

Extended Le Chatelier's formula for carbon dioxide dilution effect on flammability limits

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

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

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Abstract

Carbon dioxide dilution effect on the flammability limits was measured for various flammable gases. The obtained values were analyzed using the extended Le Chatelier's formula developed in a previous study. As a result, it has been found that the flammability limits of methane, propane, propylene, methyl formate, and 1,1-difluoroethane are adequately explained by the extended Le Chatelier's formula using a common set of parameter values. Ethylene, dimethyl ether, and ammonia behave differently from these compounds. The present result is very consistent with what was obtained in the case of nitrogen dilution.

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1. Introduction

Le Chatelier's formula [1] is commonly used to predict the flammability limits of blended gases of various fuels. According to this law, the lower flammability limit L of a blended gas is given by the following equation:

$$\frac{1}{L} = \frac{c_1}{L_1} + \frac{c_2}{L_2} + \frac{c_3}{L_3} + \dots \quad (1)$$

Here, c_1, c_2, c_3, \dots are mole fractions of component gases in the blend whose lower flammability limits are L_1, L_2, L_3, \dots , respectively. The sum of the mole fractions, c_1, c_2, c_3, \dots , is unity.

$$c_1 + c_2 + c_3 + \dots = 1 \quad (2)$$

A similar equation is said to be valid for the upper flammability limits. Recently, we have applied the Le Chatelier's formula to newly measured values of flammability limits of various mixtures prepared from nine kinds of compounds [2]. As a result, it has been found that in general Le Chatelier's formula can very well predict the values of lower flammability limits and can rea-

sonably well predict the upper flammability limits. In addition, it has been shown that Le Chatelier's formula can be modified so that the upper flammability limits of various blended gases may be fitted pretty accurately [2].

However, since Le Chatelier's formula is per se for blended gases containing only flammable compounds, it is not applicable as it is to dilution effect of inert gases. In a previous paper, we have developed Le Chatelier's formula to apply to the inert gas dilution effect [3]. As a result, it has been found that the nitrogen dilution effect on the flammability limits of a wide variety of fuel gases can be explained by the extended Le Chatelier's formula using a common set of parameter values.

Dilution with nitrogen is a typical way of ensuring safety in the use of flammable gases. Carbon dioxide is another typical gas to be used for the same purpose. It is of interest whether the carbon dioxide dilution effect on various fuel gases can be explained similarly as in the case of nitrogen dilution. If a similar result is obtained for the carbon dioxide case, we can expect that dilution effects of various inert gases on a variety of flammable gases be explained by the extended Le Chatelier's formula using a common set of parameter values.

Data of carbon dioxide dilution effects on various flammable gases are reported in the literature such as Refs. [4,5]. However, it is well known that the values of flammability limits are dependent upon the experimental apparatus and condition used for the

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

measurement. In order to make a reliable numerical analysis, it is indispensable to utilize accurate and in particular consistent data of flammability limits in the analysis. In the present study, carbon dioxide dilution effects on the same eight compounds as used in the preceding study [3] were measured carefully, and a similar analysis was carried out using the extended Le Chatelier's formula.

2. Experimental method

The experimental setup is the same as in a previous study, which basically follows that of the revised version of ASTM-E681 [6–8]. The explosion vessel is a 12-l spherical glass flask which is enclosed in an air-bath kept at 35 °C. In the present apparatus, 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. 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. The fuel gas was introduced into the vessel first, followed by carbon dioxide and then air. Two types of MKS baratron, 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 connected 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. In case this cannot relieve the pressure quickly enough, the vessel is equipped with a 1/2 in. (1.27 cm) relief valve set at 5 psi (34.5 kPa) in relief pressure. The vessel is equipped with a pair of tungsten electrodes 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.

The flammability limits of methane, propane, ethylene, propylene, methyl ether, methyl formate, 1,1-difluoroethane, and ammonia were measured at various levels of carbon dioxide dilution. Sample gases were purchased from Nippon Sanso Co. and Tokyo Kasei Co. Purities of fuel gases were 99% or better except for methyl formate. Purity of methyl formate was at least 98%. Purity of carbon dioxide was better than 99.9%. Air was of G2 grade of Nippon Sanso Co. All sample materials were used without further purification.

3. Results and discussion

The flammability limits of eight compounds, i.e., methane, propane, ethylene, propylene, dimethyl ether, methyl formate, 1,1-difluoroethane, and ammonia, were measured at various levels of dilution with carbon dioxide. The flammability limits of sample gases themselves were measured in a previous study under the same experimental condition [2]. The result of these measurements is summarized in Table 1. In this table, L_{fuel} is the concentration of the fuel gas only in the lower flammability limit mixture of the blend gas and air, and similarly, U_{fuel} is the concentration of the fuel gas only in the upper flammability limit mixture of the blend gas and air. In addition, both the fuel inertization point (FIP) and air inertization point (AIP) were determined. These are shown in Table 2. As in the preceding paper [3], FIP is defined as 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. The diluent here is carbon dioxide. If the fuel contents in the upper and lower flammability limit mixtures are plotted against diluent content in the blend, they become coincident to each other at the FIP. Likewise, AIP is defined as the point on the envelope of the flammable region in fuel–air–diluent system which has the maximum ratio of air to diluent concentration that never gives flammable mixtures whatever the fuel concentration. In Figs. 1–8, the observed values of FIPs are plotted as open circles, AIPs as filled circles, and all other data of flammability limits as open triangles. Differently from the case of nitrogen dilution, the lower flammability limit alters considerably as the concentration of carbon dioxide increases. Similarly, the upper flammability limit alters more conspicuously for carbon dioxide dilution than for nitrogen dilution.

