

An Inertization of Combustible Gaseous Mixtures by Inert or Chemically Active Agents as a Tool of Fire and Explosion Safety Ensuring

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ABSTRACT

Various aspects of inertization of gaseous mixtures by inert or chemically active agents have been considered. Combustible mixtures containing elevated concentrations of oxygen or nitrous oxide as an oxidizer were experimentally investigated. Some aspects of inhibition of combustion processes by modern ozone-safe gaseous diluents were explored. An effect of chemical induction (promotion of oxidation of fluorinated hydrocarbons by combustion of hydrogen - air and methane - air mixtures) has been revealed. An inertization of combustible gaseous mixtures by gas - aerosol compositions produced by burning of special solid fuels was considered. Flammability limits and laminar burning velocities of mixtures of hydrogen-oxygen-diluent at elevated pressures and temperatures have been experimentally determined.

INTRODUCTION

One of perspective methods of fire and explosion prevention in industrial rooms and technological equipment is an inertization of gaseous mixtures by inert or chemically active agents. An elevation of lower flammability limits (LFL) and a decrease of upper flammability limits (UFL) with an introduction of diluents in combustible mixtures take place until lower and upper branches of flammability curve joint in one point called inertization point. Also a decrease of such parameters as maximum explosion pressure, maximum explosion pressure rise rate, laminar burning velocity takes place for the most part of combustible gaseous mixtures. Many scientists in the world investigated phenomena and mechanisms of inertization of combustible gaseous mixtures (for example, G. Dixon-Lewis, P. Van Tiggelen, N.Saito, C.K. Law etc).

The investigations of russian scientists in this area of fire safety science are less known in the world, because results of their investigations were published mainly in russian scientific journals. Large contribution has been made by V.V. Azatyan, A.N. Baratov, A.Ya. Korolchenko, V.T. Monahov etc. In this paper we shall consider the main achievements obtained in All Russian Scientific Research Institute for Fire Protection last years in the area of gaseous mixtures inertization.

INERTIZATION AND INHIBITION OF COMBUSTION OF GASES AND VAPOURS IN OXYGEN ENRICHED ATMOSPHERES

Conditions for inertization of combustion of gases and vapours in air and oxygen enriched atmospheres by chemically inert agents at room temperature and atmospheric pressure are described in scientific literature rather well (see, for example, [1,2]). Therefore an attention of many investigators was aimed on determination of flammability limits in mixtures of combustible - oxidizer (air or oxygen enriched atmosphere) - halogenated diluent. Rather complete data for the case of combustion in air are presented in [3].

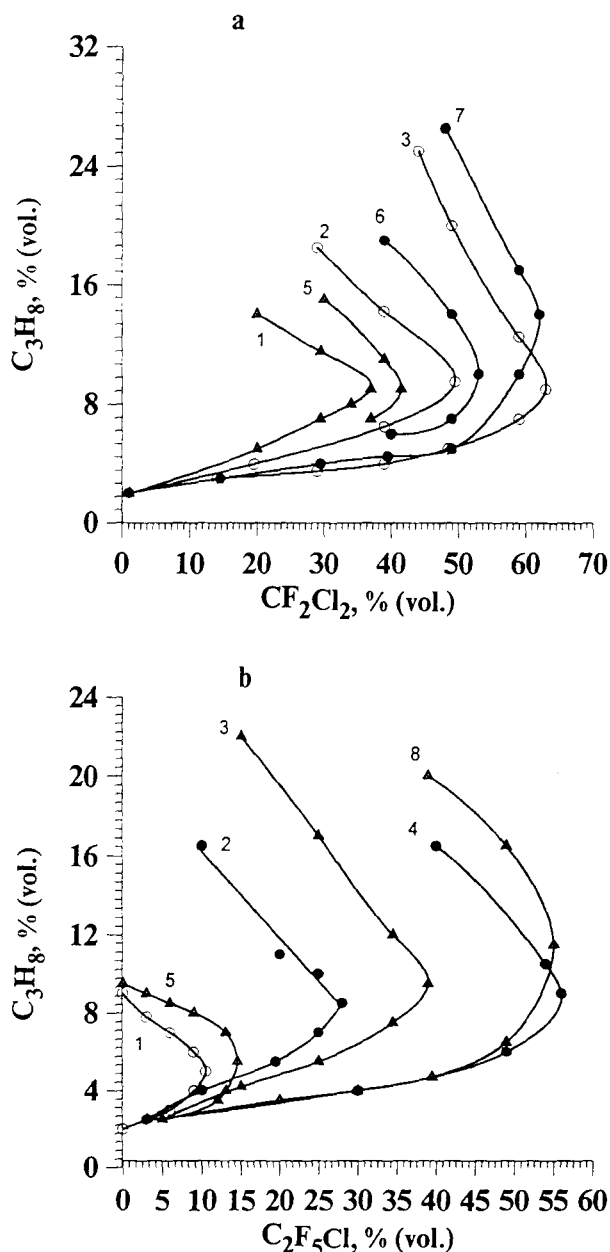


Fig.1. Flammability limits in mixtures of organic fuel-oxidizer-halogenated diluent.

a- propane - $C_2F_2Cl_2$ - oxidizer; b - propane - C_2F_5Cl - oxidizer. Oxygen concentration in oxidizer 20.6 (1, 5), 40(2, 6), 60(3, 7), 100(4, 8) % (vol.). 1, 2, 3(a) AND 1, 2, 3, 4(b) - data, obtained on the set-up "KP".

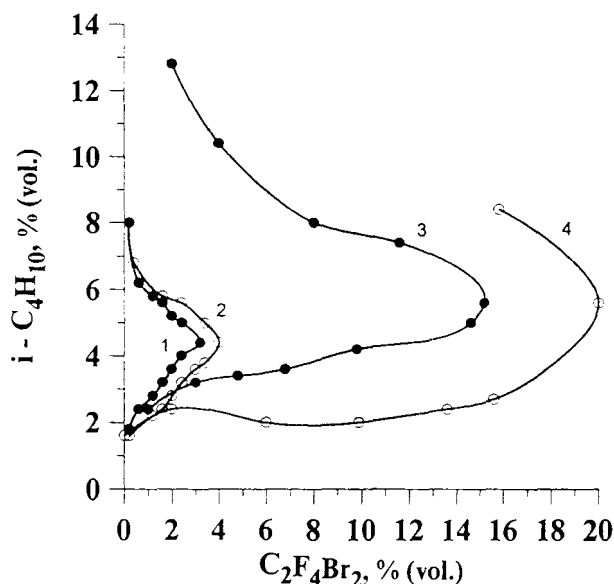


Fig.2. Flammability limits in mixtures of isobutane-C₂F₄Br₂-oxidizer. Oxygen concentration 20.6(1,2) and 40(3,4) % (vol.). Data have been obtained on the set-up “KP” (1,3) and “Limit” (2,4).

