



Short communication

On the temperature dependence of flammability limits of gases

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ABSTRACT

Flammability limits of several combustible gases were measured at temperatures from 5 to 100 °C in a 12-l spherical flask basically following ASHRAE method. The measurements were done for methane, propane, isobutane, ethylene, propylene, dimethyl ether, methyl formate, 1,1-difluoroethane, ammonia, and carbon monoxide. As the temperature rises, the lower flammability limits are gradually shifted down and the upper limits are shifted up. Both the limits shift almost linearly to temperature within the range examined. The linear temperature dependence of the lower flammability limits is explained well using a limiting flame temperature concept at the lower concentration limit (LFL) – ‘White’s rule’. The geometric mean of the flammability limits has been found to be relatively constant for many compounds over the temperature range studied (5–100 °C). Based on this fact, the temperature dependence of the upper flammability limit (UFL) can be predicted reasonably using the temperature coefficient calculated for the LFL. However, some compounds such as ethylene and dimethyl ether, in particular, have a more complex temperature dependence.

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1. Introduction

The experimental flammability limits are more or less dependent upon the apparatus and condition with which they are measured [1–4]. Recently, American Society of Heating, Refrigerating, and Air-conditioning Engineers (ASHRAE) [5,6] proposed a modification of ASTM E-681 method in order to measure the flammability limits of combustible refrigerants. They recommend using a 12-l spherical vessel instead of 5 l one. In addition their criterion for flame propagation has been so determined that the resulting values of flammability limits of methane and propane coincide with the values measured using jumbo vessels [2,7,8]. This indicates that the values obtained by this method are valid in large industrial vessels or in open space.

Indeed, the flammability limits are dependent upon the experimental condition such as temperature and pressure as well [1]. Recently, we have done some study on the pressure dependence of flammability limits of a few compounds [9]. As for temperature, it is known that the flammable range becomes wide if the temperature is raised: the lower limit becomes lower and the upper limit becomes higher. There are some data of temperature dependence of flammability limits such as reported in the literature [1]. In connection with the temperature dependence of flammability limits, White reported that the limit flame temperature is kept constant independently of the experimental temperature [10]. If it is the

case, the lower flammability limits change linearly to temperature [11–13]. Among others, Zabetakis investigated systematically to demonstrate the linear temperature dependence of lower flammability limits of saturated hydrocarbons [12]. Recently, Ciccarelli et al. investigated the flammability limits of ammonia-hydrogen mixture at elevated initial temperatures [14]. It is of particular interest to know whether the upper flammability limits of various compounds behave similarly to lower flammability limits.

In this paper, we report the result of measurement and analysis of temperature dependence of upper and lower flammability limits for various combustible gases. ASHRAE method mentioned in the above is suitable for the present purpose because it can accurately detect small shifts of flammability limits resulting from the temperature change.

2. Experiments

The measurement system of flammability limits is the same as in our previous studies [15–17], which basically follows the ASHRAE method [5,6]. Fig. 1 shows a schematic diagram of the experimental setup. 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 ASHRAE method the flange is held on the top by spring-loaded clamps. The vessel is connected to a soda lime tower 15 cm in diameter and 35 cm in height through a plastic tube 3/8-inch (0.95 cm) in diameter and approximately 100 cm in length.

The 12-l spherical glass flask was placed in an air-bath to hold at a certain temperature between 20 and 100 °C. The temperature of the head part of the vessel, which was out above the air-bath