In the preceding paper [3], we have developed an extended Le Chatelier's formula to explain the inert gas dilution effect on the flammability limits of flammable gases. The equations are specifically applicable to blend gases consisting of one

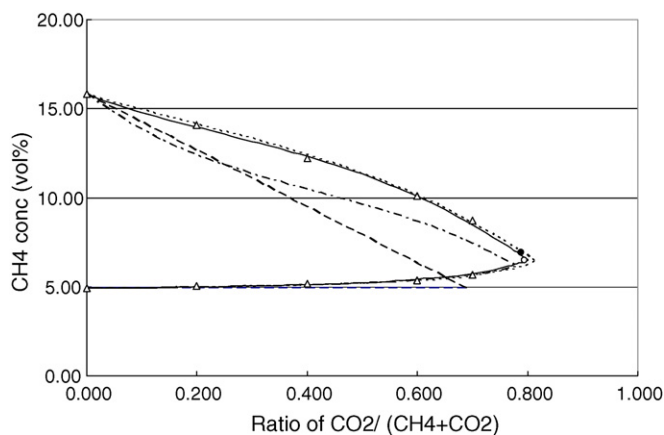


Fig. 1. Comparison between the observed and calculated values of flammability limits of methane–carbon dioxide blend of various compositions. (---) Calc 1; (—) Calc 2; (- - -) Calc 3; (· · ·) Calc 4; (○) FIP; (●) AIP; (△) other observed points.

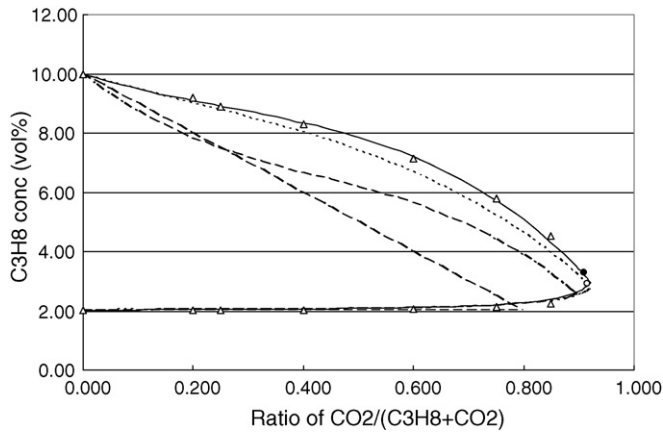


Fig. 2. Comparison between the observed and calculated values of flammability limits of propane-carbon dioxide blend of various compositions. (---) Calc 1; (—) Calc 2; (- - -) Calc 3; (· · ·) Calc 4; (○) FIP; (●) AIP; (Δ) other observed points.

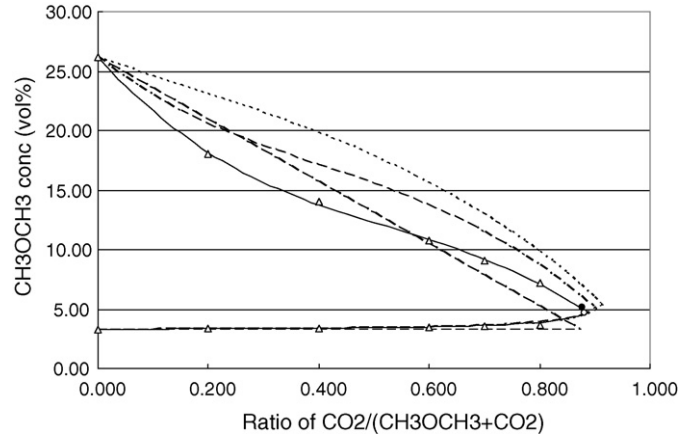


Fig. 5. Comparison between the observed and calculated values of flammability limits of dimethyl ether-carbon dioxide blend of various compositions. (---) Calc 1; (—) Calc 2; (- - -) Calc 3; (· · ·) Calc 4; (○) FIP; (●) AIP; (Δ) other observed points.

