Available online at www.sciencedirect.com
ScienceDirect
Journal of Hazardous Materials 155 (2008) 440–448
Journal of Hazardous Materials
www.elsevier.com/locate/jhazmat

A study on flammability limits of fuel mixtures

Shigeo Kondo*, Kenji Takizawa, Akifumi Takahashi, Kazuaki Tokuhashi, Akira Sekiya

National Institute of Advanced Industrial Science and Technology (AIST), Central 5, Higashi 1-1-1, Tsukuba, Ibaraki 305-8565, Japan

Received 3 October 2007; received in revised form 21 November 2007; accepted 22 November 2007
Available online 21 February 2008

Abstract

Flammability limit measurements were made for various binary and ternary mixtures prepared from nine different compounds. The compounds treated are methane, propane, ethylene, propylene, methyl ether, methyl formate, 1,1-difluoroethane, ammonia, and carbon monoxide. The observed values of lower flammability limits of mixtures were found to be in good agreement to the calculated values by Le Chatelier's formula. As for the upper limits, however, some are close to the calculated values but some are not. It has been found that the deviations of the observed values of upper flammability limits from the calculated ones are mostly to lower concentrations. Modification of Le Chatelier's formula was made to better fit to the observed values of upper flammability limits. This procedure reduced the average difference between the observed and calculated values of upper flammability limits to one-third of the initial value.

Keywords: Flammability limits; Fuel mixtures; Modified Le Chatelier's formula; ASHRAE method

1. Introduction

The flammability limit is a widely used index for representing flammability of gases and vapors. There is a large amount of flammability limits data such as the ones by Coward and Jones [1], Zabetakis [2], and by NFPA [3]. In particular, Coward and Jones [1] and the numerous articles cited therein include the flammability limits data of various mixtures as well. On the other hand, various kinds of alternatives to chloro-fluoro-carbon (CFC) are now under development in order to cope with the global environmental problem. They sometimes include blended gases. If it is a blended gas, flammability limits have to be measured individually for that particular concentration. It may be of great help if there is a reliable method for predicting the flammability limits of mixtures.

This situation reminds us of Le Chatelier's formula for calculating the flammability limits of fuel mixtures [4]. According to this formula, the lower flammability limit of a blended gas of n kinds of fuel gases is given by the following equation:

$$\frac{1}{L} = \sum_{i=1}^{n} \frac{c_i}{L_i} \tag{1}$$

Here, c_1, c_2, c_3, $\cdots$, c_n are the mole fractions of component gases whose lower flammability limits are L_1, L_2, L_3, $\cdots$, and L_n, respectively. A similar equation is said to be valid for the upper flammability limits as well [1].

Le Chatelier's formula is based on the assumption that the heat of combustion per mole of the flammability limit mixture is the same for all component fuels as well as for the resulting mixture. If the heat of combustion per mole is Q_1 for the 1st component, Q_2 for the 2nd, Q_3 for the 3rd, and so forth, this assumption is given as follows:

$$Q_1 L_1 = Q_2 L_2 = Q_3 L_3 = \cdots = QL = k \tag{2}$$

Here, Q is the heat of combustion per mole for the resulting mixture and k is a constant. This equation can be rewritten as follows:

$$Q_1 = \frac{k}{L_1}; Q_2 = \frac{k}{L_2}; Q_3 = \frac{k}{L_3}; \cdots; Q = \frac{k}{L} \tag{3}$$

On the other hand, the heat of combustion of the resulting mixture is given by the following equation:

$$Q = \sum_{i=1}^{n} c_i Q_i \tag{4}$$

Eq. (1) is readily obtained by substituting Eq. (3) into Eq. (4). A similar reasoning may be possible for the upper flammability

* Corresponding author. Tel.: +81 29 861 4770; fax: +81 29 861 4770.
E-mail address: s.kondo@aist.go.jp (S. Kondo).

0304-3894/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2007.11.085

limits and the following equation is obtained:

$$\frac{1}{U} = \sum_{i=1}^{n} \frac{c_i}{U_i} \tag{5}$$

Here, c_1, c_2, c_3, $\cdots$, c_n are the mole fractions of component gases whose upper flammability limits are U_1, U_2, U_3, $\cdots$, and U_n, respectively.

Now, it is of interest to examine the validity of Le Chatelier's formula using the experimental data. Coward and Jones [1] have listed a large amount of data on the flammability limits of various fuel mixtures. In general, the experimental values of lower flammability limits shown in those figures seem to agree well with the calculated values by Le Chatelier's formula. However, agreement with the calculated values is not guaranteed at the upper flammability limits.

On the other hand, in order to make a more quantitative evaluation of the predictability of Le Chatelier's formula, it is necessary to obtain accurate experimental data. As regards the experimental values of flammability limits, there is a well-known problem that they are dependent upon various experimental factors. The most important ones are explosion vessels and ignition sources [5–7]. It is desirable for the analysis to utilize a set of experimental data consistently taken with the same explosion vessel and ignition source under the same experimental condition with the same criterion for judgment in one laboratory. Recently, Liekhus et al. [8] have measured the lower flammability limits of gaseous mixtures containing hydrogen and a few volatile organic compounds. As far as the blended gases containing only flammable components are concerned, the observed values were in good agreement with the calculated ones with Le Chatelier's formula. It is desirable to carry out a similar study for upper flammability limits as well. More recently, Markus et al. studied flammability limits of CH_4–CH_3OH–air premix flames and stated that Le Chaterier's rule was not applicable to the upper flammability limits of this system [9]. On the other hand, Wierzba and Wang studied flammability limits of H_2–CO–CH_4 mixtures at elevated temperature, and found that Le Chaterier's rule can be applied with fair accuracy to the mixtures [10].

The purpose of the present study is to measure both the upper and lower flammability limits of mixtures of a number of typical flammable gases consistently with the ASHRAE method [11], and to compare the values to the calculated ones by Le Chatelier's formula in order to reexamine the predictability of this equation. Since the agreement between the observed and calculated values of flammability limits may not be very good for the upper flammability limits, it is possible that some reasoning is required to modify Le Chatelier's formula adequately to better interpret the observed values.

2. Experimental method

The measurement of flammability limits was done essentially by the ASHRAE method [11], which is a revised version of ASTM-E681 [12]. Since the present method is the same as in a previous paper [13], only a brief summary of the method is described below.

