Flammability limits of isobutane and its mixtures with various gases

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Abstract

Flammability limits of isobutane and five kinds of binary mixtures of isobutane were measured by the ASHRAE method. Propane, nitrogen, carbon dioxide, chloroform, and HFC-125 (1,1,1,2,2-pentafluoroethane) were used as the counter part gases in the mixtures. The observed data were analyzed using the equations based on Le Chatelier's formula. The flammability limits of mixtures with propane were well explained by the original Le Chatelier's formula. The flammability limits of mixtures with nitrogen and the ones with carbon dioxide were adequately analyzed by the extended Le Chatelier's formula. It was found that the extended Le Chatelier's formula is also applicable to the flammability limits of mixtures with chloroform and HFC-125.
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1. Introduction

The global environmental problem makes it an urgent task to establish CFC alternatives. Isobutane is one of those compounds considered to be suitable for a refrigerant or for a component gas in blended refrigerants. However, since this compound is flammable, the data of flammability characteristics are indispensable. The flammability limit is one of the most important indices to access the fire and explosion hazards of flammable gases. Jones and Scott [1] have measured the flammability limits of isobutane in air with upward propagation of flame in a tube 2 in. (5.1 cm) in diameter and 6 ft (150 cm) in length at ambient pressure. They have also taken some data on the nitrogen and carbon dioxide dilution effects on the flammability limits of this compound [1]. Recently, we have investigated nitrogen and carbon dioxide dilution effects on the flammability limits of eight selected compounds [2,3]. Certainly, isobutane is as important a compound as those treated there from a refrigerant point of view.

As to the flammability limits of gaseous mixtures, they have to be determined for the individual compositions. If a mix-

ture in question contains only flammable components, the lower flammability limit can be estimated from the data of constituting compounds by using Le Chatelier's formula [4]. The lower flammability limit L of the mixture is given by the following equation.

$$\frac{1}{L} = \sum_i \frac{c_i}{L_i} \tag{1}$$

Here, c_i's are mole fractions of component gases whose lower flammability limits are $L_1, L_2, L_3, \ldots$, and satisfy the following equation.

$$\sum_i c_i = 1 \tag{2}$$

In a previous study, we have applied this equation to the flammability limits of mixtures prepared from nine different flammable gases of various kinds [5]. As a result, it has been found that Le Chatelier's formula works very well for lower flammability limits of quite a variety of compounds. A similar equation is valid to a certain extent for upper flammability limits as well. For some cases, however, discrepancy was noted between the observed and calculated values of upper flammability limits. In particular, discrepancy was noted for such mixtures as the ones containing ethylene, dimethyl ether, and carbon monoxide [5].

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On the other hand, since Le Chatelier's formula is *per se* for blended gases containing only fuel compounds, a certain extension is necessary to apply it to mixtures containing a non-flammable component. We have developed an extension of Le Chatelier's formula to interpret the inert gas dilution effects on the flammability limits [2]. The extended Le Chatelier's equation was used to interpret the nitrogen and carbon dioxide dilution effects on the flammability limits of various kinds of flammable gases [2,3]. It is of particular interest whether the equation can be applied to mixtures containing such compounds as chloroform and HFC-125, because they are non-flammable but are not inert chemicals.

Recently, Liekhus et al. [6] have measured the lower flammability limits of mixtures containing carbon tetrachloride. They have analyzed the obtained data in terms of a group contribution method combined with the Le Chatelier's formalism. The lower flammability limits of these mixtures were calculated using the scheme of Le Chatelier's formula from the lower flammability limits of individual compounds obtained by a group contribution method. One advantage of this method is that even for such a compound as carbon tetrachloride a virtual value of lower flammability limit is obtained which can be used in the Le Chatelier's formulation to calculate the lower flammability limits of such mixtures. Unfortunately, however, this method is only applicable to the lower flammability limits. Meanwhile, Shebeko et al. [7] have proposed a unique method of predicting envelopes of flammable region of mixtures. However, the calculation by this method is not very accurate. Vidal et al. [8] evaluated the lower flammability limits of fuel–air–diluent mixtures using calculated adiabatic flame temperatures for saturated and unsaturated hydrocarbons.

The purpose of the present study is at first to measure the flammability limits of isobutane and its mixtures with propane, nitrogen, carbon dioxide, chloroform, and 1,1,1,2,2-pentafluoroethane (HFC-125) consistently by one method [9–11], and secondly to analyze the obtained data with the equations based on the Le Chatelier's formula [2–4].