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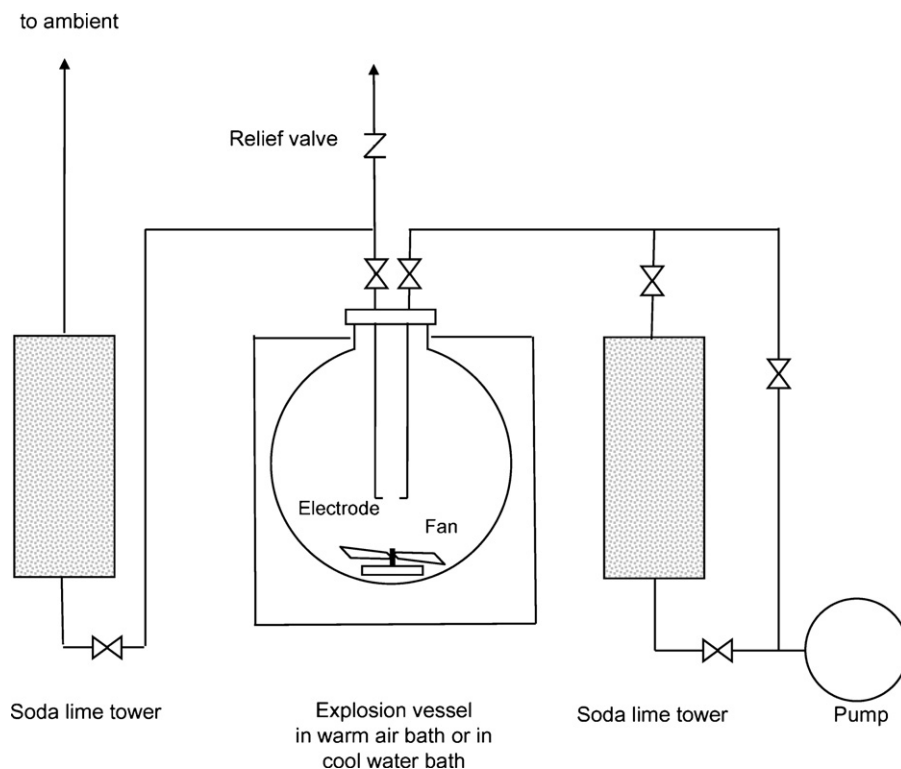


Fig. 1. Schematic diagram of experimental setup.

ceiling, was kept at the same level of temperature using a ribbon heater. The air in the air-bath was circulated continuously to keep the temperature constant. In addition, the fan to stir the gas mixture inside the vessel helped to secure the homogeneity of temperature inside the vessel. For the measurement at 5 °C, the flask was set in a cool water bath. We believe that the accuracy and homogeneity of temperature control is better than 2 °C.

For the measurement, gas mixture was 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). The fuel gas was introduced into the vessel first followed by air. Two kinds 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 eight minutes, left to settle for one minute, and balanced with the ambient pressure by opening the valve leading to the soda-lime tower just before ignition. The valve was kept open during and after the ignition. In case this cannot relieve the explosion pressure quickly enough, the vessel is equipped with a relief valve of 1/2-inch (1.27 cm) diameter set at 5 psi (34.5 kPa) relief pressure.

The vessel is equipped with a pair of tungsten electrodes for AC electric discharge, whose ends were pointed and set 1/4 inch (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 sec. This corresponds to ignition energy of approximately 10 J. This was roughly estimated by recording the electric current and voltage between the electrodes during the discharge. 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 of 90° as measured from the point of ignition.

The flammability limits of methane, propane, isobutane, ethylene, propylene, methyl ether, methyl formate, 1,1-difluoroethane

(HFC-152a), ammonia, and carbon monoxide were measured at temperatures from 5 to 100 °C. Sample gases were purchased from Chemical companies. Purities of sample gases were 99% or better except for methyl formate. Purity of methyl formate was at least 98%. The compressed air used was extra-pure and dry. All sample materials were used without further purification.

3. Results and discussion

Since the temperature range examined was relatively narrow, it was necessary to detect subtle changes in flammability limits accurately. As stated, ASHRAE method is suitable for the present purpose. The result of flammability limit measurement is summarized in Table 1. The uncertainties given to the observed numbers were estimated considering the stability and the gradient of the plot of maximum flame propagation angle versus fuel concentration in air.

It has been found that the values of both upper and lower flammability limits change moderately and almost linearly to temperature, i.e. as the temperature is raised the lower flammability limits shift to lower concentrations and the upper limits to higher concentrations. The linear regression analysis was made for each of the lower and upper flammability limits of the individual compounds. The result for the lower flammability limits is summarized in Table 2 and the one for the upper limits in Table 3.