The explosion vessel is a 12-l spherical glass flask. The vessel is settled in air-bath kept at 35 °C. A flange is fixed to the top of the vessel. The vessel is connected to a soda-lime tower through a plastic tube to treat the burnt gas resulting from the explosion. The vessel is also equipped with a relief valve 5 psi g (1 psi = 6895 Pa) in relief pressure. A pair of tungsten electrodes for ac electric discharge is positioned at the height one-third the vessel diameter. ac electric spark was initiated by a Neon transformer. The spark duration was 0.4 s. The flame propagation was observed visually in the dark. The mixture is determined to be flammable if the flame moves upward and outward from the point of ignition to reach an arc of the vessel wall subtending an angle larger than 90° as measured from the point of ignition.

In the experiments, gas mixtures were directly prepared in the explosion vessel by the partial pressure method. Fuel gases were introduced into the vessel successively and then dry air was added to it. Introduction of fuel gases was made in order of decreasing boiling point except for ammonia. Introduction of ammonia always followed that of the counterpart fuel(s) to suppress its adsorption if any to the vessel wall to the minimum. Two types of MKS baratrons, 100 Torr head and 1000 Torr head (1 Torr = 133.32 Pa), were used for the pressure measurement. Mixtures were prepared in the vessel at a total pressure a little higher than the ambient pressure, stirred with a fan for 8 min, left quiet to settle for 1 min, and balanced with the ambient pressure just before ignition by opening the vessel valve leading to the soda-lime tower. This procedure ensures that the hot gas accumulation at the vessel top resulting from the ignition process is relieved through the valve.

The sample gases of methane, propane, ethylene, propylene, methyl ether, methyl formate, 1,1-difluoroethane, ammonia, and carbon monoxide were used. The sample gases were purchased from Taiyo-Nissan Co. and Wako Chemical Co. Except for methyl formate, the purities of gases were 99% or better. Purity of methyl formate was 98%. Dry air was of G3 grade of Taiyo-Nissan Co. The sample gases were used without further purification.

3. Results and discussion

The number of fuel compounds treated in this study is nine. Although this is not a large number, a variety of compounds are included, i.e., saturated hydrocarbons (methane and propane), unsaturated hydrocarbons (ethylene and propylene), an ether (dimethyl ether), an ester (methyl formate), a halogenated compound (1,1-difluoroethane), and inorganic compounds (ammonia and carbon monoxide). For consistency, the flammability limits of the individual compounds were measured under the same experimental condition as for mixtures. In this case, measurement of carbon monoxide itself was made in moist air of 50% relative humidity corrected for 23 °C. All other measurements were done using dry air. Table 1 shows the result of measurement for pure gases.

From the nine compounds, thirty-six binary combinations are made. Since this is not a small number to do measurements, limited kinds of mixing ratios were examined. Actually, the measurements were done for two kinds of binary mixtures for each

Table 1
Observed values of flammability limits for individual compounds[a]

Gas	Purity (%)	L (vol%)	U (vol%)	Flame color		NFPA/325M (vol%)	Note
				L	U		
Methane	99.9999	4.9 (0.1)	15.8 (0.2)	Whitish blue	Orange + blue	5–15	
Propane	99.9	2.03 (0.02)	10.0 (0.3)	Whitish blue	Orange + blue	2.1–9.5	
Ethylene	99.9	2.74 (0.10)	31.5 (1.0)	Whitish blue	Orange + blue	2.7–36	
Propylene	99.8	2.16 (0.04)	11.0 (0.5)	Whitish blue	Orange red	2.0–11.1	
Dimethyl ether	99up	3.3 (0.1)	26.2 (0.5)	Whitish blue	Pale blue	3.4–27	
Methyl formate	98up	5.25 (0.10)	22.6 (0.6)	Whitish blue	Pale blue	4.5–23	
1,1-Difluoroethane	99.9	4.32 (0.05)	17.35 (0.50)	Whitish blue	Orange + blue	–	
Ammonia	99.999	15.2 (0.5)	30.0 (0.5)	Orange red	Orange red	15–28	
Carbon monoxide	99.95	12.2 (0.3)	72.5 (0.5)	Whitish blue	Whitish blue	12.5–74	[b]

[a] Numbers in parenthesis are estimated experimental uncertainties by the present measurement method.
[b] Humidity of air is 50% corrected for 23 °C.

combination of compounds: one-to-one mixture and either of one-to-three or three-to-one mixture. In addition to these binary mixtures, several kinds of ternary one-to-one-to-one mixtures were examined.

3.1. Lower flammability limits

The observed values of lower flammability limits for various fuel mixtures are listed in "Obs" column in Table 2.

. The numbers in "Calc 1" column in this table are the values calculated with Le Chatelier's formula. For most cases, agreement between the observed and calculated values is very good. The largest difference is observed for the three-to-one mixture of ammonia and carbon monoxide where the observed value is 15.2 vol% and the calculated one is 14.32 vol%. The difference is 0.88 vol% which corresponds to 5.8 relative percent. The second largest is one-to-three mixture of methyl formate and ammonia where the observed value is 10.94 vol% and the calculated one is 10.31 vol%. The difference is 0.63 vol% which also corresponds to 5.8 relative percent. The differences for other mixtures are much smaller than these values. In fact, the difference between the observed and calculated values is about 0.1 vol% for a majority of cases. The average absolute difference between the observed and calculated values of lower flammability limits for all 86 mixtures is 0.068 vol%, and the average relative differences is 1.21%. This kind of agreement between the observed and calculated values is amazingly good especially when one considers that the measurements were done for quite a variety of compounds. Thus, Le Chatelier's formula has an excellent ability of predicting lower flammability limits of a wide variety of fuel blends.

3.2. Upper flammability limits

The observed values of upper flammability limits for various mixtures are listed in "Obs" column in Table 3. The numbers in "Calc 1" column in this table are the ones calculated with Le Chatelier's formula. In this case, the differences between the observed and calculated values are large compared to those for the lower flammability limits. The differences are dependent upon the individual mixtures. It is large for some mixtures and not so much for others. The average absolute difference between the observed and calculated values of upper flammability limits over 86 mixtures in all is 1.66 vol%, and the average relative difference is 7.19 relative percent. These values are much larger than the corresponding ones of 0.068 vol% and 1.21 relative percent, respectively, for the lower limits. It is noteworthy, however, that most of the observed values of upper flammability limits are lower than the respective calculated ones. In addition, for the exceptional cases where the observed values are higher than the calculated ones, the differences between them are negligibly small.