2. Experimental method

It is well known that the experimental flammability limits are dependent on the size and shape of the explosion vessel used in the measurement. Except for a type of vessels which measures a sort of quenching limit of concentration for a given cylindrical diameter like the one known as US Bureau of Mines type [12], in general the larger the vessel size, the narrower the experimental flammable range obtained from the measurement, and then, the experimental flammable range approaches a certain limit value [13]. This limit value should be the flammable range valid in the real living space or in free space. It is desirable to utilize an explosion vessel of a certain size. If it is a cylindrical vessel, it is desirable that the diameter is at least 30 cm and the height is at least 60 cm [13].

The experimental setup used in the present study is the same as that used in our previous studies [2–4], which basically follows that of the revised version of ASTM-E681 [9–11]. The explosion vessel is a 12 l spherical glass flask. In the present setting, the vessel flange is fixed to the top of the vessel, while in the ASTM method the flange is held on the top by spring-loaded clamps. Though the size of this vessel may not be large enough to realize the equivalent environment to free space, the decision criteria of the present method as well as the revised version of ASTM method have been so determined that the resulting flammable ranges for methane and propane are consistent with the measurements in jumbo vessels [10,12]. The explosion vessel is enclosed in an air-bath kept at 35 °C. The vessel is connected to a soda lime tower 30 cm in diameter and 50 cm in height through a plastic tube 3/8 in. (0.95 cm) in diameter and approximately 50 cm in length.

In the experiments, the gas mixtures were directly prepared in the explosion vessel by the partial pressure method. Before introduction of gases, the vessel was evacuated to 5×10^{-2} Torr (1 Torr = 133.32 Pa) or lower. For the preparation of sample mixtures containing chloroform vapor, chloroform vapor was introduced into the vessel first, followed by isobutane, and then air. For other cases, isobutane was introduced first followed by counterpart gas, and then air. Two types of MKS baratrons, 100 and 1000 Torr heads, were used for the pressure measurement. Gas 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 to settle for 1 min, and balanced with the ambient pressure just before ignition.

By opening the valve leading to the soda lime tower just before ignition, the hot gas accumulation at the ceiling produced by the ignition process is relieved through the plastic tube. The vessel is also equipped with a 1/2 in. (1.27 cm) relief valve set at 5 psi (34.5 kPa) in relief pressure. A pair of tungsten electrodes was set for AC electric discharge, the ends of which were pointed and set 1/4 in. (0.63 cm) apart. The electrodes were positioned one-third from the bottom to the shoulder of the vessel. An AC electric spark was initiated by a 15 kV neon transformer. The spark duration was 0.4 s. This corresponds to an ignition energy of approximately 10 J. 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.

Samples of isobutane, propane, nitrogen, carbon dioxide, chloroform, and 1,1,1,2,2-pentafluoroethane (HFC-125) were used. Sample materials of isobutane, propane, nitrogen, carbon dioxide, as well as dry-air were purchased from Nippon Sanso Co. HFC-125 is from Showa Denko Co. and chloroform from Wako Chemical Co. Purities of fuel gases were at least 99% except for chloroform. Purity of chloroform was 98% or better. Air was of G3 grade of Nippon Sanso Co. All sample materials were used without further purification.

3. Results and discussion

3.1. Isobutane itself and its mixtures with propane

In order to calculate the flammability limits of various mixtures using Le Chatelier's formula or relevant equations, it is necessary to utilize the data consistently taken with the same

Table 1
Observed and calculated values of flammability limits of isobutane-propane mixtures

Blend ratio	Lower flammability limit (vol%)			Upper flammability limit (vol%)		
C3H8:iC4H10	Obs	Calc[a]	Obs − Calc	Obs	Calc[a]	Obs − Calc
0.0:1.0	1.68 (0.02)	–	–	7.8 (0.4)	–	–
0.2:0.8	1.733 (0.010)	1.74	0.00	8.2 (0.4)	8.16	0.04
0.4:0.6	1.79 (0.01)	1.80	−0.01	8.6 (0.4)	8.55	0.05
0.6:0.4	1.86 (0.02)	1.87	−0.01	9.0 (0.4)	8.99	0.01
0.8:0.2	1.94 (0.02)	1.95	−0.01	9.4 (0.3)	9.47	−0.07
1.0:0.0	2.03 (0.02)	–	–	10.0 (0.3)	–	–