Typical data on flammability limits in oxygen enriched atmospheres, which are mixtures of O₂ and N₂, are shown in Figs. 1,2. These data are characterized by the following peculiarities. Firstly, inertization concentrations for halogenated hydrocarbons are much lower than for chemically inert diluents (this is the result of comparison of data in Figs. 1,2 with those published in [1,2]). Secondly, it is clear, that for halogenated hydrocarbons an influence of instrument factors for low volume installation is sufficient. Concentration flammability regions determined on the set-up “Limit” (reaction vessel in the form of vertical cylinder with internal diameter 300 and height 800 mm [4]) are sufficiently wider, that obtained on the set-up “KP” (reaction vessel in the form of vertical tube with diameter 50 and height 1500 mm [6]). As it has been shown in [4], flammability limits data obtained on the set-up “Limits” are close to those determined in large - scale apparatus with volume of a reaction vessel of several m³.

Inertization concentrations determined on the set-up “Limit” are sufficiently higher than obtained on the set-up “KP”. But with an elevation of oxygen concentration in the atmosphere the relative difference between inertization concentrations determined on various apparatus diminishes, and at oxygen concentration of 40% (vol.) becomes near 10%. At almost all oxygen concentrations lower branches of flammability curves determined on various apparatus are close to each other, and the difference in concentration flammability regions is mostly due to upper branches of flammability curves. It has been noted [5], that for fully halogenated hydrocarbons containing only F and Cl atoms the qualitative behaviour of lower flammability curves does not depend significantly on the oxygen concentration (at least up to [O₂] = 60% (vol.)). The wider concentration flammability region determined on the set-up “Limit” is caused by influence of natural convection on combustion [7]. Convective and conductive heat losses at a flame propagation in large vessels are lower than in narrow tubes, and therefore the higher concentrations of diluents are required for combustible mixture inertization. The difference ΔC_d in values of inertization concentrations obtained on various installation

characterizes the difference in heat losses from a flame front at its propagation in various reaction vessels.

It is known, that heat losses are determined sufficiently by a flame velocity. At flammability limits these velocities are close to each other at defined conditions of heat exchange between a flame and environment regardless on composition of combustible mixture (for example, oxygen or diluent concentration) [8]. From this viewpoint it is evident that the difference in heat losses at flammability limits for various reaction vessels (the set-ups "Limit" and "KP") should be approximately the same for various oxygen concentrations. Therefore the ΔC_d values should be near constant. This fact is evident from Fig.1 and has been confirmed in experiments [5]. Because the inertization concentration C_d becomes higher with the increase of oxygen concentration, the ratio $\Delta C_d/C_d$ diminishes.

The qualitatively different character of influence of oxygen concentration on flammability limits has been revealed for such diluent as $C_2F_4Br_2$ (Fig.2.) With an elevation of $[O_2]$ the slope of the lower branch of flammability curve decreases due to decrease of inhibition effectiveness of this halon caused probably by its combustion. According to [9,10] 1,2 - dibromotetrafluoroethane is capable to burn in pure oxygen. The ratio of $\Delta C_d/C_d$ increases with the elevation of oxygen concentration.

INERTIZATION AND INHIBITION OF COMBUSTION OF GASES AND VAPOURS IN NITROUS OXIDE

Flame propagation in gaseous mixtures, where nitrous oxide N_2O is an oxidizer, is investigated rather poor. Experimental data which characterize this process, are sometimes contradictory. According to [1,2], LFL of organic gases and vapours in air and in nitrous oxide are close to each other, but in [11,12] much lower LFL in N_2O have been obtained. The absence of reliable experimental data on combustion characteristics of gases and vapours in nitrous oxide makes difficult a creation of analytical methods for prediction of such characteristics.

In [13] experiments have been executed on the mentioned above set-ups "Limit" and "KP" aimed on determination of flammability limits in ternary mixtures of combustible (propane, butane) - nitrous oxide - diluent (N_2 , CO_2 , C_2F_5Cl , CF_2Cl_2 , $C_2F_4Br_2$). The results are presented in Fig.3.

As in experiments described in previous section, concentration flammability regions determined on the "Limit" installation are wider than measured on the set-up "KP". It is interesting to note an unusual character of an inertization curve in the mixture of propane - nitrous oxide - 1,2 - dibromotetrafluoroethane. Rather rapid reduction of LFL of propane with elevation of halon concentration takes place at $[C_2F_4Br_2] \approx 0.2-0.5\%$ (vol.). This effect is due to a sufficient heat release at conversion of $C_2F_4Br_2$ in a flame front. But any flame propagation was not observed in mixtures of 1,2- dibromotetrafluoroethane with nitrous oxide at halon concentration up to 20% (vol.). The more slow influence of halogenated hydrocarbons on flammability limits of organic gases and vapours in comparison with the case of combustion in air is observed (the typical inertization concentration of C_2F_5Cl is near 15% (vol.) in air and near 40% (vol.) in nitrous oxide).

