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THE LIMITS OF FLAMMABILITY OF MIXTURES OF AMMONIA, HYDROGEN AND METHANE IN MIXTURES OF NITROGEN AND OXYGEN AT ELEVATED TEMPERATURES AND PRESSURES

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Summary

As part of a program investigating the flammability characteristics of ammonia in mixtures with air, nitrogen and ammonia side-products, the flammability limits of mixtures of ammonia, hydrogen and methane in air and nitrogen were experimentally determined at 150° C and pressures up to 175 bar. The flammable regions are not as large as those found in a previous study for mixtures of ammonia and hydrogen, but are still remarkably wider than the regions for ammonia alone.

1. Introduction

Synthesis gas for the production of ammonia may be obtained through partial oxidation of natural gas. This method may leave traces of methane and hydrogen in the final product. When these impurities are concentrated in consecutive processes, they may present an explosion hazard. Since flammability data at elevated temperatures and pressures are sparse, the characteristics of mixtures of ammonia, hydrogen and methane were determined experimentally, following a study reported previously in which the flammability characteristics of ammonia mixed with hydrogen were determined [1].

In the present study, the hydrogen was replaced by a mixture of 50% methane and 50% hydrogen (all percentages mentioned in this paper are molar percentages). Experiments were conducted at 150° C and 44 and 175 bar.

2. Experimental

Two apparatuses are used in this program, one for pressures up to 44 bar, and one for pressures above that value. These apparatuses and the experimental procedure are fully described in our previous paper (loc. cit.). The apparatuses consist in essence of large (8 and 6 litres, respectively) pressure

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vessels fitted with temperature and pressure measuring instruments and an ignition device. Gases can be introduced into the vessels and thoroughly mixed before an ignition attempt. Ignition is performed by melting a spiral tungsten wire. The experiments were carried out at O_2/N_2 ratios of 9/91, 12/85 and 21/79 (air). In addition, the apex of the flammable area of H_2/CH_4 = 1/1 (in mixtures with air and nitrogen) as well as some limits of flammability of methane were determined separately. The accuracy of the results is better than 1%. The flammability diagram for mixtures of ammonia and hydrogen/methane = 1/1, in mixtures of air and nitrogen, at a temperature of 150° C, and a pressure of 175 bar, was constructed from the data thus obtained.

3. Results

The results of the measurements for mixtures of hydrogen and methane in air are depicted in Fig. 1. Hydrogen and methane follow the rule of le Chatelier [2] as closely at elevated temperature and pressures as under

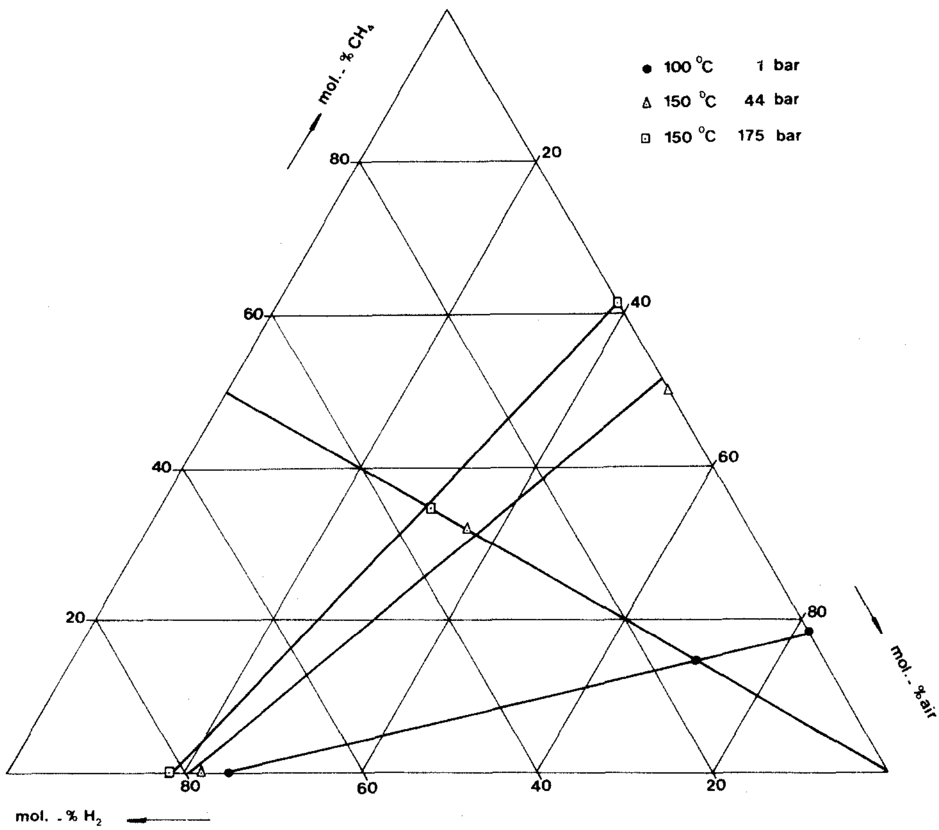

Fig. 1. The upper limits of flammability of mixtures of CH_4 and H_2 under atmospheric conditions, and at 150° C, and 44 and 175 bar.