[a] Calculated with Le Chatelier's formula.

apparatus under the same experimental condition by the same decision criterion. In conformity with this policy, the flammability limits of isobutane were re-measured in this study. The obtained values are 1.68 vol% for lower flammability limit and 7.8 vol% for upper flammability limit, while the values of 1.83 vol% and 8.43 vol% are, respectively, reported in the literature [1]. On the other hand, the flammable range from 1.5 vol% to 9.4 vol% reported in CHEMSAFE [14] is definitely wider than the present result. Apparently, the difference is primarily due to the difference in the vessel sizes used for the measurements. As pointed out in the preceding section, the experimental flammable range becomes wide if the vessel size is small [13]. As to the mixtures with propane, several compositions were examined. The result is shown in Table 1. The calculated values for the mixtures were obtained using Le Chatelier's formula. The values of 2.03 vol% and 10.0 vol% were used as the flammability limits of propane, which were obtained in the literature using the same experimental method [5]. Agreement between the observed and calculated values is excellent both for the upper and lower flammability limits. Actually, the calculated values for various compositions fall well within the experimental uncertainties. This shows that the flammability limits of propane–isobutane mixtures of arbitrary compositions can be quite accurately predicted by the Le Chatelier's formula. This fact indicates that the chemical natures and combustion reactions of the two compounds are very similar to each other.

3.2. Dilutions with nitrogen and with carbon dioxide

Flammability limits of isobutane diluted with nitrogen and with carbon dioxide were measured at various levels of concentrations. The result is summarized in Table 2, where L_{fuel} and U_{fuel} are, respectively, the concentrations of isobutane in the lower and upper flammability limit mixtures of isobutane, diluent, and air. As in a previous paper [2,3], FIP and AIP stand for fuel inertization point and air inertization point, respectively. Namely, FIP is the point on the envelope of flammable region in the triangular system of fuel–air–diluent which defines the maximum ratio of fuel to diluent concentration that never gives flammable mixtures whatever amount of air is added to or subtracted from the mixture. If the fuel contents in the upper and lower flammability limit mixtures are plotted against mole fraction of diluent in the blend (like in Figs. 1–4 shown later), they become coincident to each other at FIP. Likewise, AIP

is the point on the envelope of the flammable region in the fuel–air–diluent triangular system which has the maximum ratio of air to diluent concentration that never gives flammable mixtures whatever the fuel concentration.

In order to search for FIP, it is helpful to image an envelope of flammable range in a graph which takes isobutane concentration for ordinate scale and the ratio of added nitrogen to isobutane plus added nitrogen for abscissa scale. In this figure, FIP is located at the far end of the peninsular of flammable region, which is not difficult to find out. Similarly, AIP is located at the
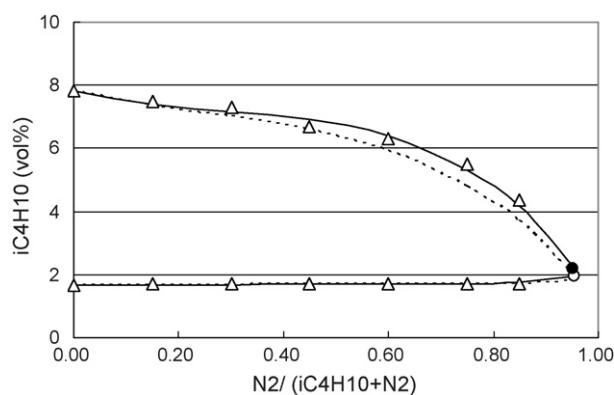

Fig. 1. Comparison between the observed and calculated values of flammability limits of isobutane–nitrogen blend of various compositions. (—) Calc 1; (· · ·) Calc 2; (○) FIP; (●) AIP; (△) other observed points.
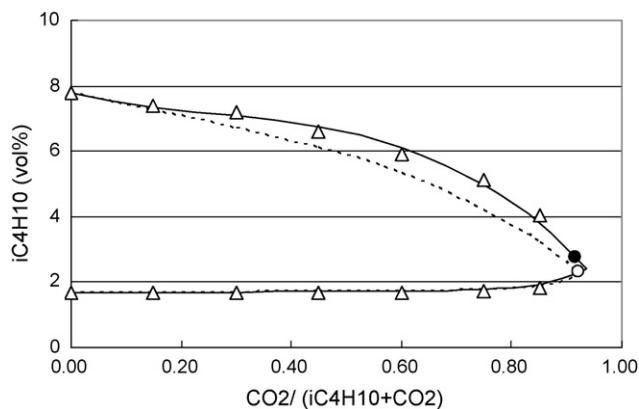

Fig. 2. Comparison between the observed and calculated values of flammability limits of isobutane–carbon dioxide blend of various compositions. (—) Calc 1; (· · ·) Calc 2; (○) FIP; (●) AIP; (△) other observed points.