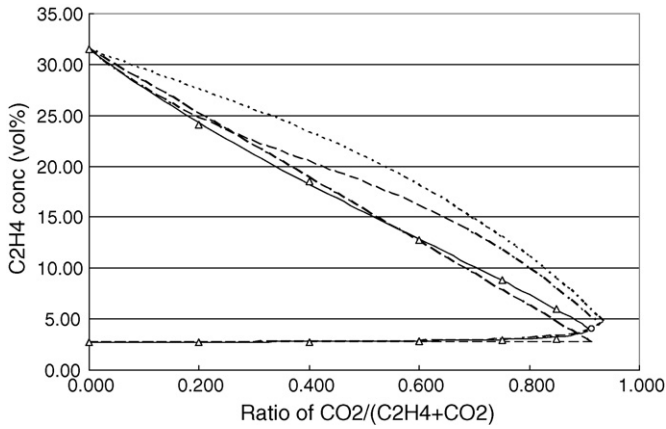


Fig. 3. Comparison between the observed and calculated values of flammability limits of ethylene-carbon dioxide blend of various compositions. (---) Calc 1; (—) Calc 2; (- - -) Calc 3; (· · ·) Calc 4; (○) FIP; (●) AIP (overlapped by FIP); (Δ) other observed points.

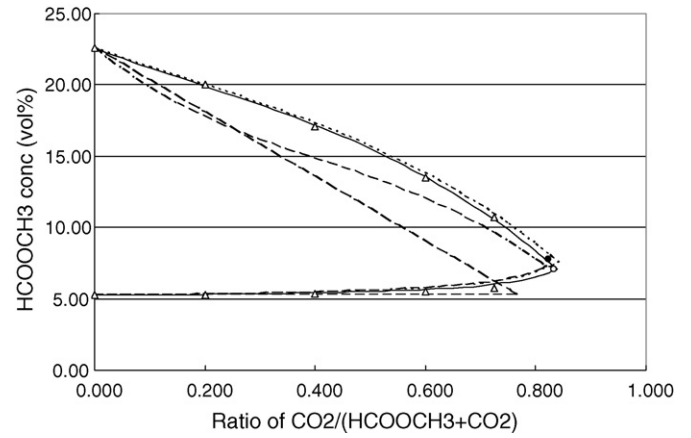


Fig. 6. Comparison between the observed and calculated values of flammability limits of methyl formate-carbon dioxide blend of various compositions. (---) Calc 1; (—) Calc 2; (- - -) Calc 3; (· · ·) Calc 4; (○) FIP; (●) AIP; (Δ) other observed points.

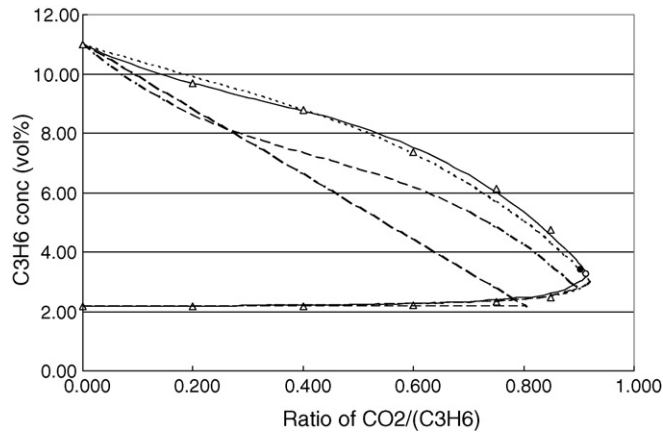


Fig. 4. Comparison between the observed and calculated values of flammability limits of propylene-carbon dioxide blend of various compositions. (---) Calc 1; (—) Calc 2; (- - -) Calc 3; (· · ·) Calc 4; (○) FIP; (●) AIP; (Δ) other observed points.

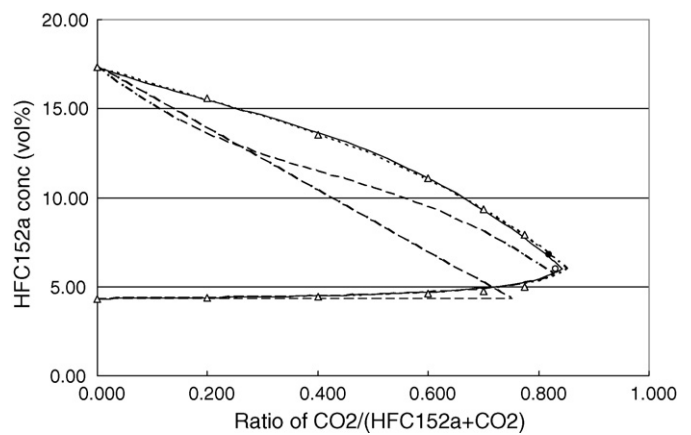


Fig. 7. Comparison between the observed and calculated values of flammability limits of 1,1-difluoroethane-carbon dioxide blend of various compositions. (---) Calc 1; (—) Calc 2; (- - -) Calc 3; (· · ·) Calc 4; (○) FIP; (●) AIP; (Δ) other observed points.

