.0	0.553	0.519	0.034	4.5	4.0	5.1	2.4	10.6
61	*Iso*-butyric acid	$(CH_3)_2CHCOOH$	2.0	9.2	0.534	0.519	0.015	4.3	4.0	5.1	2.4	10.6
62	Propylene dichloride	$CH_3CHClCH_2Cl$	3.4	14.5	0.516	0.438	0.078	7.0	4.5	6.2	3.5	10.9
63	Propylene glycol	$CH_3CHOHCH_2OH$	2.6	12.5	0.544	0.622	−0.078	5.7	5.0	6.0	2.3	15.9
64	Acetone cyanhydrin	$(CH_3)_2C(OH)CN$	2.2	12.0	0.572	0.561	0.011	5.1	3.8	4.8	2.1	10.9
65	Propylene	CH_2:$CHCH_3$	2.0	11.1	0.576	0.637	−0.061	4.7	4.5	4.7	1.7	12.9
66	Allyl chloride	CH_2:$CHCH_2Cl$	2.9	11.1	0.489	0.533	−0.044	5.7	4.7	5.7	2.7	12.2

67	1-Chloropropylene	$CH_3CH{:}CHCl$	4.5	16.0	0.470	0.533	−0.063	8.5	4.7	5.7	2.7	12.2
68	Allyl bromide	$CH_2{:}CHCH_2Br$	4.4	7.3	0.224	0.302	−0.078	5.7	4.7	6.7	4.7	9.6
69	Allyl alcohol	$CH_2{:}CHCH_2OH$	2.5	18.0	0.627	0.667	−0.040	6.7	5.0	5.6	1.9	16.8
70	Allylamine	$CH_2{:}CHCH_2NH_2$	2.2	22.0	0.684	0.601	0.083	7.0	4.2	4.7	1.9	11.8
71	Methylacrylonitrile	C_4H_5N	2.0	6.8	0.458	0.577	−0.119	3.7	3.8	4.5	1.9	10.6
72	1,3-Dichloropropene	$CHCl{:}CHCH_2Cl$	5.3	14.5	0.395	0.428	−0.033	8.8	5.0	6.8	3.9	11.9
73	2,3-Dichloropropene	CH_2CClCH_2Cl	2.6	7.8	0.423	0.428	−0.005	4.5	5.0	6.8	3.9	11.9
74	Methyl ethyl ether	$CH_3OC_2H_5$	2.0	10.1	0.555	0.607	−0.052	4.5	4.5	5.0	2.0	12.8
75	Methyl ethyl ketone	$C_2H_5COCH_3$	1.4	11.4	0.650	0.586	0.064	4.0	3.7	4.4	1.8	10.6
76	Butyraldehyde	$CH_3(CH_2)_2CHO$	1.9	12.5	0.610	0.586	0.024	4.9	3.7	4.4	1.8	10.6
77	*Iso*-butyraldehyde	$(CH_3)_2CHCHO$	1.6	10.6	0.611	0.586	0.025	4.1	3.7	4.4	1.8	10.6
78	Ethyl acetate	$CH_3COOC_2H_5$	2.0	11.5	0.583	0.562	0.021	4.8	4.0	5.1	2.2	11.6
79	Methyl propionate	$CH_3COOCH_2CH_3$	2.5	13.0	0.561	0.562	−0.001	5.7	4.0	5.1	2.2	11.6
80	Methylal	$CH_3OCH_2OCH_3$	2.2	13.8	0.601	0.633	−0.032	5.5	5.0	6.0	2.2	16.4
81	Methyl vinyl ketone	$CH_3COCH{:}CH_2$	2.1	15.6	0.633	0.643	−0.010	5.7	4.0	4.7	1.7	13.3
82	Vinyl acetate	$CH_2{:}CHOOCCH_3$	2.6	13.4	0.560	0.619	−0.059	5.9	4.5	5.6	2.1	14.6
83	Methyl acrylate	$CH_2{:}CHCOOCH_3$	2.8	25.0	0.665	0.619	0.046	8.4	4.5	5.6	2.1	14.6
84	Cyclopropane	$(CH_2)_3$	2.4	10.4	0.520	0.639	−0.119	5.0	4.5	4.7	1.7	12.9
85	Propylene oxide	OCH_2CHCH_3	2.3	36.0	0.747	0.665	0.082	9.1	5.0	5.6	1.9	16.7
86	Trioxane	$OCH_2OCH_2OCH_2$	3.6	29.0	0.648	0.717	−0.069	10.2	6.5	8.3	2.4	29.4
87	Epichlorohydrin	CH_2CHOCH_2Cl	3.8	21.0	0.575	0.556	0.019	8.9	5.3	6.8	3.0	15.3
88	Butane	$CH_3CH_2CH_2CH_3$	1.6	8.4	0.564	0.581	−0.017	3.7	3.1	3.5	1.5	8.4
89	*Iso*-butane	$(CH_3)_3CH$	1.8	8.4	0.537	0.581	−0.044	3.9	3.1	3.5	1.5	8.4
90	Butyl chloride	C_4H_9Cl	1.8	10.1	0.578	0.524	0.054	4.3	3.2	4.2	2.0	8.8
91	*Iso*-butyl chloride	$(CH_3)_2CHCH_2Cl$	2.0	8.8	0.523	0.524	−0.001	4.2	3.2	4.2	2.0	8.8
92	Butyl bromide	$CH_3(CH_2)CH_2Br$	2.6	6.6	0.372	0.398	−0.026	4.1	3.2	4.8	2.9	8.1
93	Butyl alcohol	$CH_3(CH_2)_2CH_2OH$	1.4	11.2	0.646	0.598	0.048	4.0	3.4	4.0	1.6	10.1
94	*Iso*-butyl alcohol	$(CH_3)_2CHCH_2OH$	1.7	10.6	0.600	0.598	0.002	4.2	3.4	4.0	1.6	10.1
95	*Sec*-butyl alcohol	$CH_3CH_2CHOHCH_3$	1.7	9.8	0.584	0.598	−0.014	4.1	3.4	4.0	1.6	10.1
96	*Tert*-butyl alcohol	$(CH_3)_2COHCH_3$	2.4	8.0	0.452	0.598	−0.146	4.4	3.4	4.0	1.6	10.1
97	Butylamine	$C_4H_9NH_2$	1.7	9.8	0.584	0.561	0.022	4.1	3.0	3.6	1.6	8.2
98	*Tert*-butylamine	$(CH_3)_3C{:}NH_2$	1.7	8.9	0.563	0.561	0.002	3.9	3.0	3.6	1.6	8.2
99	1-Butene	$CH_3CH_2CH{:}CH_2$	1.6	10.0	0.600	0.623	−0.023	4.0	3.4	3.8	1.4	10.0