Table 2

Results of fitting calculation to observed flammability limits of isobutane diluted with four kinds of non-flammable compounds. Calc 1 is from accurate fitting to individual combinations, and Calc 2 is obtained using parameter values from simultaneous fitting to selected five compounds in [2,3]

Non-flammable		c_i[a]	Obs			Calc 1	Obs − Calc 1	Calc 2	Obs − Calc 2	Note
			Fuel[b] (vol%)	Diluent[c] (vol%)	Air (vol%)	Fuel (vol%)	Fuel (vol%)	Fuel (vol%)	Fuel (vol%)	
Nitrogen		0.000	1.68 (0.02)	0.00	98.32	1.68	0.00	1.68	0.00	
		0.150	1.69 (0.02)	0.30	98.01	1.68	0.01	1.68	0.01	
		0.300	1.69 (0.02)	0.72	97.59	1.68	0.01	1.68	0.01	
	L_{fuel}	0.450	1.69 (0.02)	1.38	96.93	1.69	0.00	1.68	0.01	
		0.600	1.69 (0.02)	2.54	95.78	1.70	−0.01	1.69	0.00	
		0.750	1.70 (0.02)	5.10	93.20	1.71	−0.01	1.70	0.00	
		0.850	1.71 (0.02)	9.69	88.60	1.74	−0.03	1.71	0.00	
		0.955	1.95 (0.05)	41.77	56.28	1.94	0.01	1.80	0.15	FIP
		0.000	7.8 (0.4)	0.00	92.20	7.80	0.00	7.80	0.00	
		0.150	7.5 (0.4)	1.32	91.18	7.39	0.11	7.37	0.13	
		0.300	7.3 (0.3)	3.13	89.57	7.18	0.12	7.03	0.27	
		0.450	6.7 (0.4)	5.48	87.82	6.93	−0.23	6.60	0.10	
	U_{fuel}	0.600	6.3 (0.3)	9.45	84.25	6.39	−0.09	5.92	0.38	
		0.750	5.5 (0.3)	16.50	78.00	5.33	0.17	4.79	0.71	
		0.850	4.36 (0.15)	24.71	70.93	4.19	0.17	3.70	0.66	
		0.953	2.20 (0.10)	44.60	53.20	2.26	−0.06	2.00	0.20	AIP
		0.955	1.95 (0.05)	41.77	56.28	2.21	−0.26	1.95	0.00	FIP
Carbon dioxide		0.000	1.68 (0.02)	0.00	98.32	1.68	0.00	1.68	0.00	
		0.150	1.67 (0.02)	0.29	98.04	1.69	−0.02	1.69	−0.02	
		0.300	1.68 (0.02)	0.72	97.60	1.70	−0.02	1.69	−0.01	
	L_{fuel}	0.450	1.69 (0.02)	1.38	96.93	1.71	−0.02	1.71	−0.02	
		0.600	1.69 (0.02)	2.54	95.78	1.74	−0.05	1.73	−0.04	
		0.750	1.73 (0.02)	5.19	93.08	1.80	−0.07	1.78	−0.05	
		0.850	1.81 (0.02)	10.26	87.93	1.91	−0.10	1.88	−0.07	
		0.922	2.30 (0.10)	27.23	70.47	2.25	0.05	2.15	0.15	FIP
		0.000	7.8 (0.4)	0.00	92.20	7.80	0.00	7.80	0.00	
		0.150	7.4 (0.4)	1.31	91.29	7.36	0.04	7.23	0.17	
		0.300	7.2 (0.4)	3.09	89.71	7.08	0.12	6.70	0.50	
		0.450	6.6 (0.3)	5.40	88.00	6.73	−0.13	6.09	0.51	
	U_{fuel}	0.600	5.9 (0.2)	8.85	85.25	6.08	−0.18	5.30	0.60	
		0.750	5.1 (0.2)	15.30	79.60	4.94	0.16	4.20	0.90	
		0.850	4.05 (0.15)	22.95	73.00	3.78	0.27	3.22	0.83	
		0.917	2.78 (0.10)	30.62	66.60	2.74	0.04	2.38	0.40	AIP
		0.922	2.30 (0.10)	27.23	70.47	2.65	−0.35	2.30	0.00	FIP
Chloroform		0.000	1.68 (0.02)	0.00	98.32	1.68	0.00			
		0.150	1.64 (0.02)	0.29	98.07	1.61	0.03			
		0.300	1.60 (0.02)	0.69	97.71	1.55	0.05			
		0.450	1.56 (0.02)	1.28	97.16	1.52	0.04			
	L_{fuel}	0.600	1.54 (0.02)	2.30	96.16	1.51	0.03			
		0.750	1.53 (0.03)	4.59	93.88	1.59	−0.06			
		0.800	1.59 (0.02)	6.36	92.05	1.67	−0.08			
		0.850	1.80 (0.05)	10.20	88.00	1.87	−0.07			
		0.852	2.00 (0.05)	11.51	86.49	1.88	0.12			FIP
		0.000	7.8 (0.4)	0.00	92.20	7.80	0.00			
		0.150	7.4 (0.4)	1.30	91.30	7.38	0.01			
		0.300	7.1 (0.04)	3.06	89.80	7.12	0.02			
		0.450	6.7 (0.5)	5.49	87.80	6.67	0.04			
	U_{fuel}	0.600	5.6 (0.3)	8.34	86.11	5.70	−0.14			
		0.750	3.92 (0.15)	11.77	84.31	3.95	−0.03			
		0.800	3.24 (0.06)	12.96	83.80	3.16	0.08			
		0.820	2.90 (0.10)	13.21	83.89	2.62	0.28			AIP
		0.850	2.17 (0.05)	12.29	85.54	2.24	−0.07			
		0.852	2.00 (0.05)	11.51	86.49	2.20	−0.20			FIP

