FLAMMABILITY LIMITS OF THE SYSTEM CH_3Cl—CH_2Cl_2—HCl—Cl_2

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Summary

In this paper, experimental work to determine flammability limits of the four-component system CH_3Cl—CH_2Cl_2,—HCl—Cl_2 is reported. The limit determinations were carried out at atmospheric pressure and at temperatures of 20÷30°C in a 50-mm internal-diameter vertical flame tube. The temperature of 30°C was needed to prevent condensation of methylene chloride from the gaseous mixture. The results show an irregular rich-flammability limit. The limits agree well with the literature data for two-component systems. Measurements of flammability limits at higher temperatures and pressures will be carried out in the near future.

Introduction

Thermal chlorination of methane and methyl chloride is a reaction that is carried out commercially at large scale in the chemical industry. Both from experimental work and factory incidents it is known that mixtures of methane or methyl chloride and chlorine can explode and even detonate [1—5].

Surprisingly, little or no work has been published concerning the flammability limits of these systems. The only published data originate from Russian investigations [2—4]. This lack of data has motivated the present work — both experimental and theoretical — on the flammability and reactivity of chlorine-containing systems.

The reported experiments form a part of a larger study covering a range of techniques from flame tube and bomb work to detonation experiments, determination of ignition temperatures, burning velocities and quenching diameters. In the present work the flammability limits of the four-component system methyl chloride—methylene chloride—hydrogen chloride—chlorine are reported.

Experimental

Apparatus

The experimental apparatus consisted of a vertical flame tube with an inner diameter of 50 mm and a length of 1500 mm, the same in principle as the tube

described in Bulletin 503 of the Bureau of Mines. The tube was closed to the atmosphere during preparation of the mixture to be tested and was opened at the bottom just before testing (Fig. 1). The gases were metered with rotameters and mixed in an inlet tube. The operating pressure of the rotameters was fixed by means of an H_2SO_4 column of constant height. Methylene chloride, being a liquid (B.Pt. 39.8°C) was continuously pumped into an evaporator by means of a double acting injection pump (pulse-free) which allowed flows from 0.05 up to 9 ml/min.
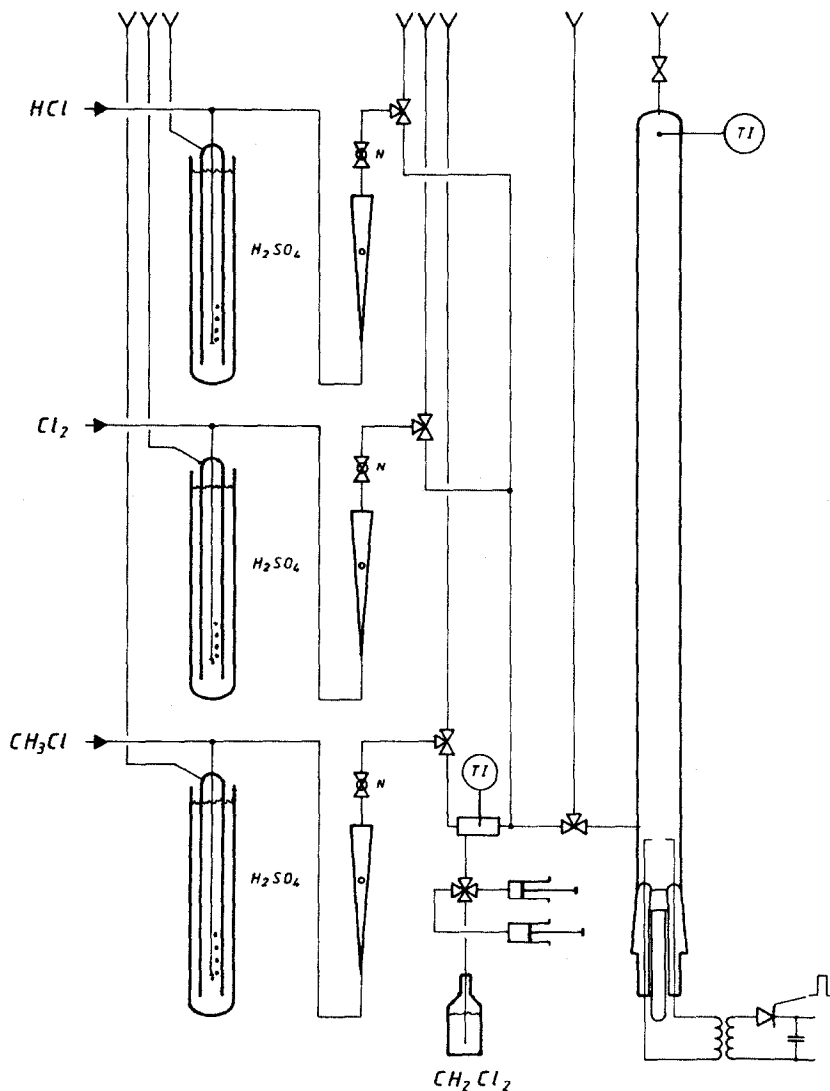