Table 1
Observed values of flammability limits for fuel–carbon dioxide mixtures of eight kinds of fuels

Fuel	c_{in}^a	L_{fuel}^b (vol%)	U_{fuel}^b (vol%)
Methane	0.000	4.90	15.8
	0.200	5.05 (0.10)	14.06 (0.15)
	0.400	5.15 (0.10)	12.2 (0.1)
	0.600	5.35 (0.10)	10.08 (0.10)
	0.700	5.65 (0.10)	8.7 (0.1)
Propane	0.000	2.03	10.0
	0.200	2.02 (0.02)	9.2 (0.3)
	0.250	2.02 (0.02)	8.9 (0.3)
	0.400	2.03 (0.03)	8.3 (0.2)
	0.600	2.07 (0.02)	7.15 (0.15)
	0.750	2.14 (0.02)	5.8 (0.1)
	0.850	2.24 (0.02)	4.53 (0.06)
Ethylene	0.000	2.74	31.5
	0.200	2.735 (0.04)	24.1 (1.0)
	0.400	2.77 (0.04)	18.5 (1.0)
	0.600	2.83 (0.04)	12.75 (0.50)
	0.750	2.92 (0.03)	8.8 (0.2)
	0.850	3.08 (0.03)	6.03 (0.15)
Propylene	0.000	2.16	11.0
	0.200	2.18 (0.03)	9.7 (0.5)
	0.400	2.17 (0.02)	8.8 (0.3)
	0.600	2.22 (0.02)	7.35 (0.15)
	0.750	2.30 (0.02)	6.13 (0.15)
	0.850	2.45 (0.02)	4.75 (0.15)
Methyl ether	0.000	3.30	26.2
	0.200	3.33 (0.04)	18.0 (0.7)
	0.400	3.35 (0.03)	14.0 (0.7)
	0.600	3.42 (0.04)	10.74 (0.25)
	0.700	3.51 (0.03)	9.1 (0.2)
	0.800	3.68 (0.03)	7.15 (0.15)
Methyl formate	0.000	5.25	22.6
	0.200	5.31 (0.05)	20.0 (0.7)
	0.400	5.33 (0.04)	17.1 (0.5)
	0.600	5.48 (0.05)	13.5 (0.5)
	0.725	5.75 (0.05)	10.75 (0.20)
	1,1-Difluoroethane	0.000	4.32
0.200		4.37 (0.04)	15.6 (0.5)
0.400		4.41 (0.03)	13.5 (0.5)
0.600		4.58 (0.04)	11.1 (0.5)
0.700		4.73 (0.03)	9.35 (0.20)
0.775		5.00 (0.03)	7.9 (0.2)
Ammonia	0.000	15.2	30.0
	0.100	16.5 (0.5)	26.3 (0.3)
	0.200	18.0 (0.5)	23.3 (0.3)

^a c_{in} is the mole fraction of inert gas in fuel–inert gas blend, where inert gas means carbon dioxide.

^b Numbers in parentheses are experimental uncertainties.

flammable gas and one diluent gas, though the extension to other cases can easily be made as necessary. Actually, the concentration of the fuel gas L_{fuel} in the lower flammability limit mixture of the blend gas and air is given by the following equation:

$$\frac{c_1}{L_{fuel}} = \frac{c_1}{L_1} + pc_{in} \quad (3)$$

where L_1 is the lower flammability limit of the fuel gas in air, c_1 the mole fraction of the fuel gas in the fuel–inert blend,

Table 2
Measurement of fuel inertization point (FIP) and air inertization point (AIP) for eight kinds of fuels using carbon dioxide as the inert diluent

Fuel	FIP ^a		AIP ^a	
	Inert/ (fuel + inert) (%)	Fuel/ total ^b	Inert/ (air + inert) (%)	Fuel/total ^b
Methane	79.4 (1.0)	At 6.47%	27.7 (0.7)	At 6.9%
Propane	91.5 (0.5)	At 2.9%	34.1 (0.9)	At 3.3%
Ethylene	91.3 (0.4)	At 4.0%	44.0 (1.0)	At 4.0%
Propylene	90.6 (0.3)	At 3.25%	33.0 (1.0)	At 3.4%
Methyl ether	88.2 (0.2)	At 4.68%	38.3 (0.7)	At 5.1%
Methyl formate	83.3 (0.5)	At 7.1%	39.2 (0.8)	At 7.8%
1,1-Difluoroethane	83.0 (0.5)	At 6.0%	33.1 (0.5)	At 6.8%
Ammonia	25.5 (0.5)	At 20.5%	9.4 (0.4)	At 21.0%

^a “Inert” means carbon dioxide, and numbers in parentheses are experimental uncertainties.

^b “Total” means fuel plus carbon dioxide plus air.

$c_{in} = 1 - c_1$ the mole fraction of inert gas in the fuel–inert blend, and p is a parameter to be determined experimentally. Similarly, the concentration of the fuel gas U_{fuel} in the upper flammability limit mixture of the blend gas and air is given by the following equation:

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

Here, U_1 is the upper flammability limit of the fuel gas in air, n_1 the moles of oxygen consumed by 1 mol of the fuel gas in the upper flammability limit region of this fuel, and q , r , and s are parameters to be determined experimentally. The value of n_1 is estimated from the upper flammability limit concentration U_1 of the fuel gas itself in air.