Now, according to a limiting flame temperature concept (White's rule) [10], the heat required to warm one mole of unburnt mixture from 25 to t °C is equal to the difference of the heats of combustion per mole of unburnt mixture between 25 and t °C. Then, if the temperature is raised from 25 to t °C, the lower flammability limit L at temperature t is expressed as follows.

$$L = L_{25} - \frac{100C_{p,L}}{Q}(t - 25) = L_{25} \left\{ 1 - \frac{100C_{p,L}}{L_{25} \cdot Q}(t - 25) \right\} \quad (1)$$

Table 1
Observed values of flammability limits at various temperatures for various compounds.

Compound	Temp °C	L		U		G
		vol%	±	vol%	±	vol%
Methane	5	5.00	0.10	15.50	0.10	8.80
	21	4.95	0.10	15.70	0.1	8.82
	35	4.94	0.06	15.82	0.10	8.84
	50	4.88	0.10	16.00	0.1	8.84
	75	4.74	0.10	16.20	0.10	8.76
	100	4.70	0.06	16.50	0.10	8.81
Propane	5	2.07	0.02	9.7	0.3	4.48
	20	2.05	0.02	9.8	0.4	4.48
	35	2.02	0.02	9.81	0.30	4.45
	50	1.99	0.02	9.90	0.30	4.44
	75	1.96	0.02	9.97	0.20	4.42
	100	1.92	0.02	10.04	0.30	4.39
Iso-butane	5	1.698	0.01	7.8	0.4	3.64
	20	1.68	0.01	7.9	0.5	3.64
	35	1.67	0.01	7.66	0.4	3.57
	50	1.63	0.01	7.86	0.30	3.58
	75	1.61	0.01	7.78	0.20	3.54
	100	1.58	0.01	8.05	0.30	3.57
Ethylene	5	2.77	0.03	30.1	0.8	9.13
	20	2.75	0.020	30.5	1.0	9.15
	35	2.72	0.02	30.8	0.8	9.15
	50	2.68	0.02	31.4	0.8	9.17
	75	2.62	0.03	32.4	0.8	9.21
	100	2.57	0.02	34.0	0.8	9.35
Propylene	5	2.21	0.03	10.1	0.3	4.72
	20	2.18	0.010	10.3	0.3	4.74
	35	2.17	0.02	10.5	0.5	4.77
	50	2.15	0.015	10.4	0.4	4.72
	75	2.09	0.015	10.5	0.3	4.68
	100	2.05	0.015	10.7	0.3	4.68
Dimethyl ether	5	3.37	0.03	23.40	0.8	8.88
	20	3.35	0.05	25.20	0.7	9.19
	35	3.30	0.10	25.90	0.7	9.24
	50	3.23	0.02	27.10	0.7	9.36
	75	3.17	0.02	29.50	1.0	9.67
	100	3.10	0.03	31.00	1.0	9.80
Methyl formate	5	5.36	0.03	22.7	0.5	11.03
	20	5.30	0.05	22.4	0.4	10.90
	35	5.23	0.03	22.9	0.5	10.94
	50	5.15	0.03	23.3	0.4	10.95
	75	5.07	0.03	23.6	0.5	10.94
	100	4.95	0.04	24.0	0.5	10.90
HFC-152a	5	4.43	0.03	17.20	0.5	8.73
	20	4.39	0.03	17.20	0.4	8.69
	35	4.29	0.03	17.3	0.5	8.61
	50	4.26	0.03	17.5	0.5	8.63
	75	4.16	0.02	17.7	0.5	8.58
	100	4.07	0.02	18.0	0.5	8.56
Ammonia	5	15.6	0.3	29.3	0.2	21.38
	20	15.5	0.2	29.55	0.20	21.40
	35	15.4	0.4	30.0	0.3	21.49
	50	15.2	0.3	30.2	0.2	21.43
	75	15.0	0.2	30.7	0.2	21.46
	100	14.8	0.2	31.15	0.15	21.47
Carbon monoxi	5	12.67	0.20	72.04	0.15	30.21
	20	12.3	0.2	72.7	0.2	29.90
	35	12.16	0.20	73.1	0.1	29.81
	50	12.0	0.2	73.47	0.10	29.69
	75	11.8	0.2	74.2	0.2	29.59
	100	11.5	0.2	75.0	0.2	29.37