Table 1 (*Continued*)

	Gas	Chemical formula	L_{obs}	U_{obs}	F_{obs}	F_{calc}	$F_{obs} - F_{calc}$	$\sqrt{(UL)_{obs}}$	C_{st}	$\sqrt{(UL)_{est}}$	L_{est}	U_{est}
100	*Cis*-2-butene	$CH_3CH{:}CHCH_3$	1.7	9.0	0.565	0.623	−0.058	3.9	3.4	3.8	1.4	10.0
101	*Trans*-2-butene	$CH_3CH{:}CHCH_3$	1.8	9.7	0.569	0.623	−0.054	4.2	3.4	3.8	1.4	10.0
102	2-Methylpropene	$CH_2{:}C(CH_3)CH_3$	1.8	9.6	0.567	0.623	−0.056	4.2	3.4	3.8	1.4	10.0
103	2-Chlorobutene-2	$CH_3CCl{:}CHCH_3$	2.3	9.3	0.503	0.547	−0.044	4.6	3.5	4.5	2.0	9.9
104	1-Crotyl chloride	$CH_3CH{:}CHCH_2Cl$	4.2	19.0	0.530	0.547	−0.017	8.9	3.5	4.5	2.0	9.9
105	Methallyl chloride	$CH_2C(CH_3)CH_2Cl$	3.2	8.1	0.371	0.547	−0.175	5.1	3.5	4.5	2.0	9.9
106	Crotyl bromide	$CH_3CH{:}CHCH_2Br$	4.6	12.0	0.381	0.377	0.004	7.4	3.5	5.2	3.3	8.4
107	Crotonyl alcohol	$CH_3CH{:}CHCH_2OH$	4.2	35.3	0.655	0.645	0.010	12.2	3.7	4.4	1.6	12.3
108	Vinyl ethyl alcohol	$CH_2{:}CH(CH_2)_2OH$	4.7	34.0	0.628	0.645	−0.017	12.6	3.7	4.4	1.6	12.3
109	1,3-Butadiene	$CH_2{:}CHCH{:}CH_2$	2.0	12.0	0.592	0.665	−0.074	4.9	3.7	4.1	1.4	12.1
110	2-Chloro-1,3-butadiene	$CH_2CCl{:}CHCH_2$	4.0	20.0	0.553	0.556	−0.003	8.9	3.8	4.9	2.2	11.0
111	2,3-Dichlorobutadiene-1,3	$CH_2{:}C(Cl)C(Cl){:}CH_2$	1.0	12.0	0.711	0.447	0.264	8.5	4.0	5.8	3.2	10.4
112	Ethyl ether	$C_2H_5OC_2H_5$	1.9	36.0	0.770	0.601	0.170	8.3	3.4	4.0	1.6	10.1
113	Methyl propyl ketone	$CH_3COC_3H_7$	1.5	8.2	0.572	0.585	−0.013	3.5	2.9	3.7	1.5	8.8
114	Propyl acetate	$C_3H_7OOCCH_3$	1.7	8.0	0.539	0.567	−0.028	3.7	3.1	4.2	1.8	9.6
115	*Iso*-propyl acetate	$(CH_3)_2CHOOCCH_3$	1.8	8.0	0.526	0.567	−0.041	3.8	3.1	4.2	1.8	9.6
116	Butyl formate	$HCOOC_4H_9$	1.7	8.2	0.545	0.567	−0.022	3.7	3.1	4.2	1.8	9.6
117	*Iso*-butyl formate	$HCOOCH_2CH(CH_3)_2$	1.7	8.0	0.539	0.567	−0.028	3.7	3.1	4.2	1.8	9.6
118	Ethyl propionate	$C_2H_5COOC_2H_5$	1.9	11.0	0.584	0.567	0.017	4.6	3.1	4.2	1.8	9.6
119	Diethylamine	$(C_2H_5)_2NH$	1.8	10.1	0.578	0.579	−0.001	4.3	3.0	3.6	1.5	8.5
120	Methyl cellosolve acetate	$CH_3COOC_2H_4OCH_3$	1.7	8.2	0.545	0.587	−0.042	3.7	3.4	4.7	2.0	11.5
121	Propionic anhydride	$(CH_3CH_2CO)_2O$	1.3	9.5	0.630	0.571	0.059	3.5	2.9	4.3	1.8	9.9
122	Ethyl acetoacetate	$C_2H_5CO_2CH_2COCH_3$	1.4	9.5	0.616	0.571	0.045	3.7	2.9	4.3	1.8	9.9
123	Glycol diacetate	$(CH_2OOCCH_3)_2$	1.6	8.4	0.564	0.553	0.011	3.7	3.1	4.8	2.2	10.8
124	Diethylene triamine	$NH_2CH_2CH_2NHCH_2CH_2NH_2$	2.0	6.7	0.454	0.539	−0.086	3.7	2.8	3.8	1.7	8.1
125	Ethyl acrylate	$CH_2{:}CHCOOC_2H_5$	1.4	14.0	0.684	0.609	0.075	4.4	3.4	4.5	1.7	11.4
126	Vinyl ethyl ether	$CH_2{:}CHOC_2H_5$	1.7	28.0	0.754	0.643	0.111	6.9	3.7	4.4	1.6	12.2
127	Methyl methacrylate	$CH_2{:}C(CH_3)COOCH_3$	1.7	8.2	0.545	0.609	−0.065	3.7	3.4	4.5	1.7	11.4
128	Tetrahydrofuran	$OCH_2CH_2CH_2CH_2$	2.0	11.8	0.588	0.644	−0.056	4.9	3.7	4.4	1.6	12.3
129	1,2-Butylene oxide	$H_2COCHCH_2CH_3$	1.7	19.0	0.701	0.644	0.057	5.7	3.7	4.4	1.6	12.3
130	2,3-Butylene oxide	$CH_3HCOCHCH_3$	1.5	18.3	0.714	0.644	0.070	5.2	3.7	4.4	1.6	12.3
131	*p*-Dioxane	$OCH_2CH_2OCH_2CH_2$	2.0	22.0	0.698	0.664	0.035	6.6	4.0	5.1	1.7	15.1
132	Morpholine	$OC_2H_4NHCH_2CH_2$	1.4	11.2	0.646	0.642	0.004	4.0	3.5	4.4	1.6	12.4
133	Divinyl ether	$(CH_2{:}CH)_2O$	1.7	27.0	0.749	0.685	0.064	6.8	4.0	4.7	1.5	15.1
134	Crotonaldehyde	$CH_3CH{:}CHCHO$	2.1	15.5	0.632	0.669	−0.037	5.7	3.4	4.2	1.4	12.6