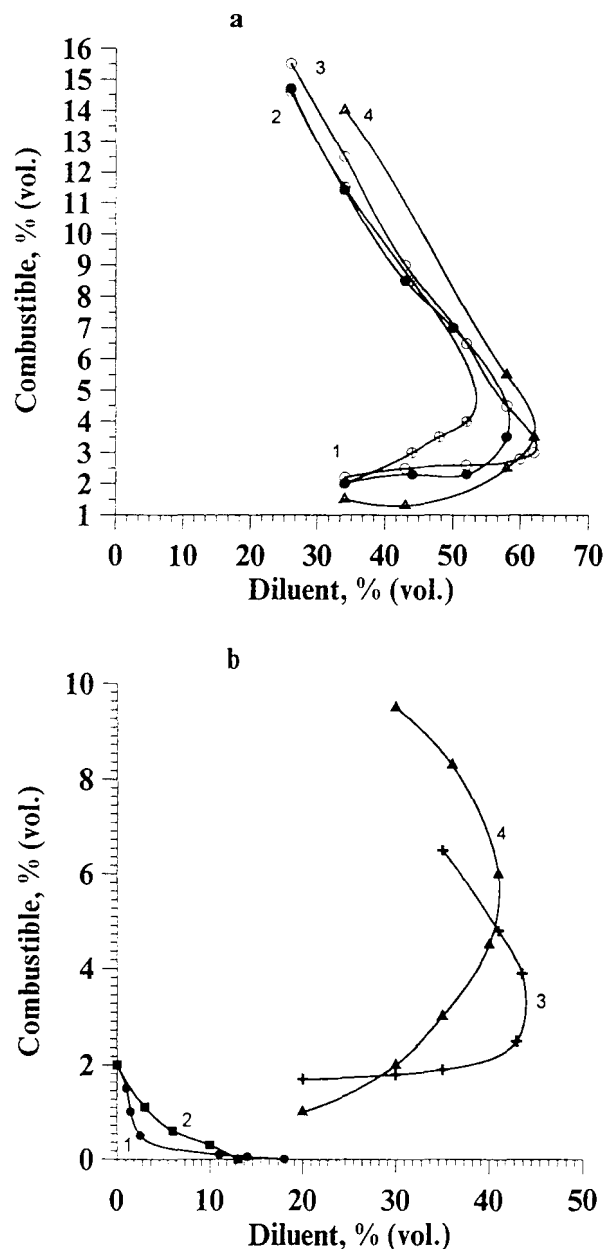


Fig.3. Flammability limits in mixtures of combustible-nitrous oxide-diluent.
 a - $C_3H_8-N_2O$ -chemically inert diluents (1,2 - CO_2 ; 3,4 - N_2).
 1, 3 - data, obtained on the set-up "KP", dashed line - data, obtained on the set-up "Limit".
 b - combustible - N_2O - halogenated diluent (1 - $C_3H_8 - N_2O - C_2F_4Br_2$),
 2 - $i - C_4H_{10} - N_2O - C_2F_4Br_2$, 3 - $i - C_4H_{10} - N_2O - C_2F_5Cl$, 4 - $C_3H_8 - N_2O - CF_2Cl_2$). Data were obtained on the set-up "KP".

THE PECULIARITIES OF INHIBITION OF COMBUSTION OF HYDROGEN

During last years in Institute of Structural Macrokinetics of Russian Academy of Sciences some new ecologically clean inhibitors of combustion of hydrogen have been proposed, which are safe for ozone layer of the Earth. In this section of the paper some

results of investigations of influence of one of such inhibitor (Inh x) on combustion characteristics of hydrogen in air have been described.

Experiments have been executed on the set-up "Variant" which was described in detail in [14]. This set-up has a spherical reaction vessel with internal diameter of 20 cm (volume of 4.2 dm³) made from stainless steel, which give a possibility to perform experiments at initial pressures of gaseous mixtures up to 4 MPa. The set-up also has a system for preparing of combustible mixture, which includes vacuum pumping, tubes and valves. Combustible mixtures were prepared immediately in the reaction vessel by partial pressures after an evacuation till residual pressure not higher than 0,5 kPa. Fused nichrom wire placed in the center of the reaction vessel was used as an ignition source. A flame propagation was detected by a system including pressure detector with a time constant near $3 \cdot 10^{-3}$ s and storing oscilloscope. It has been accepted that a flame propagation takes place, if a pressure increase is higher than 30 kPa. Processing of experimental data was made according to standard [15]. Experiments have been executed at room temperature and atmospheric pressure. Flammability limits, maximum explosion pressure ΔP_{\max} and maximum explosion pressure rise rate $(dp/dt)_{\max}$ have been determined.

In Fig.4 flammability limits of mixtures of hydrogen - air - Inh x are presented. Data for mixtures of hydrogen-air-C₂F₄Br₂ are presented for comparison too. With an elevation of halon concentration the concentration flammability region narrows sufficiently (mainly due to a reduction of UFL). The inhibitor Inh x causes more strong influence on UFL. But this inhibitor is a flammable gas, because it has his own flammability limits. In the case of C₂F₄Br₂ gaseous mixture in the inertization point is lean. This result coincides qualitatively with experimental data [17,18]. This effect is due to a preferential diffusion of hydrogen in lean mixtures because of sufficiently high diffusion coefficient of hydrogen in comparison with O₂, N₂ and C₂F₄Br₂ [19-21].

In Figs. 5,6 experimental data are presented, which characterize the dependence of maximum explosion pressure ΔP_{\max} and maximum explosion pressure rise rate $(dp/dt)_{\max}$ on inhibitors concentrations. For convenience these data are shown in the dimensionless form.

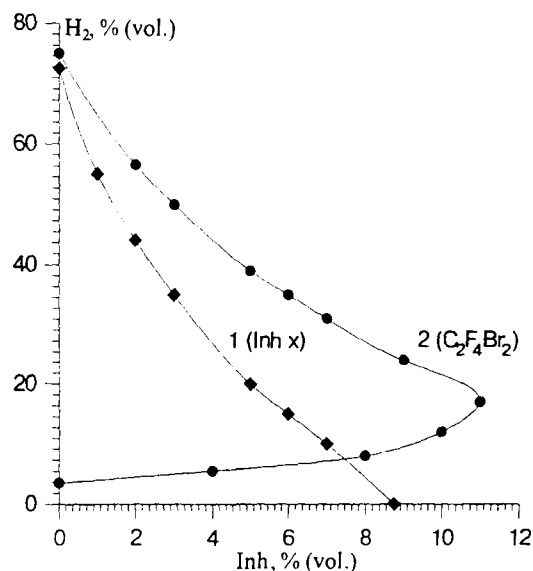


Fig.4. Flammability limits in mixtures of H₂ - air - inhibitor. 1- Inh x; 2 - C₂F₄Br₂.

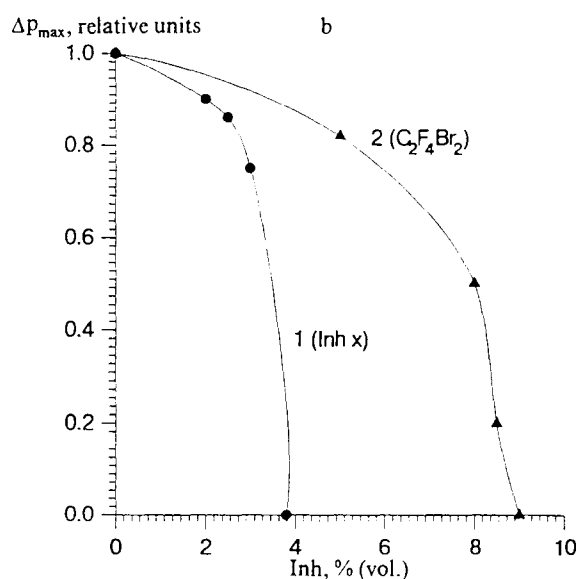
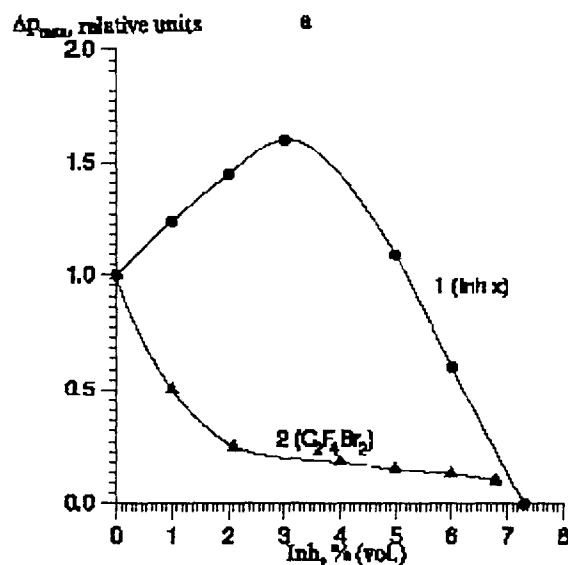


Fig. 5. Dependence of maximum explosion pressure ΔP_{\max} on concentration of Inh x (1) and $C_2F_4Br_2$ (2) for hydrogen content in air 10 (a) and 30 (b) % (vol.).