3.3. Modification of Le Chatelier's formula

As is pointed out in the above, in most cases the observed values of upper flammability limits are lower than the values calculated with Le Chatelier's formula. Actually, in eighty-four cases out of eighty-six in all the observed values are smaller than the calculated ones. For the remaining two, the difference between the observed and calculated values is negligibly small. It seems a general trend that the observed values of the upper flammability limits of blended fuels are lower than or at most equal to the prediction by Le Chatelier's formula.

If we consider a similar scheme to the one employed to interpret the lower flammability limit in Section 1, we may have the following equation for the upper flammability limit:

$$Q'_1 U_1 = Q'_2 U_2 = Q'_3 U_3 = \cdots = Q' U = k' \tag{6}$$

Here, Q'_1, Q'_2, Q'_3 and so forth are the effective heat of combustion per mole at the upper flammability limit region of the respective fuels, and k' is a constant. Q' is the "theoretical" heat of combustion per mole at the upper flammability limit region of the resulting mixture, and is given by the following equation:

$$Q' = \sum_{i=1}^{n} c_i Q'_i \tag{7}$$

It should be noticed here that the values of heat of combustion in these equations are quite different from the corresponding ones in Eq. (2). While the latter can be considered as the values for complete combustion, the former are the ones for incomplete

Table 2
Observed and calculated values of lower flammability limits of various fuel mixtures[a]

No.	Relative volume ratio of compound in mixture on air-free basis									Obs (vol%)	ε (vol%)	Calc 1 (vol%)	Δ1 (vol%)	Calc 2 (vol%)	Δ2 (vol%)
	CH_4	C_3H_8	C_2H_4	C_3H_6	Ether	Ester	152a	NH_3	CO						
1	0.5	0.5	0	0	0	0	0	0	0	2.9	0.1	2.87	0.03	2.88	0.02
2	0.75	0.25	0	0	0	0	0	0	0	3.70	0.05	3.62	0.08	3.64	0.06
3	0.5	0	0.5	0	0	0	0	0	0	3.55	0.10	3.51	0.04	3.49	0.06
4	0.25	0	0.75	0	0	0	0	0	0	3.07	0.04	3.08	−0.01	3.07	0.00
5	0.5	0	0	0.5	0	0	0	0	0	3.06	0.04	3.00	0.06	3.02	0.04
6	0.75	0	0	0.25	0	0	0	0	0	3.82	0.05	3.72	0.10	3.75	0.07
7	0.5	0	0	0	0.5	0	0	0	0	4.25	0.07	3.94	0.31	3.93	0.32
8	0.25	0	0	0	0.75	0	0	0	0	3.63	0.04	3.59	0.04	3.58	0.05
9	0.5	0	0	0	0	0.5	0	0	0	5.22	0.10	5.07	0.15	5.14	0.08
10	0.75	0	0	0	0	0.25	0	0	0	5.15	0.05	4.98	0.17	5.04	0.11
11	0.5	0	0	0	0	0	0.5	0	0	4.66	0.05	4.59	0.07	4.61	0.05
12	0.25	0	0	0	0	0	0.75	0	0	4.48	0.05	4.45	0.03	4.47	0.01
13	0.5	0	0	0	0	0	0	0.5	0	7.53	0.15	7.41	0.12	7.54	−0.01
14	0.75	0	0	0	0	0	0	0.25	0	5.89	0.10	5.90	−0.01	5.96	−0.07
15	0.5	0	0	0	0	0	0	0	0.5	7.0	0.2	6.99	0.01	7.00	0.00
16	0.25	0	0	0	0	0	0	0	0.75	8.71	0.15	8.89	−0.18	8.90	−0.19
17	0	0.5	0.5	0	0	0	0	0	0	2.33	0.02	2.33	0.00	2.33	0.00
18	0	0.75	0.25	0	0	0	0	0	0	2.18	0.03	2.17	0.01	2.17	0.01
19	0	0.5	0	0.5	0	0	0	0	0	2.08	0.02	2.09	−0.01	2.11	−0.03
20	0	0.25	0	0.75	0	0	0	0	0	2.14	0.03	2.13	0.01	2.14	0.00
21	0	0.5	0	0	0.5	0	0	0	0	2.51	0.02	2.51	0.00	2.52	−0.01
22	0	0.75	0	0	0.25	0	0	0	0	2.25	0.03	2.25	0.00	2.25	0.00
23	0	0.5	0	0	0	0.5	0	0	0	2.91	0.02	2.93	−0.02	2.97	−0.06
24	0	0.25	0	0	0	0.75	0	0	0	3.74	0.03	3.76	−0.02	3.81	−0.07
25	0	0.5	0	0	0	0	0.5	0	0	2.76	0.03	2.76	0.00	2.78	−0.02
26	0	0.75	0	0	0	0	0.25	0	0	2.36	0.03	2.34	0.02	2.35	0.01
27	0	0.5	0	0	0	0	0	0.5	0	3.54	0.05	3.58	−0.04	3.63	−0.09
28	0	0.25	0	0	0	0	0	0.75	0	6.00	0.07	5.80	0.20	5.89	0.11
29	0	0.5	0	0	0	0	0	0	0.5	3.48	0.05	3.48	0.00	3.50	−0.02
30	0	0.75	0	0	0	0	0	0	0.25	2.56	0.03	2.56	0.00	2.57	−0.01
31	0	0	0.5	0.5	0	0	0	0	0	2.40	0.04	2.42	−0.02	2.42	−0.02
32	0	0	0.75	0.25	0	0	0	0	0	2.57	0.03	2.57	0.00	2.57	0.00
33	0	0	0.5	0	0.5	0	0	0	0	3.00	0.05	2.99	0.01	2.97	0.03
34	0	0	0.25	0	0.75	0	0	0	0	3.16	0.03	3.14	0.02	3.12	0.04
35	0	0	0.5	0	0	0.5	0	0	0	3.64	0.04	3.60	0.04	3.61	0.03
36	0	0	0.75	0	0	0.25	0	0	0	3.13	0.04	3.11	0.02	3.12	0.01
37	0	0	0.5	0	0	0	0.5	0	0	3.37	0.05	3.35	0.02	3.34	0.03
38	0	0	0.25	0	0	0	0.75	0	0	3.81	0.04	3.78	0.03	3.77	0.04
39	0	0	0.5	0	0	0	0	0.5	0	4.62	0.10	4.64	−0.02	4.65	−0.03
40	0	0	0.75	0	0	0	0	0.25	0	3.35	0.10	3.45	−0.10	3.45	−0.10
41	0	0	0.5	0	0	0	0	0	0.5	4.42	0.10	4.47	−0.05	4.44	−0.02
42	0	0	0.25	0	0	0	0	0	0.75	6.44	0.20	6.55	−0.11	6.49	−0.05
43	0	0	0	0.5	0.5	0	0	0	0	2.63	0.04	2.61	0.02	2.62	0.01
44	0	0	0	0.75	0.25	0	0	0	0	2.39	0.03	2.36	0.03	2.37	0.02
45	0	0	0	0.5	0	0.5	0	0	0	3.06	0.04	3.06	0.00	3.11	−0.05
46	0	0	0	0.25	0	0.75	0	0	0	3.87	0.04	3.87	0.00	3.93	−0.06
47	0	0	0	0.5	0	0	0.5	0	0	2.88	0.03	2.88	0.00	2.91	−0.03
48	0	0	0	0.75	0	0	0.25	0	0	2.47	0.03	2.47	0.00	2.48	−0.01
49	0	0	0	0.5	0	0	0	0.5	0	3.75	0.05	3.78	−0.03	3.85	−0.10
50	0	0	0	0.25	0	0	0	0.75	0	6.31	0.10	6.06	0.25	6.19	0.12
51	0	0	0	0.5	0	0	0	0	0.5	3.66	0.04	3.67	−0.01	3.71	−0.05
52	0	0	0	0.75	0	0	0	0	0.25	2.72	0.03	2.72	0.00	2.73	−0.01
53	0	0	0	0	0.5	0.5	0	0	0	4.05	0.05	4.05	0.00	4.08	−0.03
54	0	0	0	0	0.75	0.25	0	0	0	3.65	0.04	3.64	0.01	3.66	−0.01
55	0	0	0	0	0.5	0	0.5	0	0	3.74	0.05	3.74	0.00	3.74	0.00
56	0	0	0	0	0.25	0	0.75	0	0	4.02	0.04	4.01	0.01	4.01	0.01
57	0	0	0	0	0.5	0	0	0.5	0	5.2	0.1	5.42	−0.22	5.46	−0.26
58	0	0	0	0	0.75	0	0	0.25	0	3.80	0.10	4.10	−0.30	4.12	−0.32
59	0	0	0	0	0.5	0	0	0	0.5	5.26	0.10	5.19	0.07	5.17	0.09
60	0	0	0	0	0.25	0	0	0	0.75	7.33	0.08	7.29	0.04	7.25	0.08
61	0	0	0	0	0	0.5	0.5	0	0	4.74	0.05	4.74	0.00	4.83	−0.09