atmospheric conditions [3, 4]. The increase in the upper flammability limit of methane follows the rule UEL = 15.0 + 20.4 log p, as given in ref. [4]. This increase is much greater than given in [5]. In Fig. 2 the results for mixtures of H_2/CH_4 = 1/1 in air and N_2, at 150° C, and 44 and 175 bar, are compared with the flammable area calculated from [5] for this mixture under atmospheric conditions.

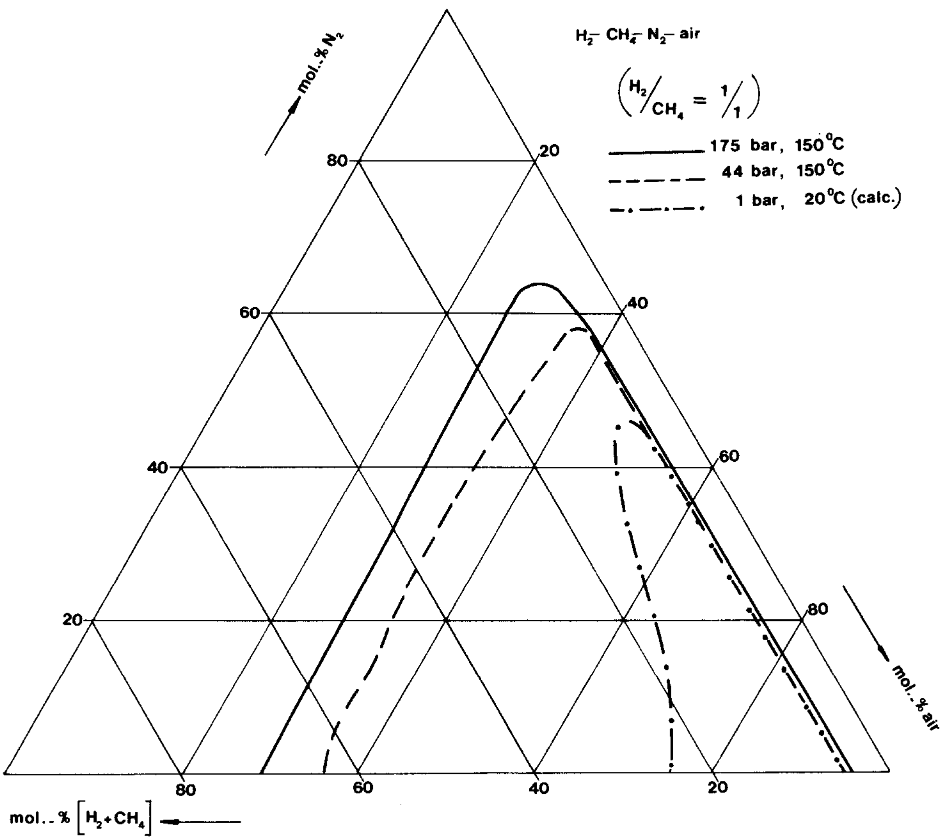

Fig. 2. The limits of flammability of a mixture of H_2 and CH_4 = 1/1 in air and nitrogen, under atmospheric conditions, and at 150° C, and 44 and 175 bar.

The increase in the upper limit of methane is the main reason for the enormous increase of the flammable area of these mixtures with increasing pressure. As could be expected from the corresponding measurements for mixtures of ammonia and hydrogen alone, mixtures with ammonia and hydrogen do not follow le Chateliers rule, although mixtures of ammonia and methane have been reported [6] to follow this rule reasonably well at 1 bar and elevated temperatures. The results found in the present investigation for mixtures of ammonia with H_2/CH_4 = 1/1 in air, at 150° C, and 44 and 175 bar, are given in Fig. 3.