For ΔP_{\max} dimensional normalizing factors for hydrogen concentrations 10 and 30% (vol.) are equal to 270 and 600 kPa, and for $(dp/dt)_{\max}$ - 3.5 and 165 MPa/s. For lean hydrogen - air mixtures a significant increase of ΔP_{\max} and $(dp/dt)_{\max}$ with an elevation of [Inh x] takes place up to certain maximum value, after this a rather rapid decrease of ΔP_{\max} and $(dp/dt)_{\max}$ occurs. For such diluent as $C_2F_4Br_2$ these maxima are absent. For stoichiometric hydrogen - air mixtures a monotone reduction of ΔP_{\max} and $(dp/dt)_{\max}$ with an elevation of [Inh x] or $[C_2F_4Br_2]$ takes place. The more rapid decrease of mentioned above parameters occurs in the case of Inh x, that is this inhibitor is more effective for stoichiometric and rich hydrogen - air mixtures than $C_2F_4Br_2$. This fact agrees qualitatively with data on flammability limits (Fig.4). The cause of such qualitative character of influence of Inh x on ΔP_{\max} and $(dp/dt)_{\max}$ is a flammability of this inhibitor.

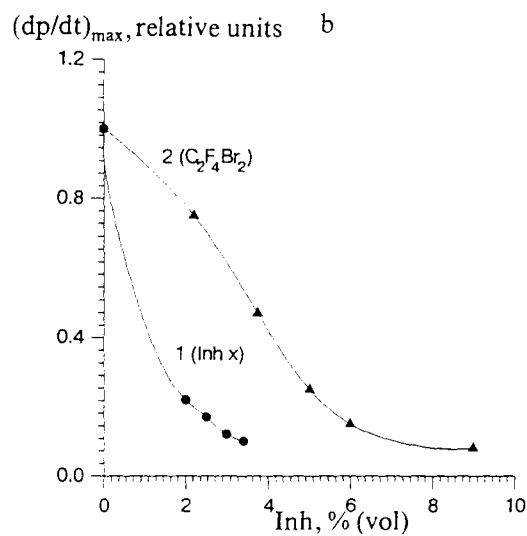
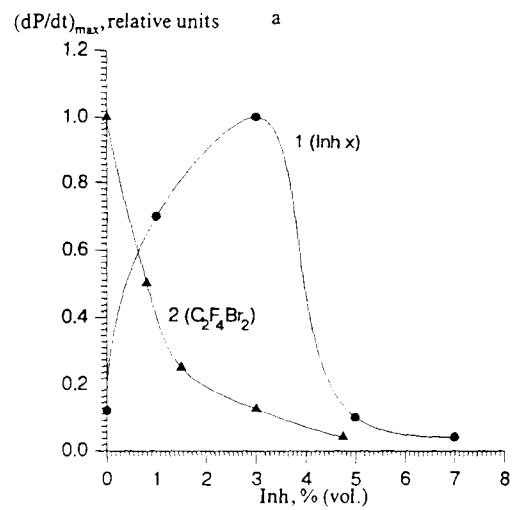


Fig.6. Dependence of maximum explosion pressure rise rate $(dp/dt)_{max}$ on concentration of Inh x (1) and $C_2F_4Br_2$ (2) for hydrogen content in air 10 (a) and 30 (b) % (vol.).

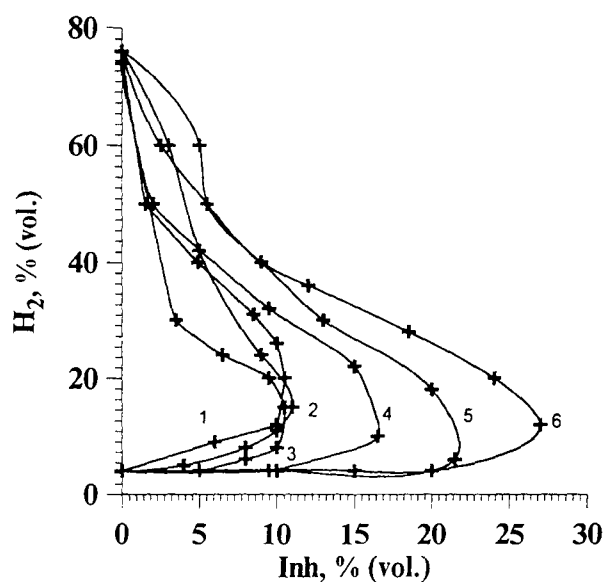


Fig.7. Flammability limits in mixtures of hydrogen - air - diluent.
1 - C_3F_7H ; 2 - $C_2F_4Br_2$; 3 - C_2F_5H ; 4 - C_4F_8 ; 5 - NAFS III; 6 - CF_3H .

ON THE CHOICE OF INHIBITORS FOR FIRE EXTINGUISHING AND EXPLOSIONS PREVENTION

Halogenated hydrocarbons are now the most effective inhibitors of combustion of hydrogen and organic substances. If these halons contain Br or I atoms, their inhibitive effectiveness is the highest one. But these diluents have some disadvantages. They often cause a destruction of ozone layer of the Earth. Sometimes these substances promote corrosion of constructive materials. At their action on flames very toxic products are formed, such as COCl_2 , COF_2 etc. Due to these disadvantages some restrictions in application of halogenated hydrocarbons for fire extinguishing and explosion prevention occur. Some advantages and disadvantages are inherent in another fire extinguishing agents (inert gases, water mists, gas-aerosol compositions etc.). Therefore it is obvious, that there is not any possibility to create an universal tool for fire extinguishing and explosion prevention applicable in all practical cases. It is more convenient to have a set of diluents of various chemical nature, from which a choice of more suitable agent can be made.

