

A theoretical investigation of iron thermochemistry in flames

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Abstract

The thermochemistry of iron in flames has been investigated theoretically using the Cantera software package. The focus was placed on the iron intermediates as well as the conditions under which condensed phases of iron or iron-species could be expected in a flame. For this purpose, equilibrium calculations were carried out for iron seeded hydrogen/oxygen/argon and propene/oxygen/argon gas mixtures at combustion relevant conditions. Varying stoichiometries over a wide range of temperatures and pressures were investigated. The results allow a prognosis which gas phase iron species may be expected in measurable concentrations at given flame conditions, and also whether condensed phases of iron or iron species are likely. Also, the effect of sampling probes on the gas mixture composition due to flame cooling is discussed.

Introduction

In recent years there has been a renewed interest in the effect of iron-containing additives, such as iron pentacarbonyl ($\text{Fe}(\text{CO})_5$) or ferrocene ($\text{Fe}(\text{C}_5\text{H}_5)_2$), on the behaviour of flames. Linteris et al. have investigated in some detail the effect of iron pentacarbonyl on the burning velocities of premixed and diffusion flames, both theoretically and experimentally [1-3]. In addition to the flame inhibiting effect of iron pentacarbonyl or ferrocene, current interest is moving towards the formation of condensed phases, soot or iron oxides. Hirasawa et al. [4] found that ferrocene addition reduced the critical sooting C/O ratio of premixed ethylene flames. However, Kim et al. [5] found that although iron addition had a soot-enhancing effect early in the flame, it caused an overall reduction in soot emissions. This was explained with an increased rate of soot oxidation in the soot burnout regime of the flame.

$\text{Fe}(\text{CO})_5$ and ferrocene have also been investigated of late as precursors for nano-particles [6, 7] or carbon nano-tubes [8-10].

Both, for the investigation of the flame effects and also for the work on nano-particles, nozzle sampling techniques are frequently employed for subsequent analysis of the gases and/or particles using molecular beam or particle mass spectrometry (See, for example [11, 12]). Paur et al. [13] used a nozzle to produce a molecular beam which they later analysed using particle mass spectrometry. However, introducing a nozzle into the flame region also introduces a surface which is considerably cooler than the flame gases. This can lead to iron and/or iron oxide condensation on the nozzle, as was found by Tian et al. [14], and can thus complicate measurements of iron species in flames. This condensation may sometimes not occur without nozzle, so that data interpretation of studies using a sampling nozzle may get delicate. The current study focuses on the limiting case of thermodynamic equilibrium, in order to see under which conditions problems with condensation may be expected.

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software package [15]. The focus was placed on the iron intermediates as well as the conditions under which condensed phases of iron or iron-species could be expected in a flame.

Specific Objectives

The objectives of this work were twofold. Firstly, equilibrium calculations help to understand which iron intermediates can be expected under flame conditions. This can aide in the design of experiments as well as the interpretation of experimental results.

Secondly, the temperature and pressure conditions under which condensed phase iron species can be expected were to be determined. This is also important information for experimenters working with iron doped flames. Deposition of condensed iron species on cooler parts of the combustion apparatus can gravely affect the measurement results if they are not accounted for. The choice of measurement technique will also be affected if condensed iron species may be expected [14].

Methodology

For this purpose, equilibrium calculations were carried out for iron seeded hydrogen/oxygen/argon and propene/oxygen/argon gas mixtures at combustion relevant conditions, using the Cantera software package. The besides the gas phase iron species FeC_3O_5 , $\text{Fe}(\text{C}_5\text{H}_5)_2$, FeO , FeO_2 , FeH , FeOH , $\text{Fe}(\text{O})\text{OH}$ and $\text{Fe}(\text{OH})_2$, the condensed phases of Fe , FeO , $\text{Fe}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$, Fe_2O_3 and Fe_3O_4 were also included in the calculation, using the NASA thermodynamic database as the source of the thermochemistry data [16]. For both gas mixtures, calculations were carried out at three different stoichiometries: $\phi = 0.37$, 1.0, and 2.31. In each case 170 ppm of iron pentacarbonyl or ferrocene were added. Temperatures were varied from 1100 K to 2500 K at pressures between 30 mbar and 10 bar.

Results and Discussion

The results of the calculations are shown in figures 1 to 4. Only those iron species are shown that have concentrations above 10^{-9} at the given temperatures. Not