135	Furfuryl alcohol	$OCH{:}CHCH{:}CCH_2OH$	1.8	16.3	0.668	0.719	−0.051	5.4	4.5	5.6	1.6	19.9
136	Furan	$CH{:}CHCH{:}CHO$	2.3	14.3	0.599	0.728	−0.129	5.7	4.5	5.2	1.4	19.2
137	Furfural	$OCH{:}CHCH{:}CHCHO$	2.1	19.3	0.670	0.732	−0.062	6.4	4.0	5.2	1.4	19.6
138	Pentane	$CH_3(CH_2)_3CH_3$	1.5	7.8	0.561	0.581	−0.020	3.4	2.6	3.0	1.3	7.3
139	*Iso*-pentane	$(CH_3)_2CHCH_2CH_3$	1.4	7.6	0.571	0.581	−0.010	3.3	2.6	3.0	1.3	7.3
140	2,2-Dimethylpropane	$(CH_3)_4C$	1.4	7.5	0.568	0.581	−0.013	3.2	2.6	3.0	1.3	7.3
141	Amyl chloride	$CH_3(CH_2)_3CH_2Cl$	1.6	8.6	0.569	0.533	0.035	3.7	2.6	3.6	1.7	7.6
142	*Iso*-amyl chloride	$(CH_3)_2CHCH_2CH_2Cl$	1.5	7.4	0.550	0.533	0.016	3.3	2.6	3.6	1.7	7.6
143	*Tert*-amyl chloride	$CH_3CH_2CCl(CH_3)CH_3$	1.5	7.4	0.550	0.533	0.016	3.3	2.6	3.6	1.7	7.6
144	Amyl alcohol	$CH_3(CH_2)_3CH_2OH$	1.2	10.0	0.654	0.595	0.059	3.5	2.7	3.4	1.4	8.5
145	*Iso*-amyl alcohol	$(CH_3)_2CHCH_2CH_2OH$	1.2	9.0	0.635	0.595	0.040	3.3	2.7	3.4	1.4	8.5
146	*Sec*-amyl alcohol	$CH_3CH_2CH_2CH(OH)CH_3$	1.2	9.0	0.635	0.595	0.040	3.3	2.7	3.4	1.4	8.5
147	2-Methyl-2-butanol	$CH_3CH_2(CH_3)_2COH$	1.2	9.0	0.635	0.595	0.040	3.3	2.7	3.4	1.4	8.5
148	3-Pentanol	$CH_3CH_2CH(OH)CH_2CH_3$	1.2	9.0	0.635	0.595	0.040	3.3	2.7	3.4	1.4	8.5
149	Amylamine	$C_5H_{11}NH_2$	2.2	22.0	0.684	0.565	0.119	7.0	2.5	3.1	1.4	7.2
150	1-Pentene	$CH_3(CH_2)CH{:}CH_2$	1.5	8.7	0.585	0.615	−0.030	3.6	2.7	3.2	1.2	8.3
151	3-Methyl-1-butene	$(CH_3)_2CHCH{:}CH_2$	1.5	9.1	0.594	0.615	−0.021	3.7	2.7	3.2	1.2	8.3
152	*Iso*-prene	$CH_2{:}C(CH_3)CH{:}CH_2$	1.5	8.9	0.589	0.649	−0.059	3.7	2.9	3.4	1.2	9.7
153	Ethyl propyl ether	$C_2H_5OC_3H_7$	1.7	9.0	0.565	0.597	−0.031	3.9	2.7	3.4	1.4	8.5
154	3-Hexanone	$C_2H_5COC_3H_7$	1.0	8.0	0.646	0.584	0.062	2.8	2.4	3.2	1.3	7.7
155	Methyl *iso*-butyl ketone	$CH_3COCH_2CH(CH_3)_2$	1.2	8.0	0.613	0.584	0.028	3.1	2.4	3.2	1.3	7.7
156	2-Ethylbutyraldehyde	$(C_2H_5)_2CHCHO$	1.2	7.7	0.605	0.584	0.021	3.0	2.4	3.2	1.3	7.7
157	Butyl acetate	$CH_3COOC_4H_9$	1.7	7.6	0.527	0.570	−0.043	3.6	2.6	3.6	1.5	8.3
158	*Iso*-butyl acetate	$CH_3COOCH_2CH(CH_3)_2$	1.3	10.5	0.648	0.570	0.078	3.7	2.6	3.6	1.5	8.3
159	*Sec*-butyl acetate	$CH_3COOCH(CH_3)C_2H_5$	1.7	9.8	0.584	0.570	0.014	4.1	2.6	3.6	1.5	8.3
160	Diacetone alcohol	$CH_3COCH_2(CH_3)_2OH$	1.8	6.9	0.489	0.598	−0.109	3.5	2.6	3.6	1.4	8.9
161	Mesityl oxide	$(CH_3)_2CCHCOCH_3$	1.4	7.2	0.559	0.618	−0.059	3.2	2.6	3.4	1.3	8.8
162	Vinyl butyrate	$CH_2{:}CHOCOC_3H_7$	1.4	8.8	0.601	0.604	−0.002	3.5	2.7	3.8	1.5	9.5
163	Cyclohexanone	$C_6H_{10}O$	1.1	9.4	0.658	0.619	0.039	3.2	2.6	3.4	1.3	8.8
164	Tetrahydrofurfuryl alcohol	$C_4H_7OCH_2OH$	1.5	9.7	0.607	0.649	−0.043	3.8	3.1	4.2	1.5	11.9
165	2,4-Hexadienal	$CH_3CH{:}CHCH{:}CHC(O)H$	1.3	8.1	0.599	0.652	−0.052	3.2	2.7	3.5	1.2	10.1
166	Hexane	$CH_3(CH_2)_4CH_3$	1.1	7.5	0.617	0.581	0.036	2.9	2.2	2.7	1.1	6.5
167	*Iso*-hexane	C_6H_{14}	1.0	7.0	0.622	0.581	0.041	2.7	2.2	2.7	1.1	6.5
168	2-Methylpentane	$(CH_3)_2CH(CH_2)_2CH_3$	1.2	7.0	0.586	0.581	0.005	2.9	2.2	2.7	1.1	6.5
169	3-Methylpentane	$CH_3CH_2CH(CH_3)CH_2CH_3$	1.2	7.0	0.586	0.581	0.005	2.9	2.2	2.7	1.1	6.5