From this viewpoint it is perspective to use the mentioned above in previous section inhibitor Inh x for explosion prevention of hydrogen - air mixtures with H_2 concentration higher than 15% (vol.). The flammability of this inhibitor is not a barrier in this case for its practical application (see, for example, investigations [22-24], where, flammable inhibitors have been explored). In fact, concentration flammability region for mixtures of hydrogen - air-Inh x with H_2 content in air higher than 15% (vol.) is more narrow than for brominated halon, which is one of the most effective inhibitor of combustion (Fig.4). For hydrogen concentration in air not lower than 30 % (vol.) Inh x decreases effectively explosion parameters of H_2 - air mixtures (maximum explosion pressure, maximum explosion pressure rise rate). The main disadvantage of Inh x is its flammability, but this disadvantage is sufficient for rather lean hydrogen - air mixtures with $[\text{H}_2] < 15\%$ (vol.). It can be seen from Fig. 4, that at concentrations of Inh x higher than 7% (vol.) hydrogen - air mixtures with $[\text{H}_2]$ from 13 to 70% (vol.) (that is mixtures, which are able to detonate) are not able to propagate flames. By other words the availability in hydrogen - air mixtures of small additions of Inh x can prevent detonation. According to [25], additions of halogenated hydrocarbons, preventing deflagrations of gaseous mixtures, in some cases at the same concentrations can not prevent a propagation of detonation waves. From this consideration a conclusion can be made, that Inh x can prevent combustion regimes with high explosion characteristics (detonation or deflagration of near - stoichiometric mixtures).

Last time fluorinated hydrocarbons are considered as an effective replace of brominated halons [26-28]. In order to determine the effectiveness of such inhibitors series of investigations has been executed for exploring of combustion characteristics of gaseous mixtures of combustible gas (hydrogen, methane) - air - fluorinated diluent. Experiments have been performed on the described above set-up "Variant" at atmospheric pressure and room temperature. Typical experimental data on flammability limits are presented in Fig.7. It can be seen, that in some cases fluorinated hydrocarbons are close in their inhibitive effectiveness to brominated halons. Therefore they can be used for fire extinguishing and explosions prevention instead of halons, which are hazardous for the ozone layer of the Earth. But these agents at their concentrations less than limiting one can increase maximum explosion pressure and maximum explosion pressure rise rate of lean hydrogen - air and methane - air mixtures [45]. This effect should be taken into account at practical application of these agents for explosion prevention in closed vessels.

INERTIZATION OF COMBUSTIBLE GASEOUS MIXTURES BY GAS-AEROSOL COMPOSITIONS

Gas-aerosol fire extinguishing compositions produced at burning of special solid combinations are now widely used in practice [29-35]. Despite of differences of such combinations produced by various organizations they contain as a rule potassium salts (KNO_3 , KClO_4 , KCl) and organic or/and inorganic combustibles (magnesium, epoxycombinations etc.). At burning of such solid fuels gas-aerosol compositions are generated, gaseous phase of which consists mainly from N_2 and CO_2 , and solid phase contains K_2CO_3 , KHCO_3 , KCl [30]. The solid phase influences on flames of organic substances by the same way as fire extinguishing powders, having at the same time significantly higher fire extinguishing effectiveness because of very small size of solid particles (mean size near $5 \mu\text{m}$ [29]). Such small particles scarcely can be produced by mechanical dispergation.

Despite of mechanism of fire extinguishing action of gas-aerosol compositions is not quite clear, there are rather extensive experimental data on minimum fire extinguishing concentrations for various combustibles. But conditions for inertization of combustible gaseous mixtures by gas-aerosol compositions are investigated much more slowly. Inertization of methane - air mixture occurs at gas - aerosol concentration near 50 g/m^3 [29]. According to [32] for inertization of stoichiometric hydrocarbon - air mixtures gas - aerosol concentrations of the order of $40\text{-}80 \text{ g/m}^3$ are required, but for hydrogen - air mixtures with H_2 content in air 20% (vol.) the minimum inertization concentration is equal to 230 g/m^3 . In this section of the paper the experimental data on inertization concentrations of gas-aerosol compositions for gaseous combustible mixtures are presented.

Experiments were carried out on the experimental set-up "Limit" which has been described in the previous section of the paper. A required quantity of solid fuel for production of gas-aerosol mixture was placed into the reaction vessel, which was then evacuated for elimination of combustion products from previous experiment. Then air was introduced up to partial pressure of 50 kPa. Burning of solid fuel was initiated by supplying of electric voltage of 15 V on nichrom wire of diameter 0.2 and length 60 mm. After 45 s from the finish of burning of solid fuel a required quantity of combustible gas or vapour (by its partial pressure) was introduced into the reaction vessel, and then air was added to atmospheric pressure. Mixing of testing combustible mixture was made convectively by short - time heating of special heater placed in the lower part of the reaction vessel. Before an ignition of the testing mixture the bottom of the reaction vessel was removed in order to avoid a destruction of the reaction vessel. The ignition was made by supplying of electric voltage of 220 V on nichrom wire of diameter of 0.2 and length 5 mm. A flame propagation in the reaction vessel was detected visually. Methane and petrol vapour were used as combustibles. Solid fuel for production of gas-aerosol composition was the combination E-1 produced by "Granit - Salamandra" organization. A relative error in the determination of flammability limits did not exceed 10%.

Experimental data of determination of flammability limits in complex mixtures of combustible-air-gas-aerosol composition are presented in Figs.8,9.

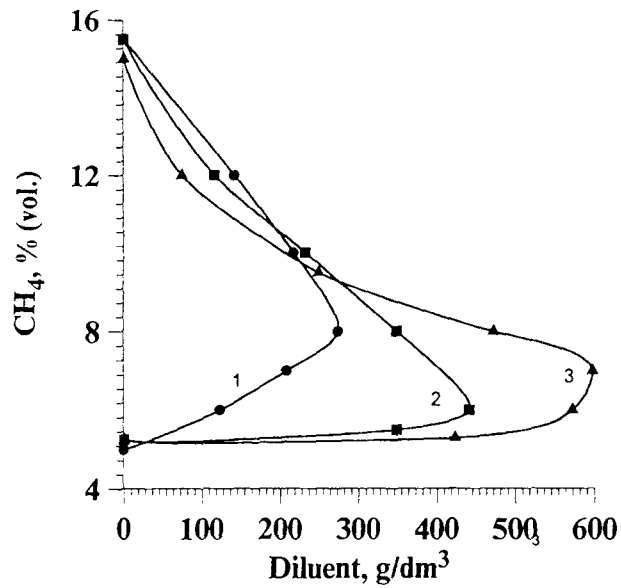


Fig.8. Flammability limits in mixtures of CH₄-air-(gas-aerosol composition) (1), CH₄-air-N₂(2) and CH₄-air-C₂HF₅ (3).