Table 2 (*Continued*)

No.	Relative volume ratio of compound in mixture on air-free basis									Obs (vol%)	ε (vol%)	Calc 1 (vol%)	Δ1 (vol%)	Calc 2 (vol%)	Δ2 (vol%)
	CH_4	C_3H_8	C_2H_4	C_3H_6	Ether	Ester	152a	NH_3	CO						
62	0	0	0	0	0	0.75	0.25	0	0	5.00	0.05	4.98	0.02	5.05	−0.05
63	0	0	0	0	0	0.5	0	0.5	0	7.94	0.05	7.80	0.14	8.13	−0.19
64	0	0	0	0	0	0.25	0	0.75	0	10.94	0.15	10.31	0.63	10.73	0.21
65	0	0	0	0	0	0.5	0	0	0.5	7.44	0.10	7.34	0.10	7.50	−0.06
66	0	0	0	0	0	0.75	0	0	0.25	6.22	0.05	6.12	0.10	6.21	0.01
67	0	0	0	0	0	0	0.5	0.5	0	6.86	0.08	6.73	0.13	6.87	−0.01
68	0	0	0	0	0	0	0.75	0.25	0	5.29	0.05	5.26	0.03	5.33	−0.04
69	0	0	0	0	0	0	0.5	0	0.5	6.45	0.10	6.38	0.07	6.42	0.03
70	0	0	0	0	0	0	0.25	0	0.75	8.48	0.08	8.38	0.10	8.43	0.05
71	0	0	0	0	0	0	0	0.5	0.5	13.6	0.5	13.54	0.06	13.98	−0.38
72	0	0	0	0	0	0	0	0.75	0.25	15.2	0.5	14.32	0.88	14.69	0.51
73	0.33	0.33	0	0.33	0	0	0	0	0	2.63	0.03	2.59	0.04	2.61	0.02
74	0.33	0.33	0	0	0	0.33	0	0	0	3.43	0.03	3.38	0.05	3.43	0.00
75	0.33	0.33	0	0	0	0	0.33	0	0	3.26	0.03	3.23	0.03	3.26	0.00
76	0.33	0	0	0.33	0	0.33	0	0	0	3.56	0.3	3.50	0.06	3.56	0.00
77	0.33	0	0	0.33	0	0	0.33	0	0	3.37	0.04	3.34	0.03	3.37	0.00
78	0.33	0	0	0	0	0.33	0.33	0	0	4.88	0.06	4.79	0.09	4.87	0.01
79	0	0.33	0	0.33	0	0.33	0	0	0	2.63	0.03	2.62	0.01	2.66	−0.03
80	0	0.33	0	0.33	0	0	0.33	0	0	2.53	0.03	2.53	0.00	2.56	−0.03
81	0	0.33	0	0	0	0.33	0.33	0	0	3.29	0.03	3.28	0.01	3.33	−0.04
82	0	0	0	0.33	0	0.33	0.33	0	0	3.40	0.04	3.39	0.01	3.45	−0.05
83	0	0.33	0.33	0	0.33	0	0	0	0	2.61	0.03	2.58	0.03	2.58	0.03
84	0	0.33	0.33	0	0	0	0	0	0.33	3.20	0.03	3.19	0.01	3.19	0.01
85	0	0.33	0	0	0.33	0	0	0	0.33	3.41	0.03	3.42	−0.01	3.43	−0.02
86	0	0	0.33	0	0.33	0	0	0	0.33	4.02	0.05	4.00	0.02	3.96	0.06

[a] Obs is observed flammability limit, ε is uncertainty in Obs, Calc 1 is calculated flammability limit for case 1, Δ1 is Obs − Calc1, Calc 2 is calculated flammability limit for case 2, and Δ2 is Obs − Calc2.

combustion under fuel excess conditions. The effective heat of combustion per mole may decrease markedly as the fuel concentration increases toward the upper flammability limit.