At first, for comparison purpose the values of lower and upper flammability limits were, respectively, calculated using Eqs. (3) and (4) but without the correction terms. The result is shown as Calc 1 dashed lines in Figs. 1–8. For the lower flammability limits, the average absolute difference between the observed and

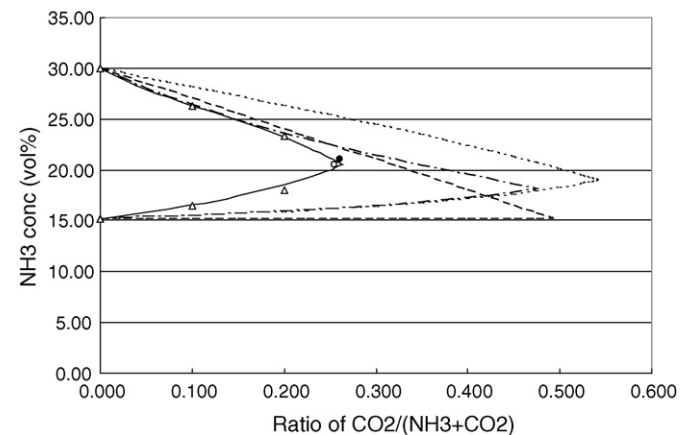


Fig. 8. Comparison between the observed and calculated values of flammability limits of ammonia–carbon dioxide blend of various compositions. (---) Calc 1; (—) Calc 2; (- · -) Calc 3; (···) Calc 4; (○) FIP; (●) AIP; (△) other observed points.

Table 3
Results of fitting procedure to observed flammability limits of fuel compounds diluted with carbon dioxide

Compounds	c_{in}^a	Obs ^b			Calc 2 fuel (vol%)	O – C2 ^c fuel (vol%)	Calc 4 fuel (vol%)	O – C4 ^c fuel (vol%)	Notes
		Fuel (vol%)	Inert (vol%)	Air (vol%)					
Methane									
L_{fuel}	0.000	4.90	0.00	95.10	4.90	0.00	4.90	0.00	
	0.200	5.05	1.26	93.69	4.98	0.07	4.97	0.08	
	0.400	5.15	3.43	91.42	5.11	0.04	5.08	0.07	
	0.600	5.35	8.03	86.63	5.40	–0.05	5.33	0.02	
	0.700	5.65	13.18	81.17	5.72	–0.07	5.60	0.05	
	0.794	6.47	24.94	68.59	6.43	0.04	6.18	0.29	FIP
U_{fuel}	0.000	15.80	0.00	84.20	15.80	0.00	15.80	0.00	
	0.200	14.06	3.52	82.43	13.96	0.10	14.12	–0.06	
	0.400	12.20	8.13	79.67	12.33	–0.13	12.40	–0.20	
	0.600	10.08	15.12	74.80	10.10	–0.02	10.10	–0.02	
	0.700	8.70	20.30	71.00	8.53	0.17	8.59	0.11	
	0.789	6.90	25.79	67.30	6.79	0.11	6.96	–0.06	AIP
0.794	6.47	24.94	68.59	6.68	–0.21	6.86	–0.39	FIP	
Propane									
L_{fuel}	0.000	2.03	0.00	97.97	2.03	0.00	2.03	0.00	
	0.200	2.02	0.51	97.48	2.04	–0.02	2.04	–0.02	
	0.250	2.02	0.67	97.31	2.05	–0.03	2.05	–0.03	
	0.400	2.03	1.35	96.62	2.07	–0.04	2.06	–0.03	
	0.600	2.07	3.11	94.83	2.11	–0.04	2.10	–0.03	
	0.750	2.14	6.42	91.44	2.20	–0.06	2.17	–0.03	
	0.850	2.24	12.69	85.07	2.38	–0.14	2.32	–0.08	
	0.915	2.90	31.22	65.88	2.83	0.07	2.67	0.23	FIP
U_{fuel}	0.000	10.00	0.00	90.00	10.00	0.00	10.00	0.00	
	0.200	9.20	2.30	88.50	9.09	0.11	9.01	0.19	
	0.250	8.90	2.97	88.13	8.92	–0.02	8.78	0.12	
	0.400	8.30	5.53	86.17	8.36	–0.06	8.02	0.28	
	0.600	7.15	10.73	82.13	7.22	–0.07	6.67	0.48	
	0.750	5.80	17.40	76.80	5.75	0.05	5.22	0.58	
	0.850	4.53	25.67	69.80	4.34	0.19	3.95	0.58	
	0.909	3.30	32.97	63.73	3.26	0.04	3.00	0.30	AIP
	0.915	2.90	31.22	65.88	3.13	–0.23	2.89	0.01	FIP
Ethylene									
L_{fuel}	0.000	2.74	0.00	97.26	2.74	0.00	2.74	–	
	0.200	2.74	0.68	96.58	2.76	–0.02	2.76	–	
	0.400	2.77	1.85	95.38	2.79	–0.02	2.80	–	
	0.600	2.83	4.25	92.93	2.86	–0.03	2.87	–	
	0.750	2.92	8.76	88.32	3.00	–0.08	3.01	–	
	0.850	3.08	17.45	79.47	3.27	–0.19	3.30	–	
	0.913	4.00	41.98	54.02	3.91	0.09	4.00	–	FIP
U_{fuel}	0.000	31.50	0.00	68.50	31.50	0.00	31.50	–	
	0.200	24.10	6.03	69.88	24.27	–0.17	27.55	–	
	0.400	18.50	12.33	69.17	18.26	0.24	23.37	–	
	0.600	12.75	19.13	68.13	12.87	–0.12	18.12	–	
	0.750	8.80	26.40	64.80	8.84	–0.04	13.06	–	
	0.850	6.03	34.17	59.80	5.97	0.06	8.95	–	
	0.913	4.00	42.24	53.76	4.00	0.00	5.90	–	AIP
	0.913	4.00	41.98	54.02	4.00	0.00	5.90	–	FIP
Propylene									
L_{fuel}	0.000	2.16	0.00	97.84	2.16	0.00	2.16	0.00	
	0.200	2.18	0.55	97.28	2.18	0.00	2.17	0.01	
	0.400	2.17	1.45	96.38	2.20	–0.03	2.19	–0.02	
	0.600	2.22	3.33	94.45	2.26	–0.04	2.24	–0.02	
	0.750	2.30	6.90	90.80	2.38	–0.08	2.32	–0.02	
	0.850	2.45	13.88	83.67	2.61	–0.16	2.49	–0.04	
	0.913	3.25	34.11	62.64	3.17	0.08	2.87	0.38	FIP
U_{fuel}	0.000	11.00	0.00	89.00	11.00	0.00	11.00	0.00	
	0.200	9.70	2.43	87.88	9.68	0.02	9.90	–0.20	