Here, L_{25} is the lower flammability limits (vol%) at 25 °C, $C_{p,L}$ is the heat capacity of unburnt gas at lower flammability limit at 25 °C, and Q is the molar heat of combustion of the fuel gas. $C_{p,L}$ and Q were assumed to be constant in the temperature range from 5 to 100 °C. The predicted values of temperature coefficient in Table 2 were obtained based on this equation, where the thermochemical data listed in Table 4 were used. As shown in Table 2, agreement between the observed and predicted values of temperature coefficient is generally very good. In the last column of this table, the

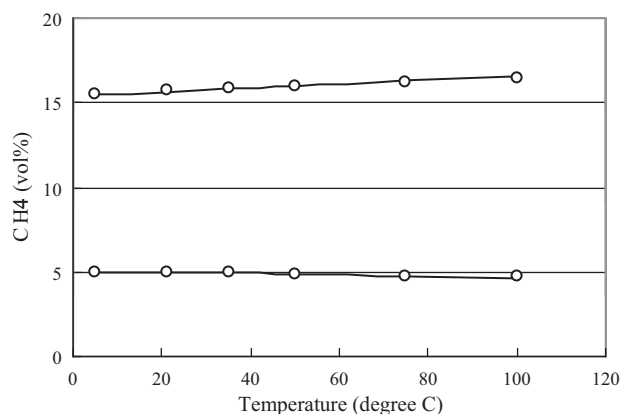


Fig. 2. Temperature dependence of flammability limits for methane, where white circles represent the observed values and solid lines for the lower and upper flammability limits are the values predicted by Eqs. (1) and (3), respectively.

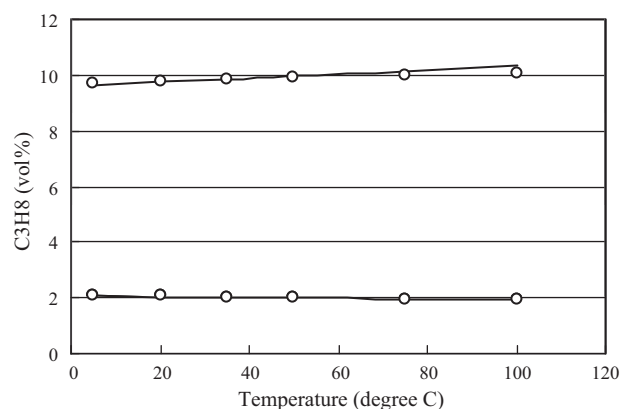


Fig. 3. Temperature dependence of flammability limits for propane, where white circles represent the observed values and solid lines for the lower and upper flammability limits are the values predicted by Eqs. (1) and (3), respectively.

values of average absolute deviation between the observed and predicted values of lower flammability limits are shown. As for the individual observations, comparison of the predicted values with the observed ones can be seen in Figs. 2–11, where open circles show the observed values and solid line (for the lower flammability limit) shows the predicted values using Eq. (1). Agreement between the observed and predicted values is excellent. The present result confirms the utility of Eq. (1) for the lower flammability limits.

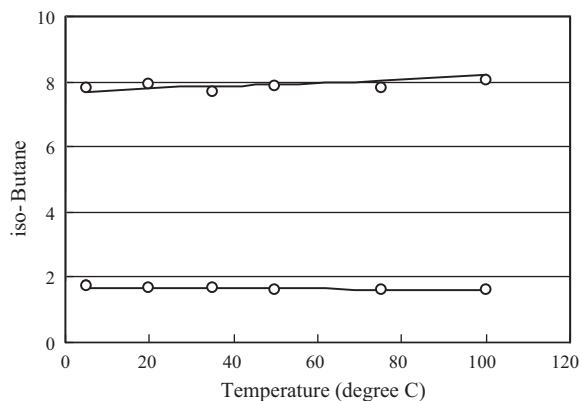


Fig. 4. Temperature dependence of flammability limits for iso-butane, where white circles represent the observed values and solid lines for the lower and upper flammability limits are the values predicted by Eqs. (1) and (3), respectively.