If the observed value of upper flammability limit of a given fuel mixture is lower than the prediction by Le Chatelier's formula, it means that the effective heat of combustion of the mixture is larger than the value given by Eq. (7). Then, it is also that the adiabatic flame temperature at the upper flammability limit region of this mixture becomes higher than what is expected from the heat of combustion given by this equation. It is quite possible that coexistence of other fuels more or less disturbs the combustion reactions of any fuel in blended gases. If it is the case, the strength of perturbation, which combustion reactions of *i*th component suffer from coexisting fuels, may become a function of $(1 - c_i)$, where c_i is the mole fraction of *i*th component itself in the blended gas. This may lead to a modification of Le Chatelier's formula to better interpret the flammability limits of fuel mixtures. As a first approximation, Le Chatelier's formula for the upper flammability limit can be modified as follows:

$$\frac{1}{U} = \sum_{i=1}^{n} \frac{c_i}{U_i}[1 + q_i(1 - c_i)] \tag{8}$$

Here, U_i is the upper flammability limit of *i*th component fuel, and q_i is the coefficient of perturbation whose value should be determined from the analysis of the observed data.

The least-squares analysis was carried out to determine the values of q_i's fitting calculated values to the observed values of upper flammability limits. The result is shown in "Calc 2" column of Table 3. A substantial improvement of agreement between the observed and calculated values is attained through this analysis. Actually, the average difference between the observed and calculated values reduced to approximately one-third of the initial value: the initial value of average absolute difference between the observed and calculated values is 1.66 vol% and the resulting one is 0.52 vol%, which correspond to 7.2 and 2.4 relative percent, respectively. This result may demonstrate the validity of the present model.

An additional test can be done to demonstrate validity of Eq. (8) by the calculation which uses a subset of the data to derive the parameter values and subsequently use the result to predict the upper flammability limits of the rest of the dataset. In this case, the way of separating the dataset is important. It is clear that the validity is tested more severely with three-component mixtures than with two-component mixtures. We did at first the fitting calculation using a subset of two-component mixtures, and then the resulting parameter values were used to predict the values of three-component mixtures (14 in total). The result is shown in "Calc 3" column of Table 3, and the parameter values in "Calc 3" column in Table 4. The average absolute deviation of the calculated values for the two-component mixtures from the observed values is 0.57 vol% which corresponds to 2.60 relative percent. On the other hand, the average absolute deviation of the predicted values from the observed ones for the three-component mixtures is 0.28 vol% which corresponds to 1.60 relative percent. It is noted that the latter values are even smaller than the former.

Table 3
Observed and calculated values of upper flammability limits of various fuel mixtures[a]