Fig. 1. Schematic experimental set up.

The ignition source used was a capacitor discharge over an automotive transformer, the secondary coil of which was connected to the electrodes. All the tests were carried out with this ignition source. The spark energy, measured on the secondary side of the transformer, was approx. 3.5 J for the spark gap used (approx. 3 mm.).

Procedure

The gas and liquid flows were adjusted to a total gas flow of 5 l/min. The mixture was fed through the flame tube for fifteen minutes from the bottom to the top in a completely dark laboratory (except for some signal lights on the apparatus). After the filling period, the gas flow was by-passed and the flame tube was then closed at the top and opened at the bottom. The diameter of the hole was approximately 10 mm, with a length of approximately 50 mm to prevent mixing with the surrounding air. The opening of the flame tube and closing of a polycarbonate shield was immediately followed by an ignition attempt. In later measurements the lower end of the tube was changed to make complete opening of the tube possible prior to, or just after, the ignition (see Fig. 2).

The mixture was considered flammable when the flame travelled the full length of the tube. This was detected by a Pt/Pt 10% Rh open-ended thermocouple at the top of the flame tube. If the flame quenched before having travelled the full length of the tube, or the mixture did not ignite in twenty
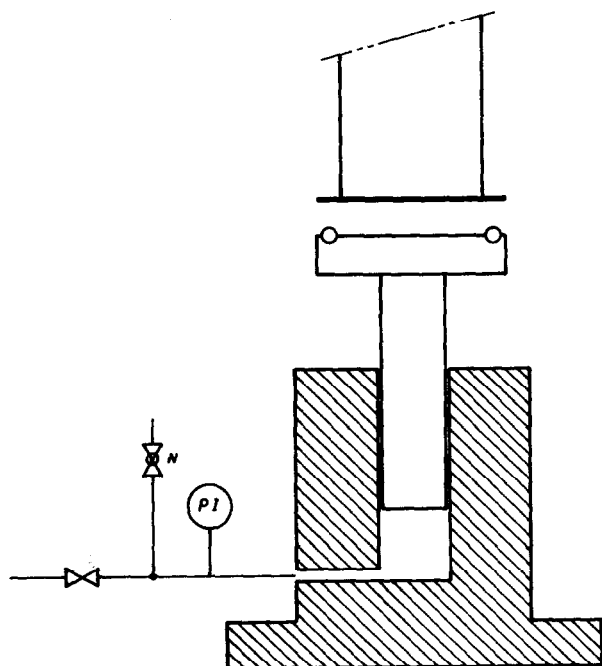
Fig. 2. Schematic pneumatic closing system.

attempts, the mixture was noted to be non-flammable. The flame often travelled 0.5 to 1 meter and then quenched, especially in limit mixtures.

Due to the termination reaction of chlorine radicals with oxygen, care was taken to prevent oxygen leaks into the apparatus. Some minor influence of oxygen can be noted, especially on the upper limit.