Table 2
Temperature dependence of lower flammability limits of various compounds. Observed and predicted values.

Compound	Regression analysis of observed values				Predicted coefficient		
	at 25 °C	s.d.	Coeff.	s.d.	Pred	Obs/Pred	Av.abs.dev.
Methane	4.95	0.02	−0.0034	0.0003	−0.0037	0.92	0.02
Propane	2.04	0.00	−0.0016	0.0001	−0.0015	1.06	0.01
Isobutane	1.67	0.00	−0.0012	0.0001	−0.0011	1.09	0.01
Ethylene	2.73	0.00	−0.0022	0.0001	−0.0022	0.97	0.01
Propylene	2.18	0.01	−0.0017	0.0001	−0.0016	1.09	0.01
Dimethyl ether	3.32	0.01	−0.0030	0.0002	−0.0023	1.31	0.02
Methyl formate	5.27	0.01	−0.0043	0.0001	−0.0034	1.27	0.03
1,1-Difluoroetha	4.35	0.01	−0.0038	0.0002	−0.0028	1.36	0.04
Ammonia	15.45	0.02	−0.0087	0.0004	−0.0095	0.92	0.03
Carbon monoxide	12.33	0.06	−0.0113	0.0010	−0.0103	1.10	0.07

Table 3
Temperature dependence of upper flammability limits of various compounds. Observed and predicted values.

Compound	Regression analysis of observed values				Predicted coefficient (1)			Predicted coefficient (2)		
	at 25 °C	s.d.	Coeff.	s.d.	Pred	Obs/Pred	Av.abs.dev.	Pred	Obs/Pred	Av.abs.de
Methane	15.72	0.02	0.0102	0.0003	0.0358	0.29	0.78	0.0117	0.88	0.05
Propane	9.79	0.02	0.0035	0.0003	0.0391	0.09	1.10	0.0071	0.49	0.11
Isobutane	7.80	0.09	0.0019	0.0016	0.0401	0.05	1.23	0.0053	0.35	0.16
Ethylene	30.63	0.22	0.0403	0.0039	0.0363	1.11	0.21	0.0249	1.62	0.38
Propylene	10.30	0.07	0.0053	0.0012	0.0365	0.14	0.94	0.0074	0.71	0.10
Dimethyl ether	25.23	0.21	0.0794	0.0037	0.0412	1.93	1.20	0.0174	4.56	1.89
Methyl formate	22.81	0.12	0.0156	0.0021	0.0395	0.40	0.75	0.0146	1.07	0.13
1,1-Difluoroetha	17.28	0.05	0.0089	0.0009	0.0391	0.23	0.95	0.0112	0.79	0.10
Ammonia	29.71	0.04	0.0196	0.0007	0.0351	0.56	0.45	0.0183	1.07	0.07
Carbon monoxide	72.74	0.06	0.0300	0.0011	0.0246	1.22	0.20	0.0612	0.49	0.96

On the other hand, in the upper flammability limit region, the heat of combustion per mole of fuel gas should be very different from the ones for complete combustion. Moreover, when the fuel concentration is increased in this region, the apparent heat of combustion per mole of fuel gas decreases and the combustion power is drastically reduced. Therefore, the assumption of constant heat of combustion per mole of fuel gas is not usable anymore in the upper flammability limit region. Instead, assumption of a constant heat of combustion per mole of oxygen could be considered. The predicted values (Pred1) of temperature coefficient for the upper flammability limits in Table 3 were obtained based on the assumption that the heat of combustion per mole of oxygen for complete combustion is applicable to the upper flammability limit region. However, as is shown in the entries in eighth column of Table 3, the average absolute difference between the observed and predicted ones are much larger than experimental uncertainties listed in Table 1.