Table 3 (Continued)

Compounds	c_{in}^a	Obs ^b			Calc 2 fuel (vol%)	O – C2 ^c fuel (vol%)	Calc 4 fuel (vol%)	O – C4 ^c fuel (vol%)	Notes
		Fuel (vol%)	Inert (vol%)	Air (vol%)					
	0.400	8.80	5.87	85.33	8.75	0.05	8.78	0.02	
	0.600	7.35	11.03	81.63	7.53	–0.18	7.28	0.07	
	0.750	6.13	18.39	75.48	6.02	0.11	5.68	0.45	
	0.850	4.75	26.92	68.33	4.55	0.20	4.27	0.48	
	0.904	3.40	31.88	64.72	3.53	–0.13	3.32	0.08	AIP
	0.913	3.25	34.11	62.64	3.34	–0.09	3.14	0.11	FIP
Dimethyl ether									
L_{fuel}	0.000	3.30	0.00	96.70	3.30	0.00	3.30	–	
	0.200	3.33	0.83	95.84	3.33	0.00	3.33	–	
	0.400	3.35	2.23	94.42	3.38	–0.03	3.38	–	
	0.600	3.42	5.13	91.45	3.50	–0.08	3.49	–	
	0.700	3.51	8.19	88.30	3.61	–0.10	3.60	–	
	0.800	3.68	14.72	81.60	3.88	–0.20	3.86	–	
	0.882	4.68	34.98	60.34	4.57	0.11	4.52	–	FIP
U_{fuel}	0.000	26.20	0.00	73.80	26.20	0.00	26.20	–	
	0.200	18.00	4.50	77.50	18.17	–0.17	23.08	–	
	0.400	14.00	9.33	76.67	13.77	0.23	19.80	–	
	0.600	10.74	16.11	73.15	10.85	–0.11	15.60	–	
	0.700	9.10	21.23	69.67	9.20	–0.10	12.95	–	
	0.800	7.15	28.60	64.25	7.06	0.09	9.80	–	
	0.877	5.10	36.35	58.55	4.96	0.14	6.93	–	AIP
	0.882	4.68	34.98	60.34	4.81	–0.13	6.73	–	FIP
Methyl formate									
L_{fuel}	0.000	5.25	0.00	94.75	5.25	0.00	5.25	0.00	
	0.200	5.31	1.33	93.36	5.31	0.00	5.33	–0.02	
	0.400	5.33	3.55	91.12	5.43	–0.10	5.46	–0.13	
	0.600	5.48	8.22	86.30	5.67	–0.19	5.74	–0.26	
	0.725	5.75	15.16	79.09	6.03	–0.28	6.19	–0.44	
	0.833	7.10	35.41	57.49	6.94	0.16	7.36	–0.26	FIP
U_{fuel}	0.000	22.60	0.00	77.40	22.60	0.00	22.60	0.00	
	0.200	20.00	5.00	75.00	19.91	0.09	20.01	–0.01	
	0.400	17.10	11.40	71.50	17.19	–0.09	17.30	–0.20	
	0.600	13.50	20.25	66.25	13.57	–0.07	13.79	–0.29	
	0.725	10.75	28.34	60.91	10.54	0.21	10.90	–0.15	
	0.822	7.80	36.14	56.06	7.68	0.12	8.16	–0.36	AIP
	0.833	7.10	35.41	57.49	7.33	–0.23	7.82	–0.72	FIP
1,1-Difluoroethane									
L_{fuel}	0.000	4.32	0.00	95.68	4.32	0.00	4.32	0.00	
	0.200	4.37	1.09	94.54	4.38	–0.01	4.37	0.00	
	0.400	4.41	2.94	92.65	4.47	–0.06	4.46	–0.05	
	0.600	4.58	6.87	88.55	4.68	–0.10	4.65	–0.07	
	0.700	4.73	11.04	84.23	4.91	–0.18	4.86	–0.13	
	0.775	5.00	17.22	77.78	5.25	–0.25	5.16	–0.16	
	0.830	6.00	29.29	64.71	5.77	0.23	5.62	0.38	FIP
U_{fuel}	0.000	17.35	0.00	82.65	17.35	0.00	17.35	0.00	
	0.200	15.60	3.90	80.50	15.47	0.13	15.48	0.12	
	0.400	13.50	9.00	77.50	13.66	–0.16	13.54	–0.04	
	0.600	11.10	16.65	72.25	11.10	0.00	10.97	0.13	
	0.700	9.35	21.82	68.83	9.32	0.03	9.29	0.06	
	0.775	7.90	27.21	64.89	7.70	0.20	7.80	0.10	
	0.819	6.80	30.85	62.35	6.63	0.17	6.81	–0.01	AIP
	0.830	6.00	29.29	64.71	6.35	–0.35	6.54	–0.54	FIP
Ammonia									
L_{fuel}	0.000	15.20	0.00	84.80	15.20	0.00	15.20	–	
	0.100	16.50	1.83	81.67	16.52	–0.02	15.49	–	
	0.200	18.00	4.50	77.50	18.53	–0.53	15.86	–	
	0.255	20.50	7.02	72.48	20.17	0.33	16.12	–	FIP