No.	Relative volume ratio of compound in mixture on air-free basis									Obs (vol%)	ε (vol%)	Calc 1 (vol%)	Δ1 (vol%)	Calc 2 (vol%)	Δ2 (vol%)	Calc 3[b] (vol%)	Δ3 (vol%)	Calc 4 (vol%)	Δ4 (vol%)
	CH_4	C_3H_8	C_2H_4	C_3H_6	Ether	Ester	152a	NH_3	CO										
1	0.5	0.5	0	0	0	0	0	0	0	12.1	0.3	12.25	−0.15	12.01	0.09	11.99	0.11	11.95	0.15
2	0.75	0.25	0	0	0	0	0	0	0	13.5	0.5	13.80	−0.30	13.57	−0.07	13.55	−0.05	13.51	−0.01
3	0.5	0	0.5	0	0	0	0	0	0	20.5	1.0	21.04	−0.54	19.57	0.93	19.55	0.95	–	–
4	0.25	0	0.75	0	0	0	0	0	0	25	1.0	25.23	−0.23	23.63	1.37	23.61	1.39	–	–
5	0.5	0	0	0.5	0	0	0	0	0	12.6	0.4	12.97	−0.37	12.69	−0.09	12.67	−0.07	12.68	−0.08
6	0.75	0	0	0.25	0	0	0	0	0	13.8	0.3	14.25	−0.45	13.99	−0.19	13.97	−0.17	13.98	−0.18
7	0.5	0	0	0	0.5	0	0	0	0	17.5	0.5	19.71	−2.21	17.26	0.24	17.20	0.30	–	–
8	0.25	0	0	0	0.75	0	0	0	0	20.1	0.8	22.50	−2.40	20.06	0.04	20.00	0.10	–	–
9	0.5	0	0	0	0	0.5	0	0	0	18.3	0.3	18.60	−0.30	18.58	−0.28	18.61	−0.31	18.21	0.09
10	0.75	0	0	0	0	0.25	0	0	0	16.6	0.3	17.09	−0.49	17.07	−0.47	17.09	−0.49	16.84	−0.24
11	0.5	0	0	0	0	0	0.5	0	0	16.0	0.5	16.54	−0.54	16.28	−0.28	16.29	−0.29	15.99	0.01
12	0.25	0	0	0	0	0	0.75	0	0	16.6	0.7	16.93	−0.33	16.73	−0.13	16.74	−0.14	16.50	0.10
13	0.5	0	0	0	0	0	0	0.5	0	19.8	0.3	20.70	−0.90	20.52	−0.72	20.57	−0.77	–	–
14	0.75	0	0	0	0	0	0	0.25	0	17.3	0.3	17.92	−0.62	17.82	−0.52	17.85	−0.55	–	–
15	0.5	0	0	0	0	0	0	0	0.5	25.0	0.5	25.95	−0.95	24.82	0.18	24.85	0.15	–	–
16	0.25	0	0	0	0	0	0	0	0.75	36.1	0.5	38.22	−2.12	36.39	−0.29	36.45	−0.35	–	–
17	0	0.5	0.5	0	0	0	0	0	0	14.7	0.7	15.18	−0.48	14.16	0.54	14.10	0.60	–	–
18	0	0.75	0.25	0	0	0	0	0	0	11.25	0.50	12.06	−0.81	11.56	−0.31	11.53	−0.28	–	–
19	0	0.5	0	0.5	0	0	0	0	0	10.5	0.5	10.48	0.02	10.17	0.33	10.13	0.37	10.37	0.13
20	0	0.25	0	0.75	0	0	0	0	0	10.5	0.5	10.73	−0.23	10.49	0.01	10.46	0.04	10.65	−0.15
21	0	0.5	0	0	0.5	0	0	0	0	13.2	0.5	14.48	−1.28	12.91	0.29	12.84	0.36	–	–
22	0	0.75	0	0	0.25	0	0	0	0	10.9	0.7	11.83	−0.93	11.01	−0.11	10.97	−0.07	–	–
23	0	0.5	0	0	0	0.5	0	0	0	13.8	0.3	13.87	−0.07	13.64	0.16	13.61	0.19	13.80	0.00
24	0	0.25	0	0	0	0.75	0	0	0	16.8	0.6	17.19	−0.39	16.92	−0.12	16.89	−0.09	17.12	−0.32
25	0	0.5	0	0	0	0	0.5	0	0	12.4	0.7	12.69	−0.29	12.35	0.05	12.33	0.07	12.49	−0.09
26	0	0.75	0	0	0	0	0.25	0	0	11.0	0.7	11.18	−0.18	10.99	0.01	10.97	0.03	11.07	−0.07
27	0	0.5	0	0	0	0	0	0.5	0	14.5	0.5	15.00	−0.50	14.65	−0.15	14.62	−0.12	–	–
28	0	0.25	0	0	0	0	0	0.75	0	18.8	0.5	20.00	−1.20	19.54	−0.74	19.50	−0.70	–	–
29	0	0.5	0	0	0	0	0	0	0.5	16.8	0.7	17.58	−0.78	16.72	0.08	16.67	0.13	–	–
30	0	0.75	0	0	0	0	0	0	0.25	12.1	0.7	12.75	−0.65	12.40	−0.30	12.38	−0.28	–	–
31	0	0	0.5	0.5	0	0	0	0	0	14.6	0.7	16.31	−1.71	15.12	−0.52	15.06	−0.46	–	–
32	0	0	0.75	0.25	0	0	0	0	0	19.5	1.0	21.49	−1.99	19.94	−0.44	19.86	−0.36	–	–
33	0	0	0.5	0	0.5	0	0	0	0	26.0	1.0	28.61	−2.61	22.09	3.91	21.92	4.08	–	–
34	0	0	0.25	0	0.75	0	0	0	0	23.0	1.0	27.35	−4.35	22.58	0.42	22.44	0.56	–	–
35	0	0	0.5	0	0	0.5	0	0	0	25.6	0.4	26.32	−0.72	24.31	1.29	24.26	1.34	–	–
36	0	0	0.75	0	0	0.25	0	0	0	27.8	1.0	28.68	−0.88	26.86	0.94	26.82	0.98	–	–
37	0	0	0.5	0	0	0	0.5	0	0	20.5	0.8	22.38	−1.88	20.51	−0.01	20.46	0.04	–	–
38	0	0	0.25	0	0	0	0.75	0	0	18.0	0.8	19.54	−1.54	18.44	−0.44	18.42	−0.42	–	–
39	0	0	0.5	0	0	0	0	0.5	0	27.2	0.8	30.73	−3.53	27.74	−0.54	27.69	−0.49	–	–
40	0	0	0.75	0	0	0	0	0.25	0	28.4	1.0	31.11	−2.71	28.76	−0.36	28.71	−0.31	–	–
41	0	0	0.5	0	0	0	0	0	0.5	37	1.0	43.92	−6.92	36.21	0.79	36.06	0.94	–	–
42	0	0	0.25	0	0	0	0	0	0.75	42.3	0.7	54.70	−12.40	45.63	−3.33	45.45	−3.15	–	–
43	0	0	0	0.5	0.5	0	0	0	0	15.0	0.5	15.49	−0.49	13.70	1.30	13.62	1.38	–	–
44	0	0	0	0.75	0.25	0	0	0	0	12.4	0.5	12.87	−0.47	11.90	0.50	11.85	0.55	–	–
45	0	0	0	0.5	0	0.5	0	0	0	14.9	0.5	14.80	0.10	14.52	0.38	14.49	0.41	14.79	0.11
46	0	0	0	0.25	0	0.75	0	0	0	18.1	0.5	17.88	0.22	17.58	0.52	17.55	0.55	17.88	0.22