As for the temperature dependence of flammability limits, the upper limit U and the lower limit L generally change in reverse fashion to each other. In this sense, the temperature dependence of geometric mean G of both limits is interesting, where G is defined as follows:

$$G = \sqrt{UL} \quad (2)$$

Now, a linear regression analysis was carried out for the temperature dependence of geometric mean G fitting to the observed data of flammability limits. The result is shown in Table 5. For most of the compounds treated in this study the temperature dependence of G has been found to be negligibly small, and the value stays almost constant in the experimental range of 5–100 °C. Actually the stability of G value against temperature is particularly noted for compounds like methane, propane, isobutane, propylene, methyl formate, and 1,1-difluoroethane. Deviation from the constancy is

Table 4
Thermochemical data used to obtain the predicted values of temperature coefficients of flammability limits in Tables 2 and 3.^a

Compounds	Heat of formation (kJ/mol)	Heat of combustion (kJ/mol)	Heat capacity J/(K mol)
Nitrogen	0.0	–	29.13
Oxygen	0.0	–	29.36
79N ₂ + 21O ₂	0.0	–	29.17
Carbon dioxide	−393.5	–	37.11
Water (gas)	−241.8	–	33.58
Hydrogen fluoride	−271.1	–	29.13
Carbonyl fluoride	−634.7	–	46.82
Methane	−74.8	802	35.31
Propane	−104.5	2043	73.51
Isobutane	−134.5	2649	96.82
Ethylene	52.3	1323	43.56
Propylene	20.2	1926	63.89
Dimethyl ether	−184.05	1328	64.39
Methyl formate	−350.2	920	67.74
1,1-Difluoroethane	−478.2	1093	67.80
Ammonia	−46.1	317	35.06
Carbon monoxide	−110.5	283	29.14

^aThe data of inorganic compounds are from Ref. [18]. For organic compounds, heat of formation are from Ref. [19], and heat capacity from Ref. [20]. The data of heat of combustion were calculated from the heat of formation.

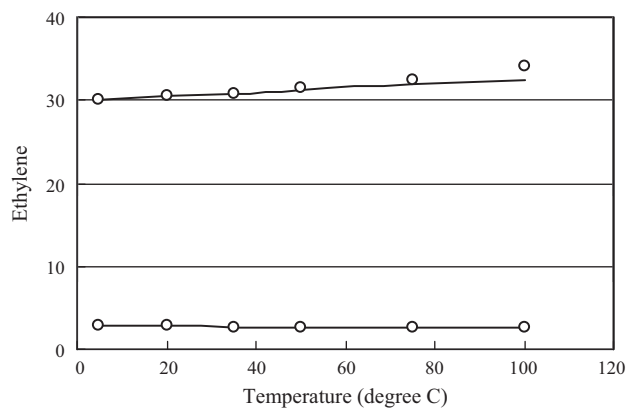


Fig. 5. Temperature dependence of flammability limits for ethylene, where white circles represent the observed values and solid lines for the lower and upper flammability limits are the values predicted by Eqs. (1) and (3), respectively.

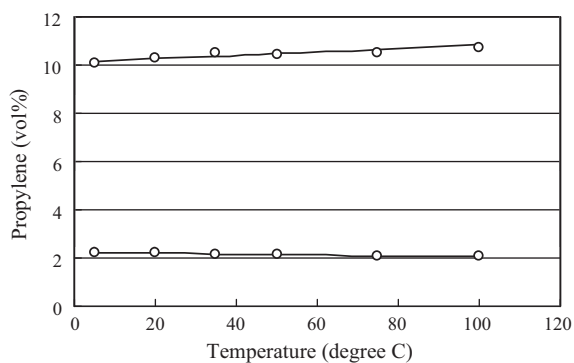


Fig. 6. Temperature dependence of flammability limits for propylene, where white circles represent the observed values and solid lines for the lower and upper flammability limits are the values predicted by Eqs. (1) and (3), respectively.

noted for such compounds as ethylene, dimethyl ether, and carbon monoxide. Ethylene is known for its tendency to thermal decomposition and dimethyl ether for its cool flame phenomenon both at high concentrations. Carbon monoxide may have too wide a flammable range to maintain a constant G value against temperature.