Table 2 (*Continued*)

Non-flammable		c_i[a]	Obs			Calc 1	Obs − Calc 1	Calc 2	Obs − Calc 2	Note
			Fuel[b] (vol%)	Diluent[c] (vol%)	Air (vol%)	Fuel (vol%)	Fuel (vol%)	Fuel (vol%)	Fuel (vol%)	
HFC−125		0.000	1.68 (0.02)	0.00	98.32	1.68	0.00			
		0.150	1.65 (0.02)	0.29	98.06	1.60	0.05			
		0.300	1.61 (0.03)	0.69	97.70	1.54	0.07			
		0.450	1.58 (0.02)	1.30	97.12	1.49	0.09			
	L_{fuel}	0.600	1.52 (0.02)	2.28	96.20	1.46	0.06			
		0.750	1.41 (0.02)	4.22	94.38	1.48	−0.07			
		0.790	1.38 (0.02)	5.20	93.42	1.52	−0.14			
		0.820	1.41 (0.02)	6.45	92.14	1.56	−0.15			
		0.850	1.65 (0.03)	9.35	89.00	1.63	0.02			
		0.851	1.80 (0.10)	10.28	87.92	1.63	0.17			FIP
		0.000	7.8 (0.4)	0.00	92.20	7.80	0.00			
		0.150	7.5 (0.4)	1.32	91.20	7.33	0.15			
		0.300	7.1 (0.4)	3.06	89.80	7.06	0.08			
		0.450	6.4 (0.3)	5.27	88.29	6.62	−0.18			
		0.600	5.4 (0.3)	8.10	86.50	5.67	−0.27			
	U_{fuel}	0.750	4.1 (0.3)	12.39	83.48	3.90	0.23			
		0.786	3.6 (0.3)	13.22	83.18	3.33	0.27			AIP
		0.790	3.5 (0.2)	13.05	83.48	3.26	0.21			
		0.820	2.84 (0.15)	12.94	84.22	2.73	0.11			
		0.850	1.98 (0.10)	11.22	86.80	2.15	−0.17			
		0.851	1.80 (0.10)	10.28	87.92	2.13	−0.33			FIP

[a] c_i is the mole fraction of diluent gas in fuel–diluent blend, where diluent means nitrogen, carbon dioxide, chloroform, or HFC125.
[b] Numbers in parentheses are experimental uncertainties.
[c] "Diluent" is nitrogen, carbon dioxide, chloroform, or HFC125.

top of the peninsular of the flammable region drawn in a graph which takes isobutane concentration for ordinate scale and the ratio of added nitrogen to air plus added nitrogen for abscissa scale. Detailed result of FIP and AIP measurement is separately listed in Table 3.