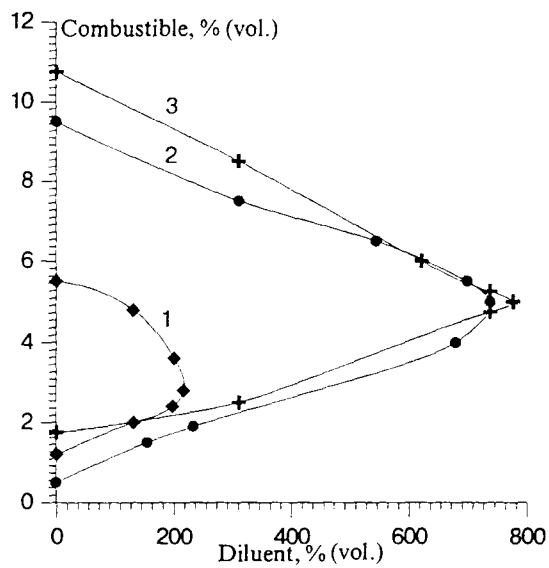
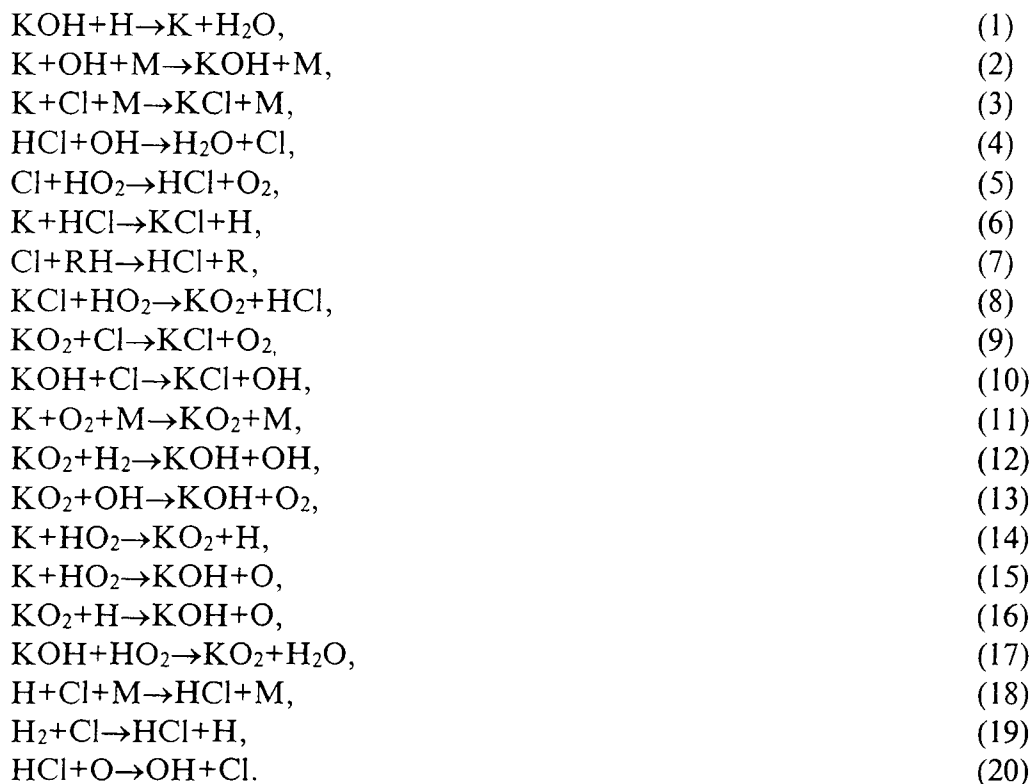


Fig.9. Flammability limits in mixtures of petrol vapour-air-(gas-aerosol composition) (1), (petrol vapour (50%) - azetone (50%)) - air - C₂F₃Cl₃ (2), (petrol vapour (50%) - ethanol (50%))- air - C₂F₃Cl₃ (3).

Experimental data [1,3] were presented for comparison too. The data [1,3] characterize flammability limits in mixtures of methane - diluent (nitrogen, pentafluoroethane)-air (Fig.8) and complex vapour combustible (mixtures of petrol vapour (50%) + acetone (50%) and petrol vapour (50%) + ethanol (50%)) - trifluorotrchloroethane - air (Fig.9). It follows from these data, that mass inertization concentration of the gas-aerosol composition is sufficiently lower, than for other diluents (including halogenated hydrocarbons). This effect is due to an inhibitive effectiveness of gas-aerosol composition, which is much higher than for other diluents. But minimum inertization concentration of E-1 gas-aerosol composition is significantly higher, than its minimum fire extinguishing concentration, which is equal to 50 g/m³ [36].

It has been found [37,38], that mixtures at inertization points for combustion of ternary compositions of organic gas or vapour - gaseous diluent - air are reach (stoichiometric in relation to combustion to CO and H₂O. But in the case of gas-aerosol composition as a diluent combustible mixtures at inertization points are lean (we took into account, that at burning of solid E-1 combination approximately 50% of its mass converts into inert gases and 50% - into solid particles [36]). We now can not explain satisfactory this difference in inertization conditions.

Mechanism of inhibitive action of gas-aerosol compositions on combustion of organic substances is close to that of fire extinguishing powders. As it has been mentioned above, one of the main components of fine aerosol particles is KCl. An evaporation of these particles in a flame front causes the following chemical reactions [35,39]:



The analysis of this reaction scheme of inhibition has been done in [39,40]. It has been found, that this homogeneous mechanism of inhibition explains qualitatively the observed in experiments variations in laminar burning velocity of methane - air mixtures at additions of gas - aerosol compositions. The main inhibitive reactions are processes (1) and (2), in the first one a recombination of H radical occurs, and in the second one a regeneration of inhibitor takes place. In [39,31] an evaluation of the role of a

heterogeneous mechanism of inhibition of methane - air flame by KCl has been done. It has been revealed, that even at instantaneous recombination of active centers on a surface of solid particles and at absence of competitive processes of adsorption of H₂O, O₂ and N₂ the influence of solid inhibitor is very slow, that is the heterogeneous mechanism is not sufficient.

INERTIZATION OF GASEOUS MIXTURES AT ELEVATED PRESSURES AND TEMPERATURES

Technological processes in many branches of industry are often realized at elevated pressures and temperatures. Therefore it is very important to investigate inertization conditions for combustible gaseous mixtures at mentioned above state parameters. In addition it is interesting to explore the possibility of application of water aerosol formed during evaporation of superheated water for inertization of gaseous mixtures. Such aerosol is successfully used for fire extinguishing [42]. Temperature of such superheated water is near 150-160°C. Aerosol has rather little droplets (mean diameter is near 50 μm), its temperature is near 50-80°C. This aerosol a priori can be used for inertization of combustible gaseous mixtures, but there is no experimental evidence of such possibility.

In this section of the paper experimental data on flammability limits of mixtures hydrogen-oxidizer (oxygen, air) - diluent at pressures up to 4.0 MPa and temperatures up to 250°C are described. Conditions for inertization of methane-air mixtures by water aerosol formed due to evaporation of superheated water are presented too.