Table 1 (*Continued*)

	Gas	Chemical formula	L_{obs}	U_{obs}	F_{obs}	F_{calc}	$F_{obs} - F_{calc}$	$\sqrt{(UL)_{obs}}$	C_{st}	$\sqrt{(UL)_{est}}$	L_{est}	U_{est}
170	2,2-Dimethylbutane	$(CH_3)_3CCH_2CH_3$	1.2	7.0	0.586	0.581	0.005	2.9	2.2	2.7	1.1	6.5
171	2,3-Dimethylbutane	$(CH_3)_2CHCH(CH_3)_2$	1.2	7.0	0.586	0.581	0.005	2.9	2.2	2.7	1.1	6.5
172	2-Methyl pentanol	$CH_3(CH_2)_2CH(CH_3)CH_2OH$	1.1	9.7	0.663	0.593	0.070	3.3	2.3	3.0	1.2	7.4
173	Methyl *iso*-butyl carbinol	$CH_3CHOHCH_2CHCH_3CH_3$	1.0	5.5	0.574	0.593	−0.019	2.4	2.3	3.0	1.2	7.4
174	1,4-Hexadiene	$CH_3CH{:}CHCH_2CH{:}CH_2$	2.0	6.1	0.427	0.637	−0.210	3.5	2.4	3.0	1.1	8.2
175	Benzol (benzene)	C_6H_6	1.3	7.9	0.594	0.653	−0.059	3.2	2.7	3.3	1.2	9.5
176	Chlorobenzene	C_6H_5Cl	1.3	9.6	0.632	0.546	0.086	3.5	2.8	3.9	1.8	8.5
177	*n*-Propyl ether	$(C_3H_7)_2O$	1.3	7.0	0.569	0.594	−0.025	3.0	2.3	3.0	1.2	7.5
178	*Iso*-propyl ether	$(CH_3)_2CHOCH(CH_3)_2$	1.4	7.9	0.579	0.594	−0.015	3.3	2.3	3.0	1.2	7.5
179	Methyl amyl ketone	$CH_3CO(CH_2)_4CH_3$	1.1	7.9	0.627	0.584	0.043	3.0	2.1	2.9	1.2	6.8
180	Methyl *iso*-amyl ketone	$CH_3COCH_2CH_2CH(CH_3)_2$	1.0	8.2	0.651	0.584	0.067	2.9	2.1	2.9	1.2	6.8
181	Amyl acetate	$CH_3COOC_5H_{11}$	1.1	7.5	0.617	0.572	0.045	2.9	2.2	3.2	1.4	7.4
182	*Iso*-amyl acetate	$CH_3COOCH_2CH_2CH(CH_3)_2$	1.0	7.5	0.635	0.572	0.063	2.7	2.2	3.2	1.4	7.4
183	Di-*iso*-propylamine	$[(CH_3)_2CH]_2NH$	1.1	7.1	0.606	0.580	0.027	2.8	2.1	2.8	1.2	6.6
184	Acetal	$CH_3CH(OC_2H_5)_2$	1.6	10.4	0.608	0.607	0.001	4.1	2.4	3.4	1.3	8.6
185	Butyric anhydride	$[CH_3(CH_2)_2CO]_2O$	0.9	5.8	0.606	0.574	0.032	2.3	2.1	3.3	1.4	7.7
186	*Iso*-butyric anhydride	$[(CH_3)_2CHCO]_2O$	1.0	6.2	0.598	0.574	0.024	2.5	2.1	3.3	1.4	7.7
187	Triethylene glycol	$HOCH_2(CH_2OCH_2)_2CH_2OH$	0.9	9.2	0.687	0.632	0.055	2.9	2.7	4.2	1.6	11.5
188	Butyl acrylate	$CH_2{:}CHCOOC_4H_9$	1.5	9.9	0.611	0.600	0.011	3.9	2.3	3.3	1.3	8.3
189	Cyclohexane	C_6H_{12}	1.3	8.0	0.597	0.610	−0.013	3.2	2.3	2.8	1.1	7.3
190	Methylcyclopentane	C_6H_{12}	1.0	8.4	0.655	0.610	0.045	2.9	2.3	2.8	1.1	7.3
191	Ethylcyclobutane	$C_2H_5C_4H_7$	1.2	7.7	0.605	0.610	−0.005	3.0	2.3	2.8	1.1	7.3
192	Methylcyclopentadiene	C_6H_8	1.3	7.6	0.586	0.666	−0.080	3.1	2.6	3.1	1.0	9.4
193	Aniline	$C_6H_5NH_2$	1.3	11.0	0.656	0.616	0.040	3.8	2.6	3.4	1.3	8.8
194	*o*-Dichlorobenzene	$C_6H_4Cl_2$	2.2	9.2	0.511	0.439	0.072	4.5	2.9	4.5	2.5	8.0
195	Trichlorobenzene	$C_6H_3Cl_3$	2.5	6.6	0.385	0.332	0.053	4.1	3.0	5.1	3.4	7.7
196	Dinitrochlorobenzene	$C_6H_3Cl(NO_2)_2$	2.0	22.0	0.698	0.661	0.038	6.6	4.2	7.6	2.6	22.5
197	Phthalic anhydride	$C_6H_4(CO)_2O$	1.7	10.5	0.598	0.676	−0.078	4.2	2.7	4.2	1.4	13.0
198	Heptane	$CH_3(CH_2)_5CH_3$	1.1	6.7	0.595	0.581	0.014	2.7	1.9	2.5	1.0	5.9
199	*Iso*-heptane	$(CH_3)_2CHC_4H_9$	1.0	6.0	0.592	0.581	0.011	2.5	1.9	2.5	1.0	5.9
200	2,3-Dimethylpentane	$CH_3CH(CH_3)CH(CH_3)CH_2CH_3$	1.1	6.7	0.595	0.581	0.014	2.7	1.9	2.5	1.0	5.9
201	2-Ethylhexanol	$C_4H_9CH(C_2H_5)CH_2OH$	0.9	9.7	0.695	0.591	0.104	3.0	2.0	2.7	1.1	6.7
202	2-Ethylhexanoic acid	$C_4H_9CH(C_2H_5)COOH$	0.8	6.0	0.635	0.550	0.085	2.2	1.9	2.9	1.3	6.4
203	2-Ethylhexanal	$C_4H_9CH(C_2H_5)CHO$	0.9	7.2	0.646	0.583	0.063	2.6	1.8	2.6	1.1	6.2
204	4-Methyl-2-pentanol acetate	$CH_3COOCH(CH_3)CH_2CH(CH_3)_2$	0.9	5.8	0.606	0.573	0.033	2.3	1.9	2.9	1.2	6.7