In a previous paper [2], we have developed an extended Le Chatelier's formula to explain the inert gas dilution effect on the flammability limits of combustible gases. The equations are specifically applicable to blended gases consisting of one flammable gas and one diluent gas, though the extension to other cases can be made easily as necessary. In the present case, the concentration of isobutane L_{fuel} (vol%) in the lower flammability limit mixture of the blended gas and air can be expressed by

the following equation.

$$\frac{c_1}{L_{fuel}} = \frac{c_1}{L_1} + pc_{in} + qc_{in}^2 + rc_{in}^3 \tag{3}$$

where L_1 (vol%) is the lower flammability limit of isobutane itself in air, c_1 is the mole fraction of isobutane in the isobutane–inert blend, $c_{in} = 1 - c_1$ is the mole fraction of inert gas in the isobutane–inert blend, and p, q, and r are empirical parameters to be determined by the experiments. Similarly, the concentration of isobutane U_{fuel} (vol%) in the upper flammability limit mixture of the blended gas and air is expressed by the
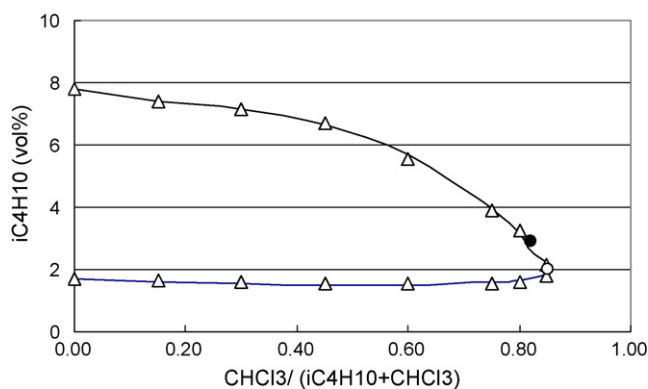

Fig. 3. Comparison between the observed and calculated values of flammability limits of isobutane-chloroform blend of various compositions. (—) Calc 1; (○) FIP; (●) AIP; (△) other observed points.
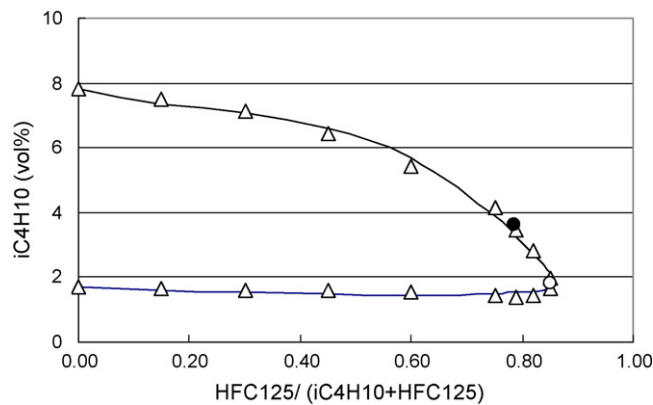

Fig. 4. Comparison between the observed and calculated values of flammability limits of isobutane-hfc125 blend of various compositions. (—) Calc 1; (○) FIP; (●) AIP; (△) other observed points.

Table 3
Details of fuel inertization point (FIP) and air inertization point (AIP) for various mixtures of isobutane[a]

Fuel	FIP[b]		AIP[b]	
	Diluent/(fuel + diluent)	Fuel/total[c]	Diluent/(air + diluent)	Fuel/total[c]
Isobutane–nitrogen	95.54 (0.10)	At 1.95 (0.05)	45.6 (0.6)	At 2.20 (0.10)
Isobutane–carbon dioxide	92.21 (0.10)	At 2.30 (0.10)	31.5 (0.7)	At 2.78 (0.10)
Isobutane–chloroform	85.2 (0.3)	At 2.00 (0.05)	13.6 (0.2)	At 2.90 (0.10)
Isobutane–HFC125	85.1 (0.3)	At 1.8 (0.10)	13.7 (0.5)	At 3.6 (0.3)

[a] Numbers are in vol%. Numbers in parentheses are experimental uncertainties.
[b] "Fuel" means isobutane and "diluent" means nitrogen, carbon dioxide, chloroform, or HFC125.
[c] "Total" means isobutane + diluent + air.