Experiments were carried out on installations "Variant", "Steam" and "Superheating". The "Variant" installation has been described in previous sections of the paper. The set-up "Steam" was used for determination of flammability limits of gaseous mixtures at pressures from 0.1 to 2.0 MPa and temperatures from 20 to 250°C. It has a closed reaction vessel in the form of vertical cylinder with internal diameter 300 and height 800 mm (volume 53 dm³). Combustible mixtures were prepared by partial pressures immediately in the reaction vessel preliminary evacuated to a residual pressure 0.1 kPa. Mixing of gaseous mixture was made convectively by local heating of a special metal tube placed in the lower part of the reaction vessel. The maximum difference in concentration of combustible gas (hydrogen) did not exceed 0,2 % (vol.). The maximum difference in temperatures in various parts of the surface of the walls of reaction vessel did not exceed 10°C. Ignition was made in the lower part of the reaction vessel by fused nichrom wire (ignition energy is near 10 J). A flame propagation was detected by a pressure transducer "Saphire-22" (time constant near 3·10⁻³ s) and thermocouples placed on the top of the reaction vessel. It was accepted, that a flame propagation takes place, if a pressure increase is higher than 10 kPa, or a temperature increase for thermocouples is higher than 100°C.

The set-up "Superheating" was used for determination of inertization conditions for gaseous mixtures by water aerosol formed due to evaporation of superheated water. It has a spherical reaction vessel of volume of 20 dm³, aerosol generator with special chamber of volume of 1 dm³ heated up to 150°C, ignition source and system for preparing of gaseous combustible mixture.

Experiments were executed by a following manner. Gaseous combustible mixture was prepared by partial pressures immediately in the reaction vessel preliminary evacuated to a residual pressure 0.1 kPa. Water was heated to temperature of 150°C in the chamber of the aerosol generator. Then after connecting of the heated chamber and the reaction vessel a required quantity of the superheated water was introduced into the

reaction vessel. This water evaporates rapidly (the evaporation time is not higher than 1 s) and gives rise to water aerosol having temperature not higher than 80°C. After 5 s from the entering of superheated water combustible mixture was ignited by fused nichrom wire (ignition energy is near 10 J). A flame propagation was detected by a pressure transducer "Sapphire-22". A relative error in determination of flammability limits of methane and mass of water aerosol did not exceed 10%.

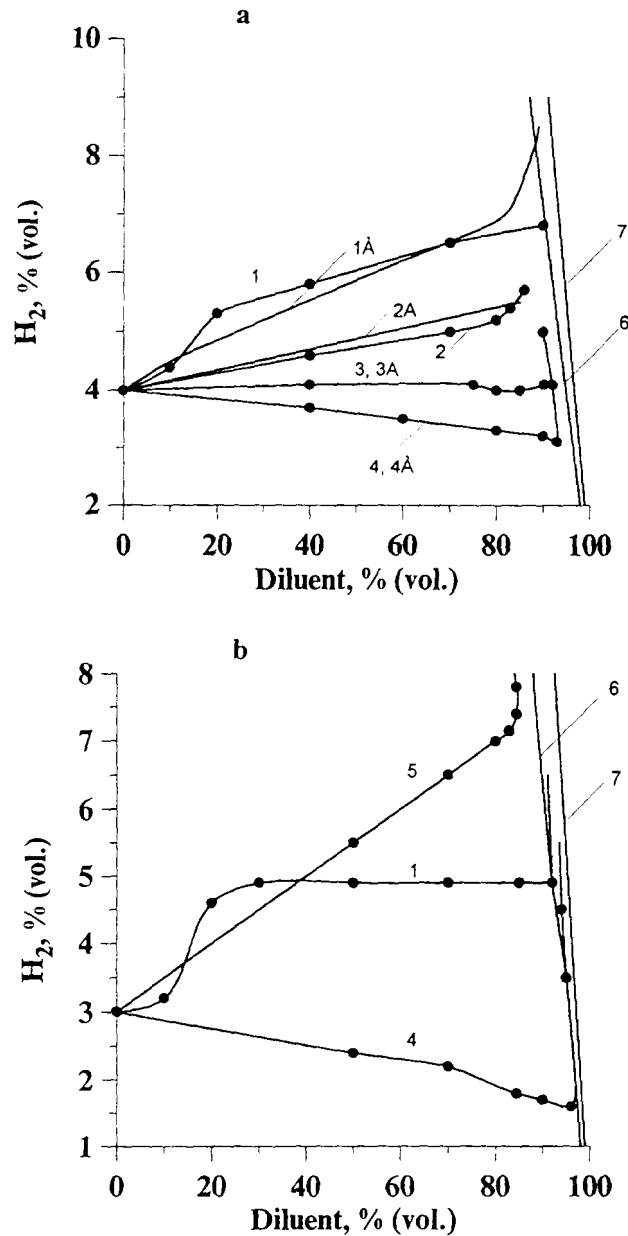


Fig. 10. Flammability limits in mixtures of hydrogen-oxygen-diluent at initial pressure 0,1 MPa and temperatures 20 (a) and 250 (b) °C.

- 1 - H₂ - He - O₂; 1a - H₂ - He - O₂ (data [18]);
- 2 - H₂ - CO₂ - O₂; 2a - H₂ - CO₂ - O₂ (data [18]);
- 3 - H₂ - N₂ - O₂; 3a - H₂ - N₂ - O₂ (data [1]);
- 4 - H₂ - Ar - O₂; 4a - H₂ - Ar - O₂ (data [18]);
- 5 - H₂ - H₂O - O₂; 6 - line of stoichiometric mixtures;
- 7 - line, restricted physically possible mixtures

In Fig. 10, 11 results of determination of flammability limits of investigated gaseous mixtures at pressures up to 2.0 MPa are presented. Data [1,18] are shown for comparison. From Fig. 10 it is obvious, that among four diluents (CO_2 , H_2O , N_2 , Ar) the most effective is that one, which has the highest molar heat capacity (carbon dioxide). If molar heat capacity C_P of diluent is higher than appropriate value for oxidizer (CO_2 , H_2O) lower flammability limit increases with an elevation of concentration of diluent. If C_P is close to molar heat capacity of oxidizer (N_2), LFL remains approximately constant up to an inertization point. If C_P is lower, than molar heat capacity of oxidizer (Ar), LFL drops with an elevation of concentration of diluent.