For ordinary compounds, Eq. (1) together with an assumption that the geometric mean G is independent of temperature can be used to predict the temperature dependence of upper flammability

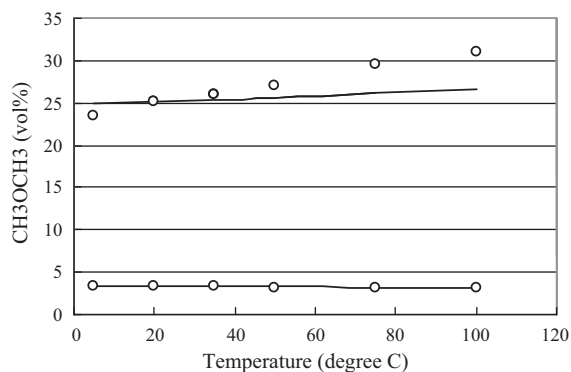


Fig. 7. Temperature dependence of flammability limits for dimethyl ether, where white circles represent the observed values and solid lines for the lower and upper flammability limits are the values predicted by Eqs. (1) and (3), respectively.

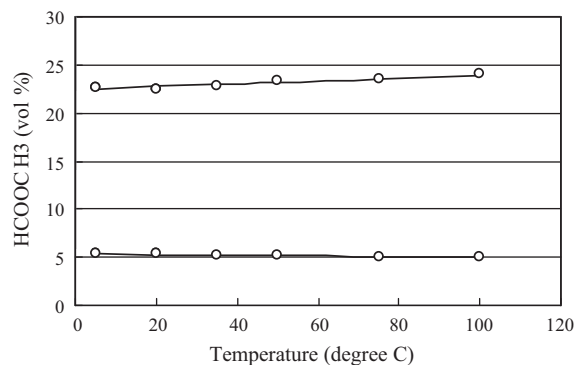


Fig. 8. Temperature dependence of flammability limits for methyl formate, where white circles represent the observed values and solid lines for the lower and upper flammability limits are the values predicted by Eqs. (1) and (3), respectively.

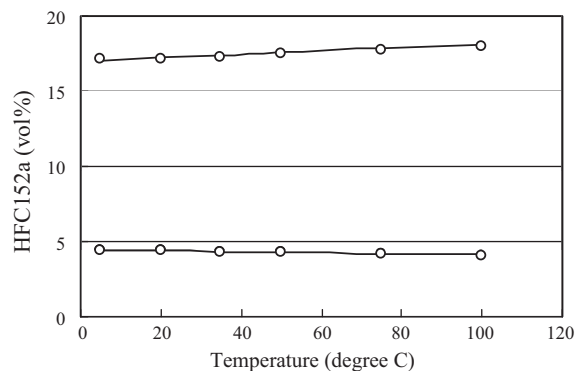


Fig. 9. Temperature dependence of flammability limits for HFC-152a, where white circles represent the observed values and solid lines for the lower and upper flammability limits are the values predicted by Eqs. (1) and (3), respectively.

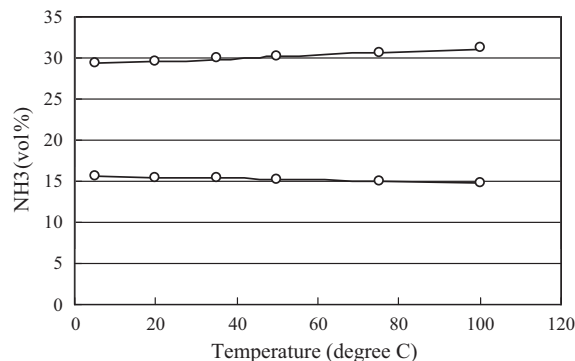


Fig. 10. Temperature dependence of flammability limits for ammonia, where white circles represent the observed values and solid lines for the lower and upper flammability limits are the values predicted by Eqs. (1) and (3), respectively.

Table 5
Temperature dependence of geometric mean G for various compounds.