47	0	0	0	0.5	0	0	0.5	0	0	13.1	0.5	13.46	−0.36	13.08	0.02	13.05	0.05	13.29	−0.19
48	0	0	0	0.75	0	0	0.25	0	0	12.0	0.5	12.11	−0.11	11.87	0.13	11.85	0.15	12.00	0.00
49	0	0	0	0.5	0	0	0	0.5	0	15.5	0.5	16.10	−0.60	15.68	−0.18	15.65	−0.15	–	–
50	0	0	0	0.25	0	0	0	0.75	0	19.8	0.5	20.95	−1.15	20.42	−0.62	20.38	−0.58	–	–
51	0	0	0	0.5	0	0	0	0	0.5	17.8	0.7	19.10	−1.30	18.07	−0.27	18.02	−0.22	–	–
52	0	0	0	0.75	0	0	0	0	0.25	13.1	0.7	13.96	−0.86	13.54	−0.44	13.51	−0.41	–	–
53	0	0	0	0	0.5	0.5	0	0	0	20.5	0.5	24.27	−3.77	20.84	−0.34	20.75	−0.25	–	–
54	0	0	0	0	0.75	0.25	0	0	0	21.2	1.0	25.20	−4.00	22.34	−1.14	22.26	−1.06	–	–
55	0	0	0	0	0.5	0	0.5	0	0	18.5	1.0	20.88	−2.38	17.98	0.52	17.91	0.59	–	–
56	0	0	0	0	0.25	0	0.75	0	0	17.4	0.7	18.95	−1.55	17.08	0.32	17.03	0.37	–	–
57	0	0	0	0	0.5	0	0	0.5	0	22.4	0.5	27.97	−5.57	23.31	−0.91	23.20	−0.80	–	–
58	0	0	0	0	0.75	0	0	0.25	0	21.3	1.0	27.06	−5.76	23.63	−2.33	23.55	−2.25	–	–
59	0	0	0	0	0.5	0	0	0	0.5	29.0	1.0	38.49	−9.49	29.02	−0.02	28.81	0.19	–	–
60	0	0	0	0	0.25	0	0	0	0.75	36.7	0.6	50.28	−13.51	38.10	−1.40	37.83	−1.13	–	–
61	0	0	0	0	0	0.5	0.5	0	0	19.6	0.8	19.63	−0.03	19.42	0.18	19.44	0.16	19.50	0.10
62	0	0	0	0	0	0.75	0.25	0	0	20.9	0.8	21.01	−0.11	20.83	0.07	20.85	0.05	20.90	0.00
63	0	0	0	0	0	0.5	0	0.5	0	25.0	0.5	25.78	−0.78	25.79	−0.79	25.84	−0.84	–	–
64	0	0	0	0	0	0.25	0	0.75	0	26.6	0.4	27.73	−1.13	27.74	−1.14	27.78	−1.18	–	–
65	0	0	0	0	0	0.5	0	0	0.5	33.3	0.7	34.46	−1.16	32.96	0.34	32.99	0.31	–	–
66	0	0	0	0	0	0.75	0	0	0.25	26.6	0.6	27.30	−0.70	26.58	0.02	26.60	0.00	–	–
67	0	0	0	0	0	0	0.5	0.5	0	20.8	0.7	21.99	−1.19	21.56	−0.76	21.58	−0.78	–	–
68	0	0	0	0	0	0	0.75	0.25	0	18.9	0.9	19.39	−0.49	19.14	−0.24	19.16	−0.26	–	–
69	0	0	0	0	0	0	0.5	0	0.5	26.9	1.0	28.00	−1.10	26.34	0.56	26.35	0.55	–	–
70	0	0	0	0	0	0	0.25	0	0.75	37.7	0.8	40.40	−2.70	37.82	−0.12	37.83	−0.13	–	–
71	0	0	0	0	0	0	0	0.5	0.5	42.0	0.5	42.44	−0.44	39.61	2.39	39.68	2.32	–	–
72	0	0	0	0	0	0	0	0.75	0.25	34.7	0.3	35.15	−0.45	33.66	1.04	33.69	1.01	–	–
73	0.33	0.33	0	0.33	0	0	0	0	0	11.6	0.6	11.80	−0.20	11.43	0.17	11.39	0.21	11.51	0.09
74	0.33	0.33	0	0	0	0.33	0	0	0	14.2	0.4	14.46	−0.26	14.19	0.01	14.18	0.02	14.14	0.06
75	0.33	0.33	0	0	0	0	0.33	0	0	13.3	0.6	13.58	−0.28	13.20	0.10	13.18	0.12	13.15	0.15
76	0.33	0	0	0.33	0	0.33	0	0	0	14.8	0.7	15.12	−0.32	14.81	−0.01	14.80	0.00	14.82	−0.02
77	0.33	0	0	0.33	0	0	0.33	0	0	13.7	0.6	14.16	−0.46	13.74	−0.04	13.72	−0.02	13.75	−0.05
78	0.33	0	0	0	0	0.33	0.33	0	0	17.6	0.5	18.16	−0.56	17.94	−0.34	17.96	−0.36	17.66	−0.06
79	0	0.33	0	0.33	0	0.33	0	0	0	12.7	0.7	12.76	−0.06	12.38	0.32	12.34	0.36	12.66	0.04
80	0	0.33	0	0.33	0	0	0.33	0	0	12.0	0.8	12.07	−0.07	11.62	0.38	11.58	0.42	11.87	0.13
81	0	0.33	0	0	0	0.33	0.33	0	0	14.7	0.6	14.86	−0.16	14.49	0.21	14.46	0.24	14.68	0.02
82	0	0	0	0.33	0	0.33	0.33	0	0	15.3	0.7	15.56	−0.26	15.14	0.16	15.11	0.19	15.42	−0.12
83	0	0.33	0.33	0	0.33	0	0	0	0	15.0	0.7	17.66	−2.66	14.92	0.08	14.81	0.19	–	–
84	0	0.33	0.33	0	0	0	0	0	0.33	18.3	0.7	20.61	−2.31	18.50	−0.20	18.41	−0.11	–	–
85	0	0.33	0	0	0.33	0	0	0	0.33	16.7	0.5	19.74	−3.04	16.82	−0.12	16.72	−0.02	–	–
86	0	0	0.33	0	0.33	0	0	0	0.33	27.5	1.0	35.84	−8.34	26.04	1.46	25.82	1.68	–	–

[a] Obs is observed flammability limit, ε is uncertainty in Obs, Calc 1 is calculated flammability limit for case 1, $\Delta 1$ is Obs − Calc1, Calc 2 is calculated flammability limit for case 2, $\Delta 2$ is Obs − Calc2, Calc 3 is calculated flammability limit for case 3, and $\Delta 3$ is Obs − Calc3, Calc 4 is calculated flammability limit for case 4, and $\Delta 4$ is Obs − Calc4.

[b] For three-component mixtures, Calc 3 means the predicted value.

Table 4
Parameter values resulting from the least-squares analysis using Eq. (8) for upper flammability limits

No.	Parameter	Calc 2		Calc 3		Calc 4	
		q_i	S.E.	q_i	S.E.	q_i	S.E.
1	Methane	0.015	0.028	0.012	0.032	0.091	0.023
2	Propane	0.056	0.019	0.063	0.027	0.025	0.019
3	Ethylene	0.420	0.102	0.435	0.106	–	–
4	Propylene	0.065	0.027	0.072	0.031	0.015	0.020
5	Dimethyl ether	0.730	0.091	0.756	0.095	–	–
6	Methyl formate	−0.017	0.039	−0.020	0.043	−0.027	0.032
7	1,1-Difluoroethane	0.051	0.025	0.051	0.028	0.044	0.025
8	Ammonia	0.021	0.084	0.016	0.082	–	–
9	Carbon monoxide	0.438	0.155	0.439	0.156	–	–

Calc 2 is for the analysis of all the blend mixtures, Calc 3 is for the analysis of two-component mixtures, and Calc 4 is for five selected compounds (see the text).