The behavior of lower branches of flammability curves of H_2 - O_2 - He mixtures is rather unusual (Fig. 11 b). At low concentration of He a rapid increase of LFL occurs, and then speed of LFL elevation drops remarkably. This effect was observed as at pressure of 0.1 MPa both at higher pressure, and is caused by preferential diffusion of hydrogen molecules, which is important for combustion of very lean ($[\text{H}_2] < 8\%$ (vol.)) mixtures containing hydrogen. It has been found that flammability limits of mixtures of hydrogen-oxygen-diluent (nitrogen, steam) do not change with pressure in the pressure range from 2.0 to 4.0 MPa.

Qualitative explanations of mentioned above peculiarities of flammability limits of mixtures of hydrogen- oxygen-diluent have been presented in [43].

In Fig. 12 a dependence of flammability limits of methane in air on mass concentration of aerosol formed due to rapid evaporation of superheated water is presented. A flammability curve for methane - air - steam mixture [1] is shown for comparison too. It can be seen, that inertization effectiveness of water aerosol is much less, than of steam. This effect is caused, for our opinion, by slow influence of water droplets on thermal balance and chemical kinetics in a narrow flame front. In diffusion flames of combustible liquids, for which fire extinguishing effectiveness is high, water droplets are evaporated mainly in combustion products with appropriate decrease of their temperature and radiative heat flux to a liquid surface. Therefore the liquid surface is cooled, and combustion is ceased. In the case of premixed flames a cooling of combustion products does not play a significant role in a flame propagation. Relatively large water droplets are not able to evaporate sufficiently in a narrow flame front and to influence a thermal balance and chemical kinetics in it.

CONCLUSIONS

In this paper recent results of investigations of inertization of gaseous mixtures by inert and chemically active agents are considered. Unfortunately a restricted space of the paper does not permit to analyze many works in the area of inertization of combustible mixtures, which are important for science and practice (for example, inertization of combustible dust-air mixtures, extinguishing of diffusion flames by gaseous agents etc.). Nevertheless from the presented materials conclusions can be made, that, first, inertization of gaseous mixtures is one of the perspective methods of fire and explosion safety ensuring, and, second, in this scientific area there are some unexplored questions. For example, a mechanism of inhibition of combustion processes by gas-aerosol compositions is not understood completely. There are some ecologically clean and safe for ozone layer of the Earth agents, which action on flames is not quite clear. Therefore investigations of inertization of gaseous mixtures and inhibition of combustion processes remain very actual and should be continued by specialists of various organizations.

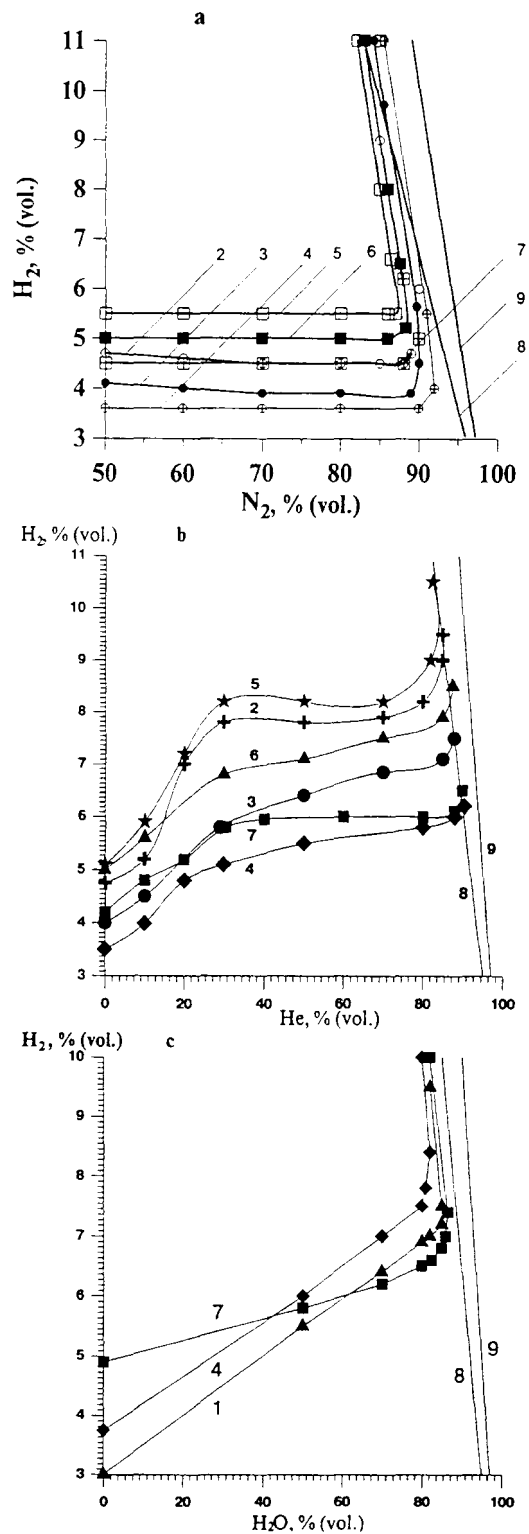


Fig. 11. Flammability limits of mixtures of hydrogen-oxygen-nitrogen (a), hydrogen-oxygen-helium (b) and hydrogen-oxygen-steam (c) at initial pressure p_0 and temperature t .

- 1 - $p_0 = 0,1 \text{ MPa}$; $t = 250^\circ\text{C}$; 2 - $p_0 = 0,6 \text{ MPa}$; $t = 20^\circ\text{C}$;
- 3 - $p_0 = 0,6 \text{ MPa}$; $t = 150^\circ\text{C}$; 4 - $p_0 = 0,6 \text{ MPa}$; $t = 250^\circ\text{C}$;
- 5 - $p_0 = 2,0 \text{ MPa}$; $t = 20^\circ\text{C}$; 6 - $p_0 = 2,0 \text{ MPa}$; $t = 150^\circ\text{C}$;
- 7 - $p_0 = 2,0 \text{ MPa}$; $t = 250^\circ\text{C}$; 8 - line of stoichiometric mixtures;
- 9 - line, restricted physically possible mixtures.

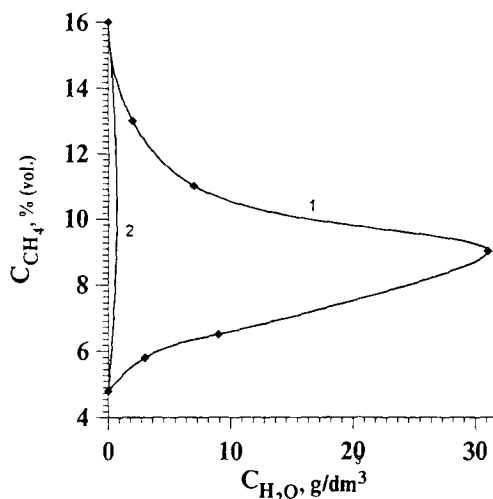


Fig. 12. Flammability limits of methane in air in dependence on mass concentration of water aerosol (1) and steam (2) [1].

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