Table 3 (Continued)

Compounds	c_{in}^a	Obs ^b			Calc 2 fuel (vol%)	O – C ^{2c} fuel (vol%)	Calc 4 fuel (vol%)	O – C ^{4c} fuel (vol%)	Notes
		Fuel (vol%)	Inert (vol%)	Air (vol%)					
U_{fuel}	0.000	30.00	0.00	70.00	30.00	0.00	30.00	–	
	0.100	26.30	2.92	70.78	26.32	–0.02	28.12	–	
	0.200	23.30	5.83	70.88	23.21	0.09	26.30	–	
	0.261	21.00	7.43	71.57	20.64	0.36	25.16	–	AIP
	0.255	20.50	7.02	72.48	20.93	–0.43	25.28	–	FIP
Average absolute deviation (vol%)						0.099		0.150	

Calc 2 is from accurate fitting to individual fuel compounds, and Calc 4 is for simultaneous fitting to selected five compounds.

^a c_{in} is the mole fraction of inert gas in fuel-inert blend, where inert gas means carbon dioxide.

^b Air is 100% minus “fuel” and “inert”.

^c O – C is observed value minus calculated value.

Calc 1 values is 0.49 vol% which corresponds to the average relative difference of 7.9 relative percent. For the upper flammability limits, the average absolute difference between the observed and Calc 1 values is 2.04 vol% which corresponds to the average relative difference of 27.6 relative percent. The agreement between the observed and calculated values is by no means good.

Then, the least-squares calculation was carried out for the observed data of carbon dioxide dilution effects using Eqs. (3) and (4) including the correction terms. The calculation was carried out for the individual compounds separately. The result is shown as Calc 2 solid lines in Figs. 1–8 for the eight compounds, respectively. The least-squares calculation gave a good agreement between the observed and calculated values for all compounds. Differently from the case of nitrogen dilution, the lower flammability limits also change considerably as the degree of dilution increases. Still the correction only with a linear term is workable. The alterations of upper flammability limits due to carbon dioxide dilution are larger than the ones for nitrogen dilution as well. More quantitative comparison can be made by the numerical data shown in Table 3. For the lower flammability limits, the average absolute difference between the observed and calculated values is 0.09 vol% and the average relative difference is 1.92 relative percent, which are very much smaller than 0.49 vol% and 7.9 relative percent, respectively, in the case of Calc 1. For the upper flammability limits, the average absolute difference is 0.11 vol% and the average relative difference is 1.39 relative percent, which are again much smaller than 2.04 vol% and 27.6 relative percent, respectively, for Calc 1.

In the next place, a similar calculation was carried out fitting to the observed values of flammability limits of eight compounds simultaneously. In this case, discrepancies between the observed and calculated values do not become so small. The result is shown as Calc 3 dot-dashed lines in Figs. 1–8. Incidentally, the overall average absolute deviation of the calculated values from the observed ones is 0.23 vol% and the average relative difference is 2.89 relative percent for the lower flammability limits, while for the upper flammability limits the average absolute difference is 1.23 vol% and the average relative difference is 14.6 relative percent.

In the preceding study [3], it was found that the nitrogen dilution effect on five compounds, i.e., methane, propane, propylene,

methyl formate, and 1,1-difluoroethane, were explained pretty well using a common set of parameter values. In the present study, a similar analysis was carried out for the same five compounds. The result is shown as Calc 4 dotted lines in Figs. 1–8. As seen in the figures, the observed values of these compounds are pretty well explained by this calculation. The numerical result is shown as Calc 4 in Table 3. After the analysis, the average absolute difference between the observed and calculated values is 0.10 vol% and the average relative difference is 2.27 relative percent for the lower flammability limits. Similarly, the average absolute difference became 0.19 vol% and the average relative difference became 2.96 relative percent for the upper flammability limits. Thus, the agreement between the observed and the calculated values is almost as good as in the case of Calc 2. Table 4 shows the obtained parameter values for the four different calculations.