The dissociation of chlorine into chlorine radicals is greatly enhanced by irradiation, especially in the visible and ultraviolet region. Light, therefore, can lead to chlorination that first produces methylene chloride plus hydrogen chloride (a well known radical reaction) and in this manner causes a higher percentage of inert components and a less reactive fuel being formed during the filling period and the time prior to ignition. To prevent this pre-reaction, which markedly decreases the reactivity of the mixture, the flammability measurements were performed in a completely darkened laboratory.

Analysis and accuracy

The composition of the mixtures is easily calculated from the component flows, but analysis of these mixtures is difficult due to the reactivity of the system. In the gas chromatograph chlorination of the column occurred. A
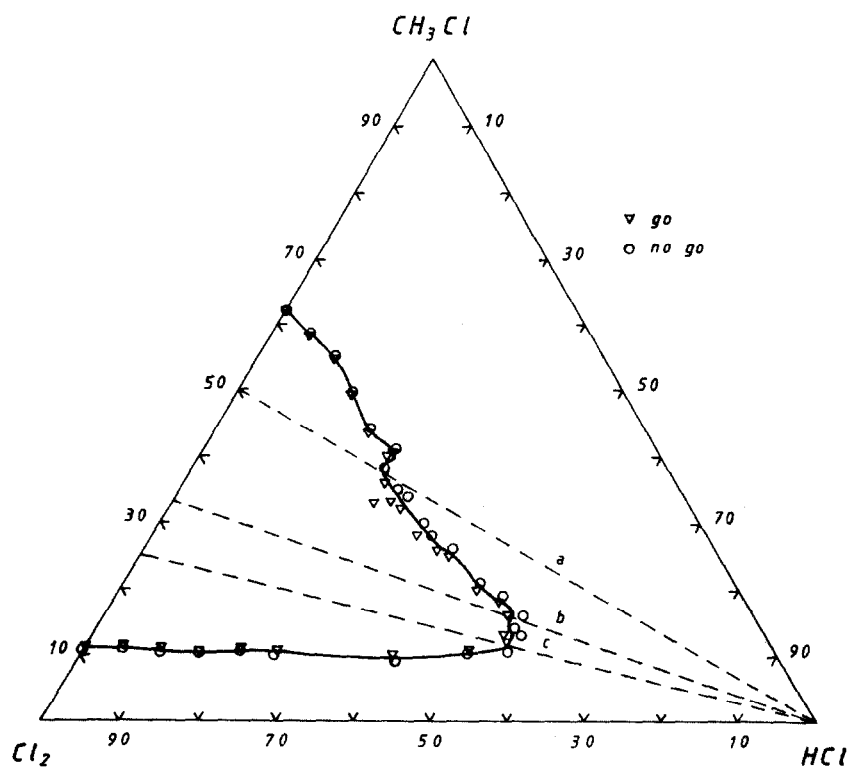