The flammable area of these mixtures is much greater than can be expected from le Chateliers rule, but smaller than that of mixtures of ammonia

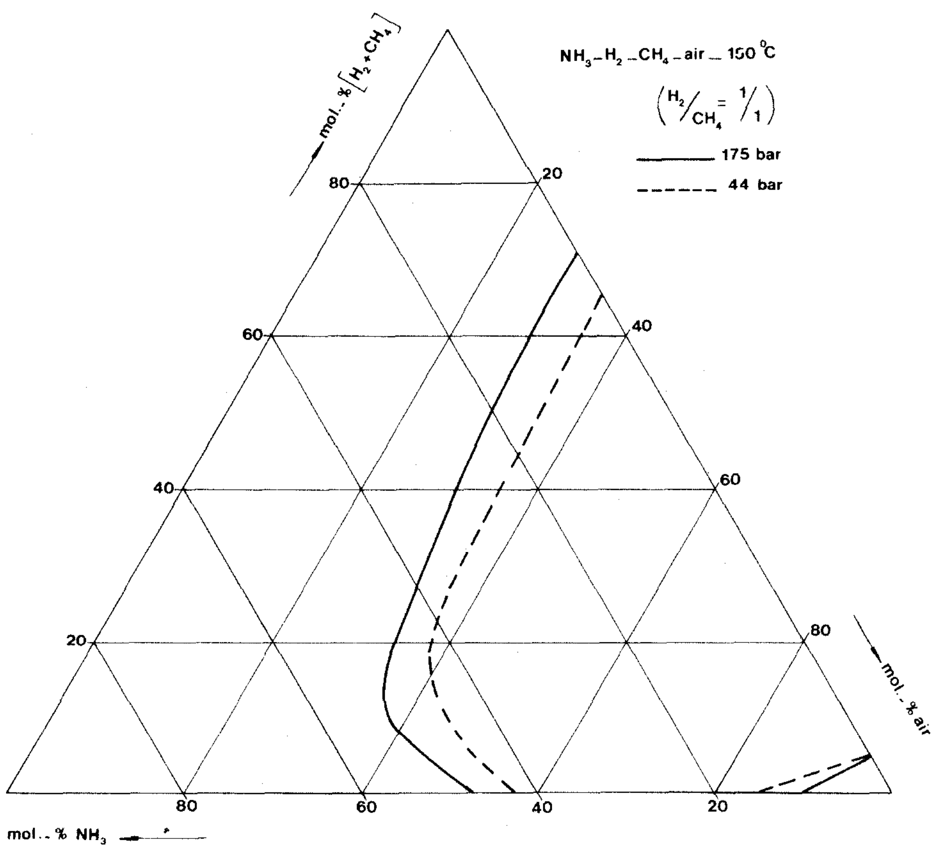

Fig. 3. The limits of flammability of mixtures of NH_3 and H_2/CH_4 = 1/1 in air, at 150° C, and 44 and 175 bar.

and hydrogen only. In Fig. 4 typical limits of flammability of mixtures of NH_3 and H_2/CH_4 = 1/1, in air and N_2, are given at 150° C and 44 and 175 bar. From the irregularity of the distance between corresponding limits at different pressures, it is apparent that a relationship between the UEL and the pressure analogous to that found for methane does not exist for the whole limit of the flammable area.