205	Cycloheptane	$CH_2(CH_2)_5CH_2$	1.1	6.7	0.595	0.606	−0.011	2.7	2.0	2.6	1.0	6.5
206	Methylcyclohexane	$CH_2(CH_2)_4CHCH_3$	1.2	6.7	0.577	0.606	−0.029	2.8	2.0	2.6	1.0	6.5
207	Ethylcyclopentane	$C_2H_5C_5H_9$	1.1	6.7	0.595	0.606	−0.011	2.7	2.0	2.6	1.0	6.5
208	Toluol	$C_6H_5CH_3$	1.2	7.1	0.589	0.643	−0.054	2.9	2.3	2.9	1.0	8.2
209	Octane	$CH_3(CH_2)_6CH_3$	1.0	6.5	0.608	0.581	0.027	2.6	1.7	2.3	1.0	5.5
210	2,2,3-Trimethylpentane	$CH_3CH_2CH(CH_3)C(CH_3)_3$	1.1	6.0	0.572	0.581	−0.009	2.6	1.7	2.3	1.0	5.5
211	2,2,4-Trimethylpentene	$(CH_3)_3CCH_2CH(CH_3)_2$	0.8	4.8	0.592	0.602	−0.010	2.0	1.7	2.4	0.9	6.0
212	Dibutyl ether	$(C_4H_9)_2O$	1.5	7.6	0.556	0.591	−0.035	3.4	1.7	2.5	1.0	6.1
213	Methyl heptyl ketone	$C_7H_{15}COCH_3$	0.9	5.9	0.609	0.583	0.026	2.3	1.6	2.4	1.0	5.8
214	Di-*iso*-butyl ketone	$[(CH_3)_2CHCH_2]_2CO$	0.8	7.1	0.664	0.583	0.081	2.4	1.6	2.4	1.0	5.8
215	Ethylcyclohexane	$C_2H_5C_6H_{11}$	0.9	6.6	0.631	0.603	0.028	2.4	1.7	2.4	0.9	6.0
216	Ethylbenzene	$C_2H_5C_6H_5$	1.0	6.7	0.614	0.635	−0.022	2.6	2.0	2.6	1.0	7.2
217	*m*-Xylene	$C_6H_4(CH_3)_2$	1.1	7.0	0.604	0.635	−0.032	2.8	2.0	2.6	1.0	7.2
218	*o*-Xylene	$C_6H_4(CH_3)_2$	1.0	7.0	0.622	0.635	−0.013	2.7	2.0	2.6	1.0	7.2
219	*p*-Xylene	$C_6H_4(CH_3)_2$	1.1	7.0	0.604	0.635	−0.032	2.8	2.0	2.6	1.0	7.2
220	Styrene	$C_6H_5CH{:}CH_2$	1.1	7.0	0.604	0.656	−0.053	2.8	2.1	2.8	1.0	8.0
221	Nonane	C_9H_{20}	0.8	2.9	0.475	0.581	−0.106	1.5	1.5	2.1	0.9	5.1
222	2,2,3,3-Tetramethyl pentane	$(CH_3)_3CC(CH_3)_2CH_2CH_3$	0.8	4.9	0.596	0.581	0.015	2.0	1.5	2.1	0.9	5.1
223	3,3-Diethyl pentane	$CH_3CH_2C(C_2H_5)_2CH_2CH_3$	0.7	5.7	0.650	0.581	0.068	2.0	1.5	2.1	0.9	5.1
224	2-Ethylhexyl acetate	$CH_3COOCH_2CH(C_2H_5)_2$	0.8	8.1	0.686	0.575	0.111	2.6	1.5	2.5	1.0	5.8
225	Trimethylbenzene	$C_6H_3(CH_3)_3$	0.9	6.4	0.625	0.629	−0.004	2.4	1.7	2.4	0.9	6.6
226	Propylbenzene	$C_3H_7C_6H_5$	0.8	6.0	0.635	0.629	0.006	2.2	1.7	2.4	0.9	6.6
227	Cumene	$C_6H_5CH(CH_3)_2$	0.9	6.5	0.628	0.629	−0.001	2.4	1.7	2.4	0.9	6.6
228	Vinyl toluene	$CH_3C_6H_4CH{:}CH_2$	0.8	11.0	0.730	0.648	0.082	3.0	1.8	2.5	0.9	7.2
229	Decane	$CH_3(CH_2)_8CH_3$	0.8	5.4	0.615	0.581	0.034	2.1	1.3	2.0	0.9	4.8
230	Diethylcyclohexane	$C_{10}H_{20}$	0.8	6.0	0.635	0.599	0.036	2.2	1.4	2.1	0.8	5.2
231	Butylbenzene	$C_6H_5C_4H_9$	0.8	5.8	0.629	0.624	0.004	2.2	1.5	2.3	0.9	6.0
232	*Iso*-butylbenzene	$(CH_3)_2CHCH_2C_6H_5$	0.8	6.0	0.635	0.624	0.010	2.2	1.5	2.3	0.9	6.0
233	*Sec*-butylbenzene	$C_6H_5CH(CH_3)C_2H_5$	0.8	6.9	0.659	0.624	0.035	2.4	1.5	2.3	0.9	6.0
234	*Tert*-butylbenzene	$C_6H_5C(CH_3)_3$	0.7	5.7	0.650	0.624	0.025	2.0	1.5	2.3	0.9	6.0
235	*p*-Diethyl benzene	$C_6H_4(C_2H_5)_2$	0.8	5.0	0.600	0.624	−0.024	2.0	1.5	2.3	0.9	6.0
236	Divinylbenzene	$C_6H_4(CH{:}CH_2)_2$	1.1	6.2	0.579	0.658	−0.079	2.6	1.7	2.4	0.8	7.1
237	Naphthalene	$C_{10}H_8$	0.9	5.9	0.609	0.651	−0.041	2.3	1.7	2.5	0.9	7.2
238	Biphenyl	$C_6H_5C_6H_5$	0.6	5.8	0.678	0.653	0.025	1.9	1.4	2.3	0.8	6.5