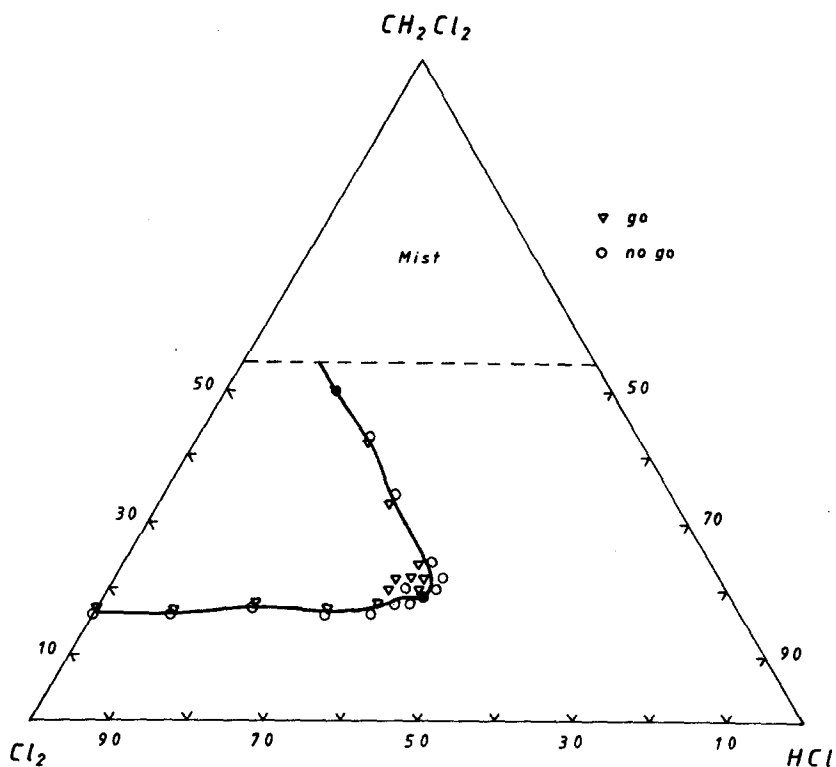Fig. 3. Flammability limits of the system CH_3Cl—Cl_2—HCl at room temperature and atmospheric pressure.

Fig. 4. Flammability limits of the system CH$_2$Cl$_2$—Cl$_2$—HCl at 293—303 K and atmospheric pressure.

sample had to be withdrawn from the apparatus in nearly complete darkness and the syringe used was painted black. The chlorine content cannot be determined by infra-red analysis, but the ratios and the absolute quantities of the other components are easily found. The analytical results confirm the calculated compositions within approximately 1% absolute at the lower limit and approximately 3% relative at the upper limit. In the diagrams, the calculated values are presented as their reproducibility was good (within ± 0.2% absolute).

The accuracy of the limit determinations (i.e. the distance between flammable and non-flammable compositions) varies, but is in general 1% and in some cases 0.25%. The total inaccuracy of the determined limits will not exceed a 5% relative error.

Results

The results of the limit determinations, carried out at atmospheric pressure and in the temperature range 20°C to 30°C, are presented graphically in Figs. 3—6. The temperature of 30°C was the limit of ambient conditions for testing

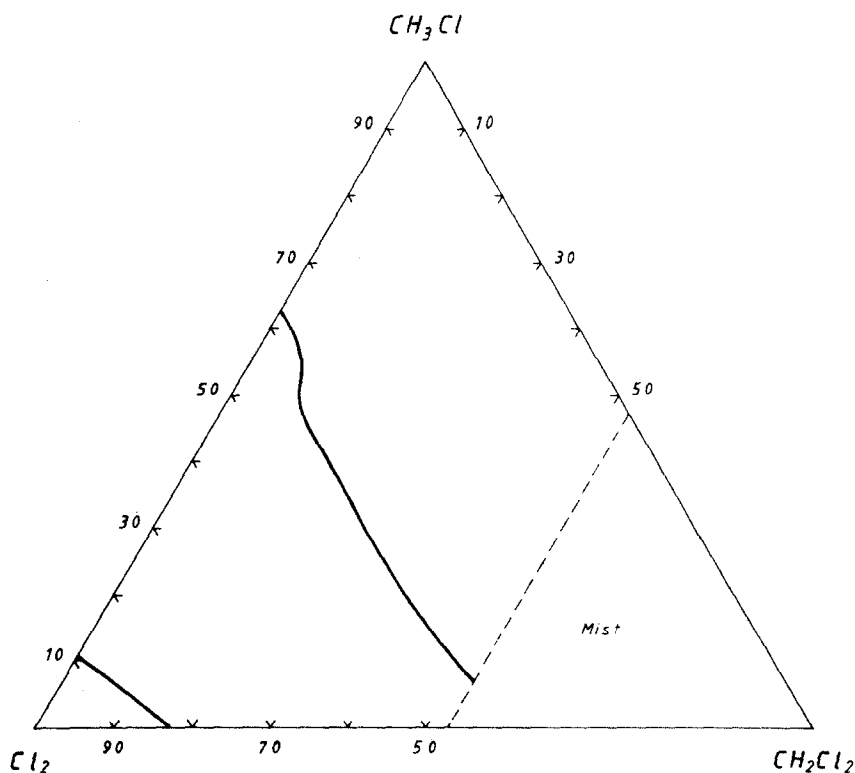Fig. 5. Flammability limits of the system CH₃Cl—CH₂Cl₂—Cl₂ at 293—303 K and atmospheric pressure.