following equation.

$$\frac{c_1 n_1}{100 - (U_{fuel}/c_1)} = \frac{c_1 n_1}{100 - U_1} + sc_{in} + tc_{in}^2 + uc_{in}^3 \quad (4)$$

Here, U_1 (vol%) is the upper flammability limit of isobutane in air, n_1 is moles of oxygen consumed by one mole of isobutane in the upper flammability limit region of isobutane, and s, t, and u are parameters to be determined experimentally. The value of n_1 is given by the following equation.

$$n_1 = \frac{0.21(100 - U_1)}{U_1} \quad (5)$$

The flammability limits of mixtures of isobutane and nitrogen were analyzed by using Eqs. (3) and (4). As in a previous paper [2,3], the parameters q and r were fixed to zero and only p was adjusted in the least squares analysis of the lower flammability limits because the alteration due to dilution is relatively gentle, while for the upper flammability limits the parameters s, t, and u were adjusted in the analysis. Comparison of the calculated values with the observed values is made in Table 2 (see Calc 1). Agreement between the observed and calculated values is good for both the upper and lower flammability limits. The average absolute deviation is 0.01 vol% for the lower flammability limit and 0.13 vol% for the upper limit. The resulting values of parameters are shown in Table 4. Fig. 1 is a visual presentation of the result, where the observed value of FIP is plotted as open circle, AIP as filled circle, and all other data of flammability limits as open triangles. Solid and dotted lines shows the calculated values. In [2], nitrogen dilution effect on the flammability limits of five selected compounds, i.e., methane, propane,

propylene, methyl formate, and 1,1-difluoroethane (HFC-152a), were analyzed simultaneously with a common set of parameter values yielding a good agreement between the observed and calculated values. Dotted line in Fig. 1 was obtained adopting this common set of parameter values in [2]. Discrepancy of this line from the observed values is a little larger than expected. The numerical values are shown as Calc 2 in Table 2. The average absolute deviation is 0.02 vol% for the lower flammability limit and 0.27 vol% for the upper limit. Incidentally, a careful inspection of the result of [2] reveals that discrepancy of the calculated values of propane by the common parameter set from the observed ones is a little larger than for the other four compounds. It would be a good idea to investigate parameter values commonly applicable to saturated hydrocarbons of large sizes.

The flammability limits of isobutane diluted with carbon dioxide were similarly analyzed using Eqs. (3) and (4). Here again, parameters q and r were fixed to zero and only p was adjusted in the analysis of the lower flammability limits, while for the upper flammability limit all of s, t, and u were used. The result is shown in Table 2. Agreement of the calculated values to the observed ones is good indeed for both the upper and lower flammability limits. The average absolute deviation is 0.04 vol% for the lower flammability limit and 0.14 vol% for the upper limit. The resulting parameter values are shown in Table 4. Fig. 2 is a visual presentation of the result. The observed value of FIP is plotted as open circle, AIP as filled circle, and all other data of flammability limits as open triangles. Solid line is the calculated values (Calc 1). As in the case of nitrogen dilution, dotted line in the figure shows the calculated values (Calc 2) utilizing a common set of parameter values obtained for the five selected compounds in [2]. Here again, discrepancy of dotted line from the observed values is a little noticed. The average absolute deviation is 0.04 vol% for the lower flammability limit and 0.44 vol% for the upper limit. This is similar to what was observed in the case of nitrogen dilution.

3.3. Mixing with chloroform and with HFC-125

The flammability limits of isobutane diluted with chloroform and HFC-125, respectively, were measured at various levels of concentrations. The result is shown in Table 2. The detailed data of FIP and AIP are listed in Table 3. Two things are noticed for the results of the mixtures with chloroform and with HFC-125 as compared to that of nitrogen and carbon dioxide dilutions.