Table 2
Parameter values obtained by the analysis

No.	Description	Obtained value	S.E.
p_1	Main coefficient	0.581	0.009
p_2	If one carbon	−0.194	0.046
p_3	Ether	0.134	0.089
p_4	Carbonyl	0.028	0.091
p_5	Ester	−0.097	0.071
p_6	NH	−0.014	0.151
p_7	Aliphatic ring	0.299	0.152
p_8	Aromatic ring	−0.125	0.296
p_9	Unsaturation	0.290	0.069
p_{10}	F	−0.344	0.114
p_{11}	Cl	−0.985	0.098
p_{12}	Br	−3.160	0.482
p_{13}	OH	0.284	0.256
p_{14}	NO_2	0.527	0.373
p_{15}	NH_2	−0.344	0.263
p_{16}	CN	−0.566	0.349
p_{17}	COOH	−0.850	0.351

carbonyl groups increases the flammability of the compound. It is interesting that insertion of an ester group to carbon skeleton decreases the flammability, though an ester group is a combination of an ether and a carbonyl groups. Insertion of an imine group to the skeleton does not bring about any remarkable effect on the flammability. Comparison between the effect of an aliphatic ring and that of an aromatic ring is also interesting. The former increases the flammability while the latter decreases it. This is because the electron resonance effect stabilizes the aromatic compounds.

The flammability-enhancing effect of unsaturated bonds is well known. For example, the flammability of ethylene is much stronger than that of ethane, and acetylene is definitely stronger than ethylene. In accord with this fact, the value of parameter p_9 has been obtained to be +0.290, which is one of the largest among parameters p_3–p_9.

Similarly, the substitution effects for hydrogen atoms can be seen in the signs of p_{10}–p_{17}. The fact that the values of p_{10}, p_{11}, and p_{12} are negative means that the substitution of halogen atoms for hydrogen atoms decreases the flammability of the corresponding gases; the substitution effect is larger for chlorine than that for fluorine, and the largest for bromine. Also, substitution of NH_2, CN, and COOH groups for hydrogen atoms decreases the flammability, while substitution of OH and NO_2 groups increases it.