In this way, the extended Le Chatelier’s formula can explain very well the carbon dioxide dilution effect on the flammability limits of the five compounds using a common set of parameter values. This is exactly the same as what was obtained in the case of nitrogen dilution. Introduction of the parameter values for Calc 4 into Eqs. (3) and (4) gives us the following equations:

$$\frac{c_1}{L_{fuel}} = \frac{c_1}{L_1} - 0.01094c_{in} \quad (5)$$

and

$$\frac{c_1 n_1}{100 - (U_{fuel}/c_1)} = \frac{c_1 n_1}{100 - U_1} + 0.00105c_{in} + 0.00106c_{in}^2 - 0.00156c_{in}^3 \quad (6)$$

It is possible that these equations can be used to predict with reasonable accuracy the carbon dioxide dilution effect on the flammability limits of such compounds as saturated hydrocarbons, olefinic hydrocarbons (other than ethylene), esters, and lightly fluorinated hydrocarbons.

On the other hand, ethylene, dimethyl ether, and ammonia were found to be exceptional from the general case. This is also the same as what happened in the case of nitrogen dilution. These compounds are known to have various characteristic flammability properties. Ethylene has a positive heat of formation and has a tendency to explosive decomposition. Due to this tendency, the

Table 4
Parameter values resulting from fitting calculation to flammability limits of various fuel compounds diluted with carbon dioxide

Case	Parameter values		
	p, q	r	s
(A) Methane			
L_{fuel}	$p = -0.01259$	–	–
U_{fuel}	$q = 0.00072$	0.00220	-0.00258
(B) Propane			
L_{fuel}	$p = -0.01293$	–	–
U_{fuel}	$q = 0.00093$	0.00234	-0.00269
(C) Ethylene			
L_{fuel}	$p = -0.01042$	–	–
U_{fuel}	$q = -0.00083$	0.00214	-0.00115
(D) Propylene			
L_{fuel}	$p = -0.01410$	–	–
U_{fuel}	$q = 0.00048$	0.00295	-0.00284
(E) Dimethyl ether			
L_{fuel}	$p = -0.01129$	–	–
U_{fuel}	$q = -0.00275$	0.00743	-0.00455
(F) Methyl formate			
L_{fuel}	$p = -0.00932$	–	–
U_{fuel}	$q = 0.00091$	0.00153	-0.00214
(G) 1,1-Difluoroethane			
L_{fuel}	$p = -0.01190$	–	–
U_{fuel}	$q = 0.00092$	0.00185	-0.00242
(H) Ammonia			
L_{fuel}	$p = -0.04733$	–	–
U_{fuel}	$q = -0.00167$	0.01367	-0.03618
(I) Eight compounds together			
L_{fuel}	$p = -0.01148$	–	–
U_{fuel}	$q = -0.00111$	0.00536	-0.00401
(J) Selected five compounds A, B, D, F, G			
L_{fuel}	$p = -0.01094$	–	–
U_{fuel}	$q = 0.00105$	0.00106	-0.00156

upper flammability limit of ethylene is considered to be much extended than what is expected from the heat of combustion. Dilution with inert gas may decrease this tendency. This must be the main cause of the discrepancy of the ethylene behavior from the general case. Dimethyl ether has a tendency to support cool flames, which may also extend the upper flammability limit beyond the value expected from its heat of combustion. This tendency may also be weakened as the degree of dilution increases. On the other hand, ammonia is an inorganic compound and has very weak flammability. There is no wonder that ammonia has a different flammability property from the ordinary organic flammable gases.

In summary, the present result together with that of nitrogen dilution effect obtained in the preceding study [3] strongly suggests that the dilution effects on the flammability limits of a wide variety of compounds such as saturated hydrocarbons, olefinic hydrocarbons (other than ethylene), lightly fluorinated compounds, and ester compounds can be explained by Eqs. (3) and (4) using a common set of parameter values for each diluent gas.

4. Conclusion

The flammability limits of eight compounds, i.e., methane, propane, ethylene, propylene, dimethyl ether, methyl formate, 1,1-difluoroethane, and ammonia, diluted with carbon dioxide at various levels were measured carefully. The obtained data were analyzed using Eqs. (3) and (4), which are the extended forms of Le Chatelier's formula. At first, the data of individual compounds were analyzed separately. The observed data were explained very well by the equations. Then, the carbon dilution effects on five compounds, i.e., methane, propane, propylene, methyl formate, and 1,1-difluoroethane, were analyzed together using a common set of parameter values. The result is that again a pretty good agreement was obtained between the observed and calculated values. This result together with a similar result obtained for the nitrogen dilution in a previous study strongly suggests that the dilution effects on the flammability limits of a wide variety of compounds can be explained by Eqs. (3) and (4) using a common set of parameter values for each diluent gas.

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