mixtures with a high methylene chloride content. At this temperature level, a maximum of approximately 53% methylene chloride in the gas phase is possible. This maximum is represented in Figs. 4, 5 and 6 as a dotted line. To prevent condensation in the feed line, a maximum CH_2Cl_2 content of 50% was used.

The four-component system methyl chloride—methylene chloride—chlorine—hydrogen chloride is found to be non-flammable when one of the following conditions is fulfilled.

(1) The chlorine content exceeds 90%.

(2) The hydrogen chloride content is higher than 55%.

(3) The methyl chloride content is higher than 64%.

(4) The chlorine content is less than 31%, provided that the methylene chloride content is smaller than 53%.

In a few tests, the flammability limits of the system methyl chloride—chlorine with up to 20% hydrogen chloride were also determined with a capacitive spark of 400 J from commercially available apparatus (SWG 400, Ciba Dynatronics GmbH.). With this hundredfold increase in spark energy, no
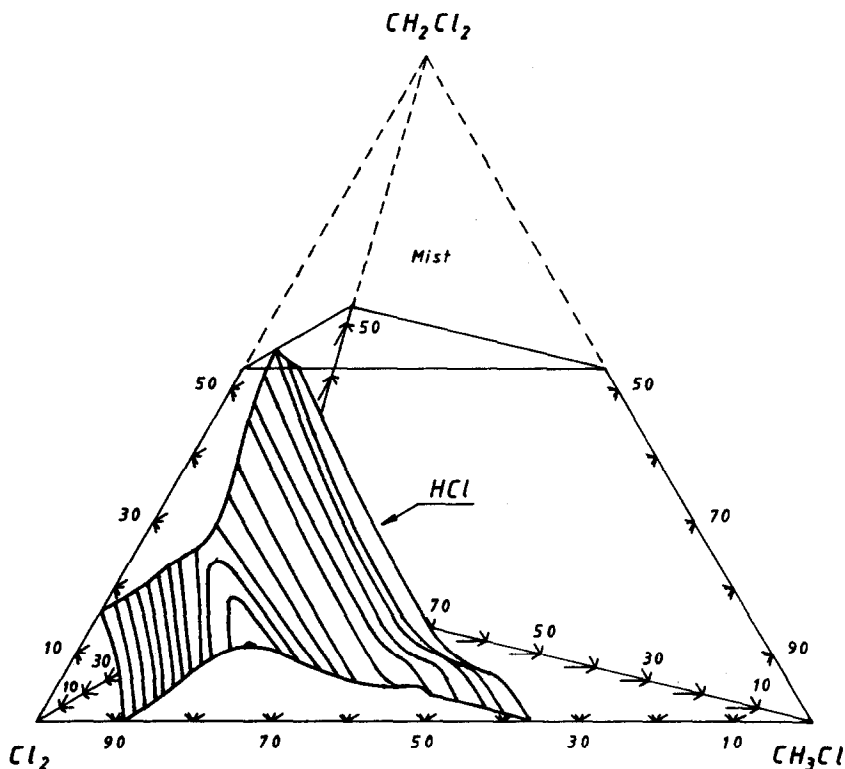
Fig. 6. Flammability region of the system CH₃Cl—CH₂Cl₂—HCl at 293—303 K and atmospheric pressure.

significant shift of the measured limits was observed. The ignition probability was high with this ignition source, the mixture ignited on the first or second attempt but otherwise did not ignite at all.