Compound	Geometric mean G			
	Intercept at 25 °C		Temperature Coeff.	
	Observed	s.d.	Observed	s.d.
Methane	8.82	0.02	-0.0003	0.0004
Propane	4.47	0.01	-0.0010	0.0001
Isobutane	3.61	0.02	-0.0009	0.0004
Ethylene	9.15	0.03	0.0021	0.0005
Propylene	4.74	0.02	-0.0007	0.0003
Dimethyl ether	9.14	0.05	0.0094	0.0009
Methyl formate	10.97	0.03	-0.0009	0.0005
1,1-Difluoroetha	8.67	0.02	-0.0017	0.0003
Ammonia	21.42	0.03	0.0008	0.0005
Carbon monoxide	29.94	0.06	-0.0079	0.0010

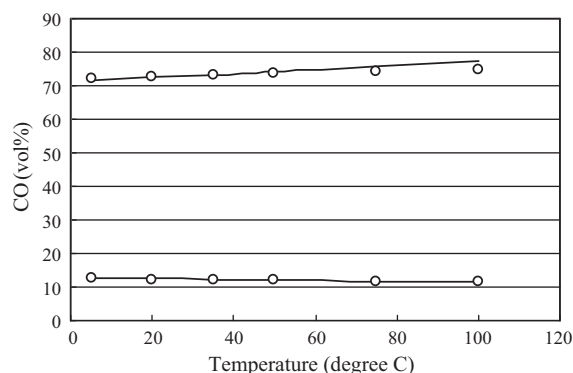


Fig. 11. Temperature dependence of flammability limits for carbon monoxide, where white circles represent the observed values and solid lines for the lower and upper flammability limits are the values predicted by Eqs. (1) and (3), respectively.

limits. By use of Eq. (1), we may obtain the following equation.

$$U = \frac{U_{25} \cdot L_{25}}{L} = \frac{U_{25}}{1 - (100C_{p,L}/L_{25} \cdot Q)(t - 25)}$$

$$\approx U_{25} \left\{ 1 + \frac{100C_{p,L}}{L_{25} \cdot Q} (t - 25) \right\} \quad (3)$$

Comparison of this equation with Eq. (1) shows that except for the sign the temperature coefficient of the relative value of upper flammability limit against the one at 25 °C is the same as for the lower limit. This result may also give support to a suggestion made by Zabetakis that the heat production at the upper flammability limit is about the same as the one at the lower flammability limit [12]. The predicted values (Pred2) of temperature coefficients for the upper flammability limits in Table 3 were obtained using Eq. (3). The average absolute differences between the observed and predicted ones are shown in eleventh column of Table 3. Except for ethylene, dimethyl ether, and carbon monoxide, they are definitely smaller than the corresponding ones for Pred1 (eighth column in Table 3). Although the values are larger than the ones for lower flammability limits, they remain about the order of or even smaller than the experimental uncertainties (see Table 1). In Figs. 2–11, the predicted values (Pred2) are visually compared with the observed ones, where open circles show the observed values and solid line for upper flammability limit shows the predicted values.

As mentioned in the above, deviation from the prediction is noted for ethylene, dimethyl ether, and carbon monoxide. Ethylene is an endothermic compound and is known for its tendency to thermal decomposition. It is possible that this tendency is enhanced at higher temperatures to pull up further the upper flammability limit. On the other hand, dimethyl ether has a tendency to support cool flames. It is known that the increase of initial temperature enhances this tendency, which may raise the upper flammability limit of this compound as well. Carbon monoxide may have too wide a flammable range to apply the present prediction scheme.

4. Conclusion

The flammability limits were measured at various temperatures between 5 and 100 °C for ten compounds. As a result, the linear temperature dependence of lower flammability limits has been found

to be predicted adequately using a limiting flame temperature concept that is constant independent of the experimental temperature [10]. In addition, for compounds like methane, propane, isobutane, propylene, methyl formate, and 1,1-difluoroethane, a limiting flame temperature concept together with an assumption that the geometric mean G is independent of temperature enables one to predict reasonably well the temperature dependence of upper flammability limits at least in the temperature range examined. However, deviation from this predicted temperature dependence is noted for the upper flammability limits of ethylene, dimethyl ether, and carbon monoxide. It should be mentioned, however, that ethylene and dimethyl ether have special burning characteristics at high concentrations. In addition, the flammable range of CO may be too wide to apply the present model to the upper flammability limit.

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