Table 4
Parameter values resulting from fitting calculation to flammability limits

Case		Parameter value		
		p	q	
		s	t	u
Isobutane–nitrogen	L_{fuel}	−0.00378	0	0
	U_{fuel}	0.00112	0.00296	−0.00321
Isobutane–carbon dioxide	L_{fuel}	−0.01275	0	0
	U_{fuel}	0.00111	0.00262	−0.00308
Isobutane–chloroform	L_{fuel}	0.1784	−0.2223	0
	U_{fuel}	0.00113	0.00322	−0.00481
Isobutane–HFC125	L_{fuel}	0.1975	−0.2284	0
	U_{fuel}	0.00089	0.00399	−0.00543

One is that at the initial stage of dilution the lower flammability limit L_{fuel} slightly goes down toward lower concentrations as the degree of mixing increases. This may indicate that these compounds are not chemically inert and actually involved in the chemical reactions in flames. The other is that AIP is located at a distance from FIP (see Figs. 3 and 4), while for nitrogen and carbon dioxide dilutions AIP is very close to FIP (see Figs. 1 and 2). The chemical reactions of non-flammable compounds such as chloroform and HFC-125 may change quite a bit toward the dilution limit of flammability. Then, the value of upper flammability limits in particular of their mixtures may become very sensitive to the concentration of non-flammable component near the dilution limit. This may be the reason why the distance between AIP and FIP is large for these mixtures compared to that for inert gas dilutions.

As to Eqs. (3) and (4), they were introduced to interpret the dilution effect of inert gases such as nitrogen and carbon dioxide [2,3]. As stated, the gases like chloroform and HFC-125 are non-flammable but not chemically inert. They may undergo chemical reactions in flames and produce certain amounts of heat. However, the correction terms in these equations may cover this effect as well. Then, similar analyses can be done using these equations for the isobutane mixtures with such compounds as chloroform and HFC-125.

For the lower flammability limits of isobutane–chloroform mixtures, the calculations were carried out adjusting two parameters, p and q, to consider the contribution from non-flammable component, where the value of r was fixed to zero. For the upper flammability limits, all the parameters of s, t, and u were adjusted in the least-squares calculation. The result of the analysis is shown in Table 2. The average absolute deviation is 0.05 vol% for the lower flammability limit and 0.09 vol% for the upper limit. Fig. 3 is a visual presentation of the result. The observed value of FIP is plotted as open circle, AIP as filled circle, and all other data of flammability limits as open triangles. Solid line shows the calculated values.

Analysis of the isobutane and HFC-125 mixtures was carried out similarly. For the upper flammability limits, the parameter values of s, t, and u were adjusted in the least-squares calculation. The result is shown in Table 4. The average absolute deviation is 0.08 vol% for the lower flammability limit and 0.18 vol% for the upper limit. Fig. 4 is a visual presentation of the result. Here again, AIP is at a distance from FIP, which is different from the cases of nitrogen and carbon dioxide.

4. Conclusion

The flammability limits of isobutane mixed, respectively, with propane, nitrogen, carbon dioxide, chloroform vapor, and HFC-125 were measured at various levels of concentration. For the mixtures of isobutane and propane, it has been found that the values of both the upper and lower flammability limits can be predicted by the Le Chatelier's formula very accurately. The average value of discrepancy of the predicted values from the observed values was 0.01 vol% for the lower flammability limit, and 0.05 vol% for the upper flammability limit. This means that the predicted values of both the lower and upper

flammability limits by Le Chatelier's formula fall well within the experimental uncertainties for the mixtures of propane and isobutane.

The flammability limits data of isobutane diluted with nitrogen were analyzed using the extended Le Chatelier's formula developed in a previous study [2]. A good agreement was obtained between the observed and calculated values. On the other hand, if a common set of parameter values determined for five selected compounds in a previous study [2] are used, deviation of the calculated values from the observed ones is very similar but a little larger than for the case of propane.

A similar analysis was carried out for isobutane–carbon dioxide mixtures using the extended Le Chatelier's formula. On the whole, quite a similar result was obtained for carbon dioxide dilution as for the nitrogen dilution. Also if a common set of parameter values determined for five selected compounds [2] are used, deviation of the calculated values from the observed ones is a little larger than for the case of propane.

The extended Le Chatelier's formula was also applied to the mixtures of isobutane with chloroform and HFC-125. One thing noted in these cases is that the alteration of the lower flammability limit due to mixing is a little larger than the ones for nitrogen and carbon dioxide dilutions. Another thing is that AIP is at a distance from FIP, while in the cases of nitrogen and carbon dioxide dilutions they are quite close to each other. This may be due to the fact that chloroform and HFC-125 are chemically active while nitrogen and carbon dioxide are not. Analyses of the flammability limits data of isobutane mixtures with chloroform vapor and with HFC-125, respectively, were done adjusting the parameter values of p, q, s, t, and u to be in good agreement between the observed and calculated values for both cases.

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