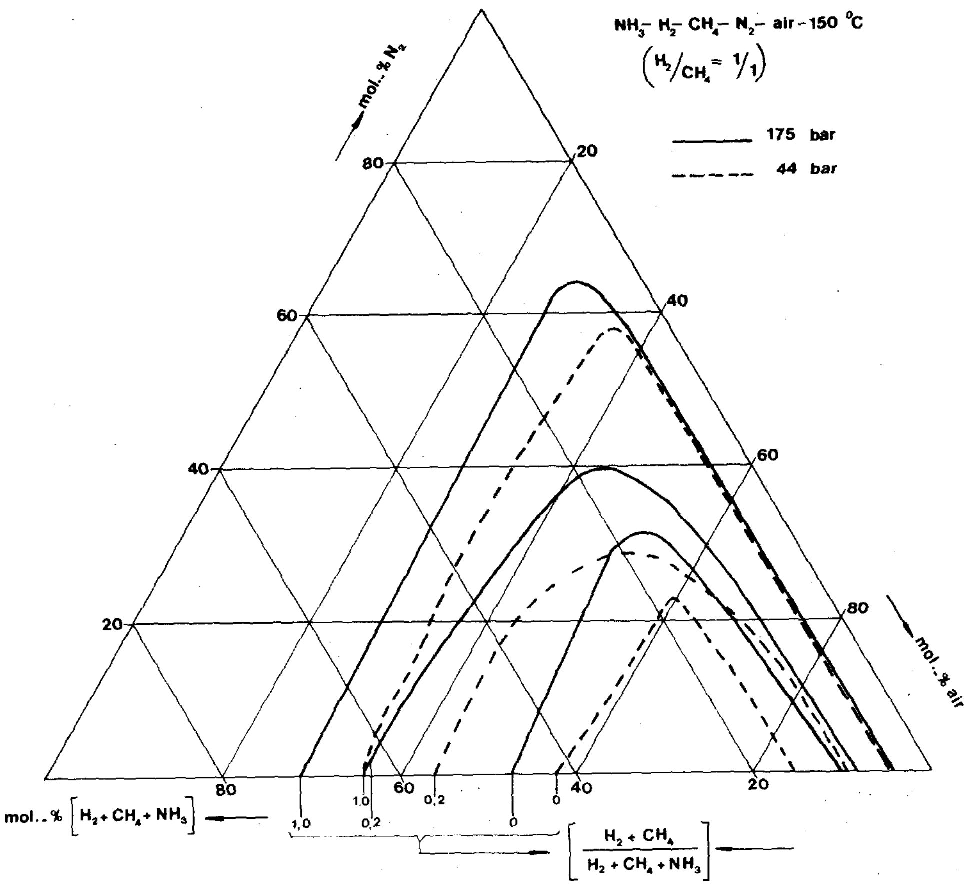

Fig. 4. The limits of flammability of mixtures of NH_3 and H_2/CH_4 = 1/1 in air and N_2, at 44 and 175 bar, and at 150° C.

The final result of the present investigation, the flammability diagram at 150° C and 175 bar, is given in Fig. 5. The diagram has the form of a fuel, nitrogen, air diagram, with the concentration of H_2/CH_4 = 1/1 in the fuel as parameter.

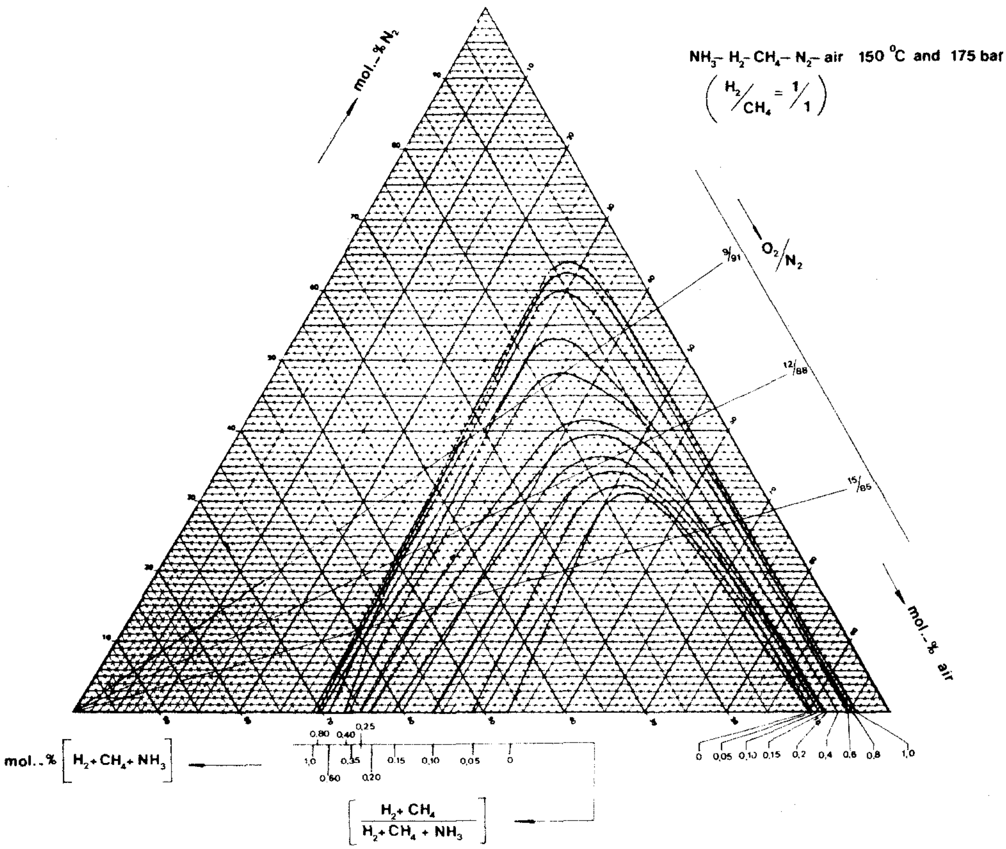

Fig. 5. The limits of flammability of mixtures of NH_3 and H_2/CH_4 = 1/1, at 150°C and 175 bar, in air and nitrogen.

4. Conclusion

The pressure dependence of the upper flammability limit, as found in this study, is in accordance with the literature. Mixtures of hydrogen and methane obey the rule of le Chatelier up to pressures of 175 bar. The flammable areas of mixtures of ammonia and H_2/CH_4 = 1/1, in air and nitrogen, are larger than can be expected from le Chatelier's rule, but smaller than those of the corresponding mixtures in which methane is replaced by hydrogen. Since it can be inferred from the literature that mixtures of ammonia and methane do not deviate very much from le Chatelier's rule, there is a strong indication that the combination ammonia—hydrogen causes the big deviations found in this study.

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Notation

UEL concentration of fuel at upper flammability limit (mol.-%)
p pressure (bar)

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