2.3. Reduction of the flammability limits values from F-number

As stated, *F*-number is calculated from the values of the flammability limits. In reverse, the values of the upper and lower flammability limits cannot be derived from a single datum of *F*-number. However, if the value of geometric mean of the upper and lower flammability limits $(UL)^{0.5}$ is known, we can calculate the values of the flammability limits by the

following equations:

$$L = (UL)^{0.5}(1 - F) \tag{3}$$

and

$$U = \frac{(UL)^{0.5}}{1 - F} \tag{4}$$

In general, it is expected that the value of $(UL)^{0.5}$ is close to the stoichiometric concentration, which is a function of the chemical formula of a generic molecule given by $C_iH_jO_kF_lCl_mBr_nN_p$.

The problem here is that the stoichiometric concentration depends on the actual oxidation reaction of the fuel. For example, if the number of H atoms, j, in the fuel molecule is larger than or equal to the sum of fluorine and chlorine atoms $(l + m)$, there is a possibility that chlorine atoms are converted to hydrogen chloride just as fluorine atoms are converted to hydrogen fluoride, whereas bromine atoms may yield bromine molecules and nitrogen atoms nitrogen molecules irrespectively of the number of hydrogen atoms. In this case, the oxidation reaction of the fuel molecule may become as

$$\begin{aligned} &C_iH_jO_kF_lCl_mBr_nN_p + [i + \tfrac{1}{4}(j - l - m - 2k)]O_2 \\ &\quad = iCO_2 + \tfrac{1}{2}(j - l - m)H_2O + lHF + mHCl + \tfrac{1}{2}nBr_2 + \tfrac{1}{2}pN_2 \end{aligned} \tag{5}$$

Then, the stoichiometric concentration may be given by the following equation:

$$C_{st} = \frac{1}{1 + 4.773[i + (j - l - m - 2k)/4]} \tag{6}$$

On the other hand, if the number of hydrogen atoms, j, is smaller than the sum of fluorine and chlorine atoms $(l + m)$, the majority of chlorine atoms may yield chlorine molecules, and the oxidation reaction may become as

$$\begin{aligned} &C_iH_jO_kF_lCl_mBr_nN_p + [i + \tfrac{1}{4}(j - l - 2k)]O_2 \\ &\quad = iCO_2 + \tfrac{1}{2}(j - l)H_2O + lHF + \tfrac{1}{2}mCl_2 + \tfrac{1}{2}nBr_2 + \tfrac{1}{2}pN_2 \end{aligned} \tag{7}$$

And the stoichiometric concentration may be given by the following equation:

$$C_{st} = \frac{1}{1 + 4.773[i + (j - l - 2k)/4]} \tag{8}$$

Further, if the number of hydrogen atoms, j, is even smaller than that of fluorine atoms, l, all the hydrogen atoms may be consumed to yield hydrogen fluoride and the remaining fluorine atoms may yield CF_4 molecule, and the oxidation reaction may become as

$$\begin{aligned} &C_iH_jO_kF_lCl_mBr_nN_p + [i + \tfrac{1}{4}(j - l - 2k)]O_2 \\ &\quad = [i - \tfrac{1}{4}(l - j)]CO_2 + \tfrac{1}{4}(l - j)CF_4 + jHF + \tfrac{1}{2}mCl_2 + \tfrac{1}{2}nBr_2 + \tfrac{1}{2}pN_2 \end{aligned} \tag{9}$$

So, the stoichiometric concentration may again become as

$$C_{st} = \frac{1}{1 + 4.773[i + (j - l - 2k)/4]} \tag{10}$$

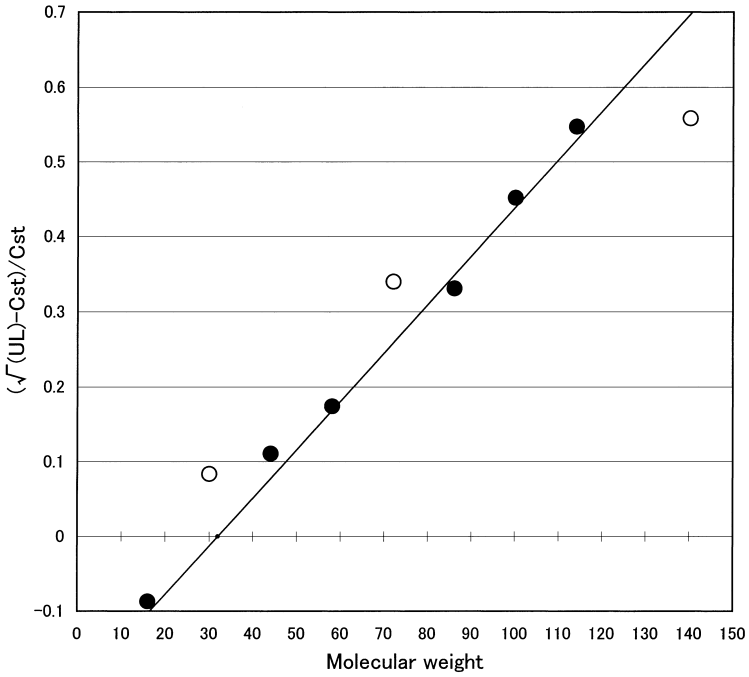

Fig. 1. Plot of relative difference between the mean of the flammability limits and stoichiometric concentration vs. molecular weight for saturated hydrocarbons: (●): methane, propane, butane, hexane, heptane, octane; (○): ethane, pentane, decane.

which is the same as Eq. (8). In other words, if all the chlorine atoms are to be converted to chlorine molecules, the stoichiometric concentration is given by Eq. (8) irrespectively of whether the number of hydrogen atoms is larger than that of fluorine atoms or not.