On the other hand, the parameter values obtained from the analysis are of particular interest. They are shown in Table 4 (in "Calc 2" column). The parameter value for dimethyl ether q_5 is the largest of all, and q_3 and q_9 which are due to ethylene and carbon monoxide, respectively, are the next largest. All other parameters are much smaller than these three. Incidentally, this situation reminds us of recent studies on nitrogen and carbon dioxide dilution effects on the flammability limits of various fuel compounds [13,14]. It has been found that the nitrogen dilution effect and carbon dioxide dilution effect on the flammability limits of methane, propane, propylene, methyl formate, and 1,1-difluoroethane can be interpreted reasonably well each with a common set of parameter values in the extended Le Chatelier's formula.

Considering this fact, we focused our attention on the upper flammability limits of the fuel mixtures which are specifically prepared from the five selected compounds, i.e., methane, propane, propylene, methyl formate, and 1,1-difluoroethane. There are thirty mixtures of such kind. For these mixtures, the average difference between the observed values and the calculated ones by the original Le Chatelier's formula is 0.26 vol% which corresponds to 1.77 relative percent. These values are even smaller than the ones obtained through the fitting procedure using Eq. (8) for all the data together, i.e., 0.52 vol% and 2.4 relative percent, respectively. Then, a similar analysis was carried out to reduce further the differences between the observed and calculated values. The result is shown in "Calc 4" column of Table 3, and the parameter values are shown in "Calc 4" column in Table 4. The average difference between the observed and calculated values is reduced from 0.26 vol% to 0.10 vol%. The latter corresponds to 0.70 relative percent. It is interesting that the rate of reduction here is almost a factor of three, which is about the same as in the case where the analysis was done over all nine compounds. Thus, the present modification is similarly valid for a set of compounds of small deviations from the original Le Chatelier's law prediction as for those of large deviations.

As necessary, we can write down a similar equation for lower flammability limits:

$$\frac{1}{L} = \sum_{i=1}^{n} \frac{c_i}{L_i}[1 + p_i(1 - c_i)] \tag{9}$$

Here, L_i is the lower flammability limit of ith component of the blended gas, and p_i is the coefficient of perturbation. For comparison, a similar analysis was made for the lower flammability limit data using this equation. The result is shown in "Calc 2" column in Table 2. The average absolute deviation of the calculated values from the observed one was 0.068 vol% originally, and the value after the analysis is 0.060 vol%. For the lower flammability limit, since the prediction by the original Le Chatelier's formula itself is very good, this analysis does not significantly improve the agreement of the calculated values to the observed ones at least for the fuel blends treated in the present study.

4. Conclusion

The flammability limits of binary and ternary mixtures prepared from nine kinds of combustible gases were measured in a 12-l spherical glass vessel. The observed values of lower flammability limits are in good agreement with the calculated values by Le Chatelier's formula. On the other hand, agreement between the observed and calculated values of upper flammability limits is not so good as for the lower flammability limits. Interestingly, however, the deviations of observed values of upper flammability limits from the calculated ones are mostly to the lower concentrations.

A modified Le Chatelier's formula was proposed to better interpret the flammability limits of fuel blends. Least squares calculation of upper flammability limits using this equation reduced the average difference between the observed and calculated values from 7.2 to 2.4 relative percent. As regards the fuel blends prepared from five selected compounds, i.e., methane, propane, propylene, methyl formate, and 1,1-difluoroethane, the average difference between the observed values and the calculated values by the original Le Chatelier's formula was relatively small, i.e., only 1.77 relative percent. A similar analysis by the modified equation reduced this to 0.70 relative percent, i.e. about one-third of the initial value.

Finally, in order to secure safety in process industries or in laboratories, the flammable properties of chemicals treated there should be directly measured under the condition actually used. In such cases, techniques of accurate prediction of their property will much reduce the cost of testing.

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, in: Fire Protection Guide on Hazardous Materials, 9th ed., NFPA, Quincy, MA, 1984, 325M.
[4] H. Le Chatelier, O. Boudouard, Limits of flammability of gaseous mixtures, Bull. Soc. Chim. (Paris) 19 (1898) 483–488.
[5] A. Takahashi, Y. Urano, K. Tokuhashi, H. Nagai, M. Kaise, S. Kondo, Fusing ignition of various metal wires for explosion limits measurement of methane/air mixture, J. Loss Prev. Process Ind. 11 (1998) 353–360.
[6] 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. Technol. 145 (1999) 1–15.
[7] A. Takahashi, Y. Urano, K. Tokuhashi, S. Kondo, Effect of vessel size and shape on experimental flammability limits of gases, J. Hazard. Mater. A105 (2003) 27–37.
[8] K.L. Liekhus, I.A. Zlochower, K.L. Cashdollar, S.M. Djordjevic, C.A. Loehr, Flammability of gas mixtures containing volatile organic compounds and hydrogen, J. Loss Prev. Process Ind. 13 (2000) 377–384.
[9] D. Markus, H.P. Schildberg, W. Wildner, G. Krdzalic, U. Maas, Flammability limits of premixed methane/methanol/air flames, Combust. Sci. Technol. 175 (2003) 2095–2112.
[10] I. Wierzba, Q. Wang, The flammability limits of H_2–CO–CH_4 mixtures in air at elevated temperatures, Int. J. Hydrogen Energ. 31 (2006) 485–489.
[11] American Society of Heating, Refrigerating and Air-conditioning Engineers, Number designation and safety classification of refrigerants, ANSI/ASHRAE Standard 34-2007, ASHRAE, Atlanta GA, 2007.
[12] American Society of Testing and Materials, Designation: E681-04, West Conshohocken, 2004.
[13] S. Kondo, K. Takizawa, A. Takahashi, K. Tokuhashi, Extended Le Chatelier's formula and nitrogen dilution effect on the flammability limits, Fire Safety J. 41 (2006) 406–417.
[14] S. Kondo, K. Takizawa, A. Takahashi, K. Tokuhashi, Extended Le Chatelier's formula for carbon dioxide dilution effect on flammability limits, J. Hazard. Mater. A138 (2006) 1–8.