The flames on the fuel-lean side of the diagrams could hardly be seen, even in the completely darkened laboratory. The fuel-rich flames were red-orange in colour and produced large amounts of soot. Other products were HCl, CCl₄, C₂Cl₄, C₂Cl₆ and minor amounts of C₆Cl₆. In most cases, the visible length of the flame was about 0.5 metres at the fuel-rich limit, due to very slow radial burning of the mixture. The flame front thickness, estimated from flames on Bunsen-type burners, is of the same order of magnitude as for flames with oxygen as oxidiser, that is approximately 0.3 mm. The estimated flame temperature (optical) is 1000—1100 K in the carbon formation zone.

Discussion

As far as the experimental results can be compared with literature data, the agreement between the two is good. Mal'tseva et al. [2,4] report flamma-

bility limits for the methyl chloride—chlorine system of 10.2% to 56.0% (this work 10.6% to 63%) and for the methylene chloride—chlorine system 16.7% to 52.9% (this work 16.5% to 52.9%). The upper limit of 52.9% for the latter system is determined by the saturated vapour pressure of methylene chloride as previously mentioned. Care must be taken at temperatures higher than 30°C because the actual upper limit will be higher than the measured value above 40°C, this being the boiling point of methylene chloride. Binary mixtures of methylene chloride and chlorine at temperatures above 40°C and high percentages of methylene chloride will become flammable when allowed to cool down below 30°C.

The flame temperatures of the systems studied were estimated to be 1000 —1100 K at the upper limit. Due to invisible flames, no estimation at the lower limit was possible with an optical pyrometer. From calculations of the adiabatic temperature with CCl_4 and HCl as products, with no dissociation taken into account, an average limit temperature of 1108 K was found ($n = 64$ points, standard deviation = 64) both for the upper and lower limit points. This adiabatic temperature is lower than the value of 1500 K that is usually found for hydrocarbons and oxygen-containing systems. The lower temperature is due to the higher radical level in chlorine and chlorinated hydrocarbons at elevated temperatures, which causes a much lower ignition temperature. Our measurements give an autoignition temperature for CH_3Cl in chlorine of approximately 215°C (AIT of CH_3Cl in air is approximately 618°C).

In the measured diagram for CH_3Cl—HCl—Cl_2, a non linear behaviour of the upper limit is found at CH_3Cl/Cl_2 ratios slightly above 1:1, 1:2 and 1:3 (lines a, b and c in Fig. 3). This behaviour can possibly be explained by the following considerations. At high temperatures CH_2Cl_2 is an unstable compound, it decomposes exothermically to form carbon and HCl, amongst other products. The intermediates, formed in the flame reaction, are believed to be mainly $CH_2Cl\cdot$ and CHCl: radicals for CH_3Cl/Cl_2 ratios of 1:0 to 1:1. These radicals form, besides carbon and HCl, partially chlorinated C_1 and C_2 compounds, because of a lack of chlorine. With high amounts of chlorine, the more stable radicals $CHCl_2\cdot$, $CCl_3\cdot$ and CCl_2: are likely to be formed, leading to products that contain more chlorine in their molecules, $CHCl_3$, CCl_4, C_2HCl_3, C_2Cl_4, etc. Below CH_3Cl/Cl_2 ratios of 1:3, the mixture contains sufficient chlorine to transform all the H atoms into HCl, and fully chlorinated products are formed (CCl_4, C_2Cl_4, C_2Cl_6 etc.).

In oxygen containing systems, the changes in intermediate radical levels usually do not give distinct regions, but it is believed that in this system a distinct change is present due to the above-mentioned low ignition temperature and change in radical types. This results in a thicker post-flame recombination zone when high levels of $CCl_2\cdot$ radicals are expected, causing more heat to be removed from the flame and therefore giving a smaller flammability diagram. This effect is diminished when an excess of chlorine radicals are present to form CCl_4.

Acknowledgement

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