Now, there is another problem that the stoichiometric concentration is not always a good approximation to the value of $(UL)^{0.5}$. It is most possible that the reason for the discrepancy is the selective diffusion between fuel molecule and oxygen molecule. In Fig. 1, the relative difference between the two quantities, Δ, is plotted against the molecular weight for a series of saturated hydrocarbons, where Δ is defined by the following equation:

$$\Delta = \frac{(UL)^{0.5} - C_{\mathrm{st}}}{C_{\mathrm{st}}} \tag{11}$$

In Fig. 1, the plotted points are mostly distributed along a linear line. However, the linear line does not seem to go through the origin of the figure. Rather, it crosses the abscissa line at a certain positive value. This may suggest that the discrepancy is primarily caused by the selective diffusion between fuel and oxygen molecules that occurs at the flame front. Actually, if one attempts to fit to a straight line that goes through the value of 32.00 at abscissa axis, it has been found that the points corresponding to methane, propane, butane,

hexane, heptane, and octane come very close to the line. Then, we may be able to estimate the value of $(UL)^{0.5}$ based on this relationship.

In order to deal with these two problems simultaneously, Δ has been expressed by the following equation:

$$\Delta = k_1 R_F + k_2 R_{Cl} + k_3 R_{Br} + k_4(M - 32.00) \tag{12}$$

Here R_F, R_{Cl}, and R_{Br} are the same as in Eq. (2), M the molecular weight of fuel, and k_1 through k_4 the parameters to be determined in the least-squares analysis. By using this equation, the flammability limits data have been analyzed again to investigate which of Eqs. (6) and (8) is more appropriate for the expression of stoichiometric concentration. The least-squares analysis has been carried out to fit to this equation utilizing the same 238 data as before, assuming each time the respective equations for the stoichiometric concentration. When Eq. (6) was assumed for the stoichiometric concentration, the values of parameters were obtained as $k_1 = -0.15 \pm 0.12$, $k_2 = -0.51 \pm 0.13$, $k_3 = 0.28 \pm 0.60$, and $k_4 = 0.00475 \pm 0.00027$. On the other hand, when Eq. (8) was assumed, the values were obtained as $k_1 = -0.15 \pm 0.14$, $k_2 = -0.07 \pm 0.18$, $k_3 = 0.27 \pm 0.60$, and $k_4 = 0.00476 \pm 0.00027$. The parameter values are very similar for the two cases except for k_2. Among the parameters k_1–k_3, the value of k_2 only has been found non-zero for the former case, while all of them are zero within the respective uncertainties for the latter. This strongly suggests that chlorine atoms in a fuel molecule are primarily converted to chlorine molecules rather than to hydrogen chloride even if the number of hydrogen atoms in the fuel molecule is enough to yield hydrogen chloride. Then, Δ becomes a unique function of molecular weight.

Therefore, we have assumed that Δ is simply proportional to the difference in the molecular weight between fuel and oxygen molecules. The least-squares analysis has again been carried out using the 238 data to determine the value of the proportionality coefficient for the relationship. As a result, we have obtained the following equation:

$$\Delta = 0.00472(M - 32.00) \tag{13}$$

The credibility of the present assumption is also assured by the fact that the values of Δ for relatively simple gases such as methane and propane are well explained by this equation, though the actual value of the coefficient has essentially been determined by the values of much heavier fuels in this case.

In Table 1, the observed values of $(UL)^{0.5}$ are listed in eighth column. The data in the ninth column shows the stoichiometric concentration and the tenth column shows the estimated values of $(UL)^{0.5}$. The numbers listed in the eleventh and twelfth columns are the estimated values of the flammability limits obtained from the calculated values of F-number combined with the estimated values of $(UL)^{0.5}$. Reasonable agreement has been obtained between the estimated and observed values of flammability limits.

It is to be noted that the present method of prediction is applicable to any of the organic gases whose molecular structure can be described by the system presented in this paper.

3. Conclusion

We have presented an empirical expression of *F*-number, which can be used to analyze the flammability characteristics of gases and vapors. *F*-number can also be used to understand the flammability characteristics of gases and vapors in a systematic way. For one thing, hazardous properties of flammable gases are classified automatically according to the *F*-number value. In addition, it can be used to predict the flammability of unknown gases. It has also been shown that the *F*-number value can be converted to the flammability limits.

In conclusion, *F*-number not only contains information on hazardous property practically equivalent to the flammability limits but also can be used much more conveniently to analyze and predict the flammable properties of gases and vapors. Finally, we would like to emphasize that adoption of the correct method for measuring the flammability limits is important to increase further the credibility of *F*-number analysis as well.

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References

[1] H.F. Coward, G.W. Jones, Limits of flammability of gases and vapors, US Bureau of Mines Bulletin 503, 1952.
[2] M.G. Zabetakis, Flammability characteristics of combustible gases and vapors, US Bureau of Mines Bulletin 627, 1965.
[3] NFPA, fire hazard properties of flammable liquids, gases, volatile solids, Fire Protection Guide on Hazardous Materials, 9th Edition, Vol. 325M, National Fire Protection Association, Quincy, MA, 1984.
[4] S. Kondo, M. Iwasaka, K. Tokuhahsi, H. Nagai, M. Kaise, A new index for expressing explosion hazards "*F*-number", J. High Pressure Gas Safety Institute Jpn 31 (1994) 272–276.
[5] E W. Heinonen, R.E. Tapscott, F.R. Crawford, Methods Development for Measuring and Classifying Flammability/Combustibility of Refrigerants: Task 3, Laboratory Test Results, New Mexico Engineering Research Institute, University of New Mexico, 1994.
[6] A. Takahashi, Y. Urano, K. Tokuhashi, H. Nagai, M. Kaise, S. Kondo, Various metal wire fusing ignition for explosion limits measurement of methane/air mixtures, J. Loss Prevent. Process Ind. 11 (1998) 353–360.
[7] S. Kondo, Y. Urano, A. Takahashi, K. Tokuhashi, Reinvestigation of flammability limits measurement of methane by the conventional vessel method with ac discharge ignition, Combust. Sci. Tech. 145 (1999) 1–15.