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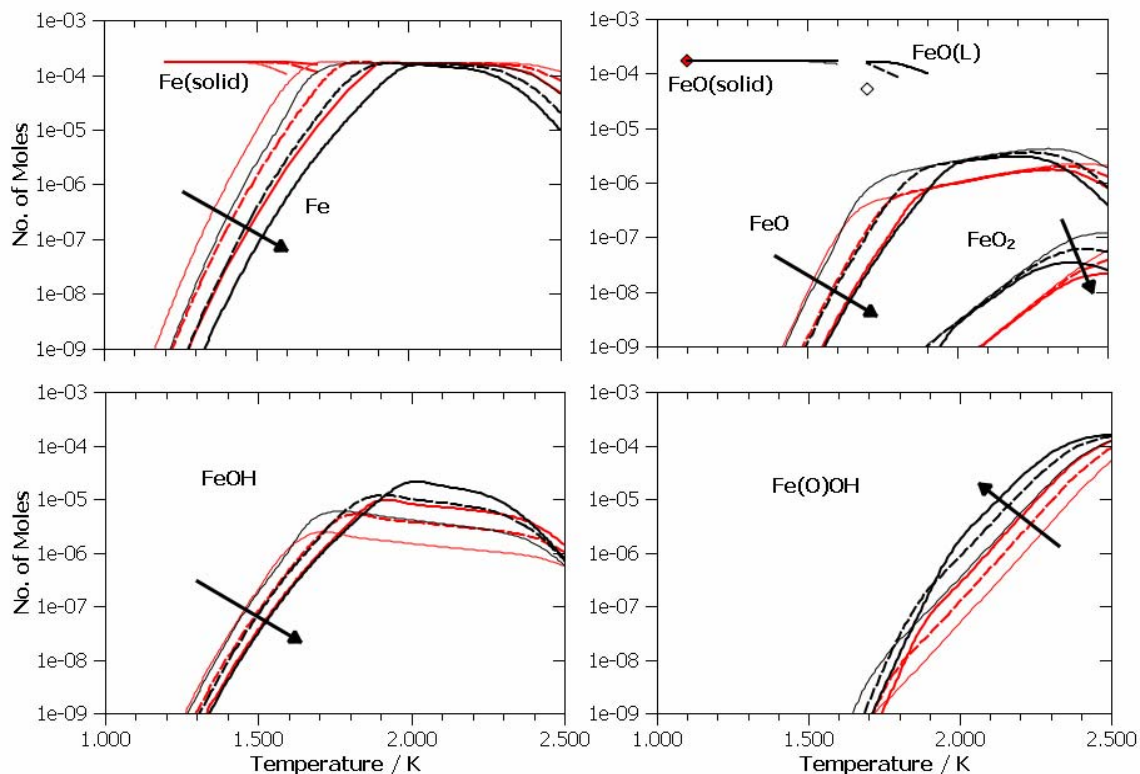


Fig. 1. Effect of fuel and pressure on iron species for fuel rich mixtures ($\phi = 2.31$) (red lines/symbols: C_3H_6 , black lines/symbols: H_2 , thin line/empty symbol: 30 mbar, dashed line: 200 mbar, thick line/solid symbol: 1 bar). The arrows indicate the direction of increasing pressure)

surprisingly, the source of the iron added (iron pentacarbonyl or ferrocene) did not have a significant impact on the equilibrium of the iron species, since such a small amount was added that the stoichiometry is not influenced noticeably. The different fuels, hydrogen and propene, were mainly studied to observe the influence

of the hydrogen to carbon ratio in the mixture on the equilibrium concentrations of iron containing compounds.

Figures 1, 2 and 3 summarise the results for fuel rich ($\phi = 2.31$), stoichiometric and lean ($\phi = 0.37$) conditions, respectively. Figure 1 shows the effect of pressure on

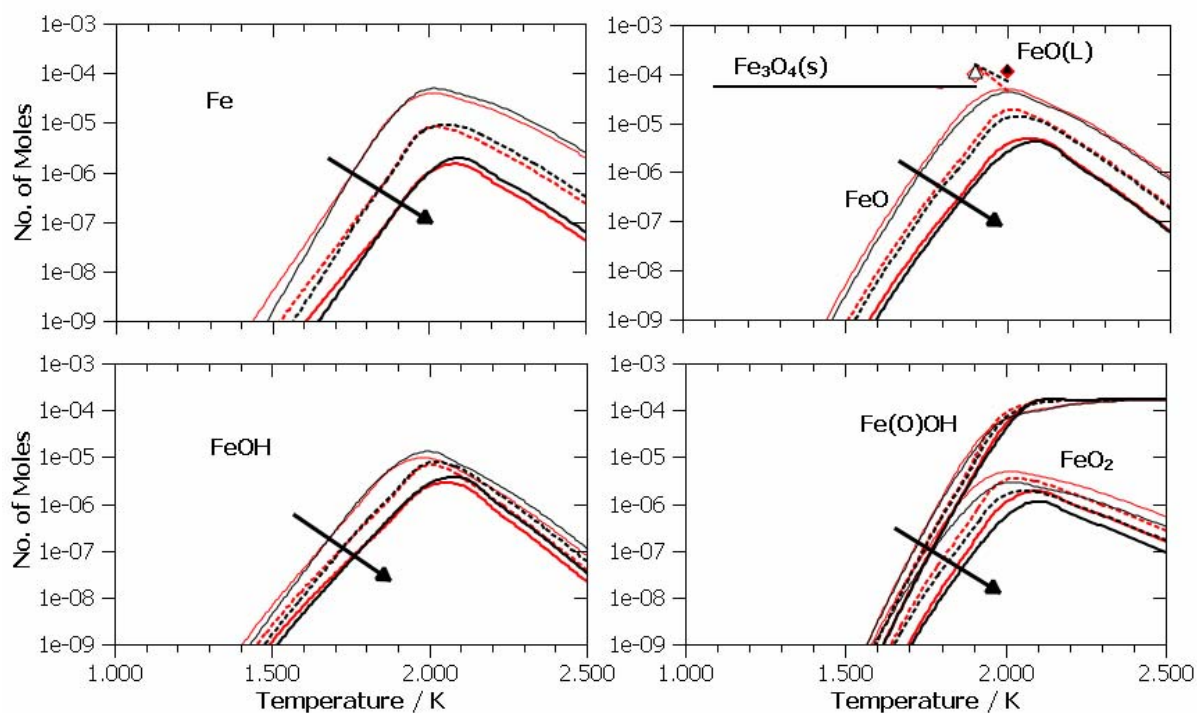


Fig. 2. Effect of fuel and pressure on iron species for stoichiometric mixtures (red lines/symbols: C_3H_6 , black lines/symbols: H_2 , thin line/empty symbol: 30 mbar, dashed line: 200 mbar, thick line/solid symbol: 1 bar)

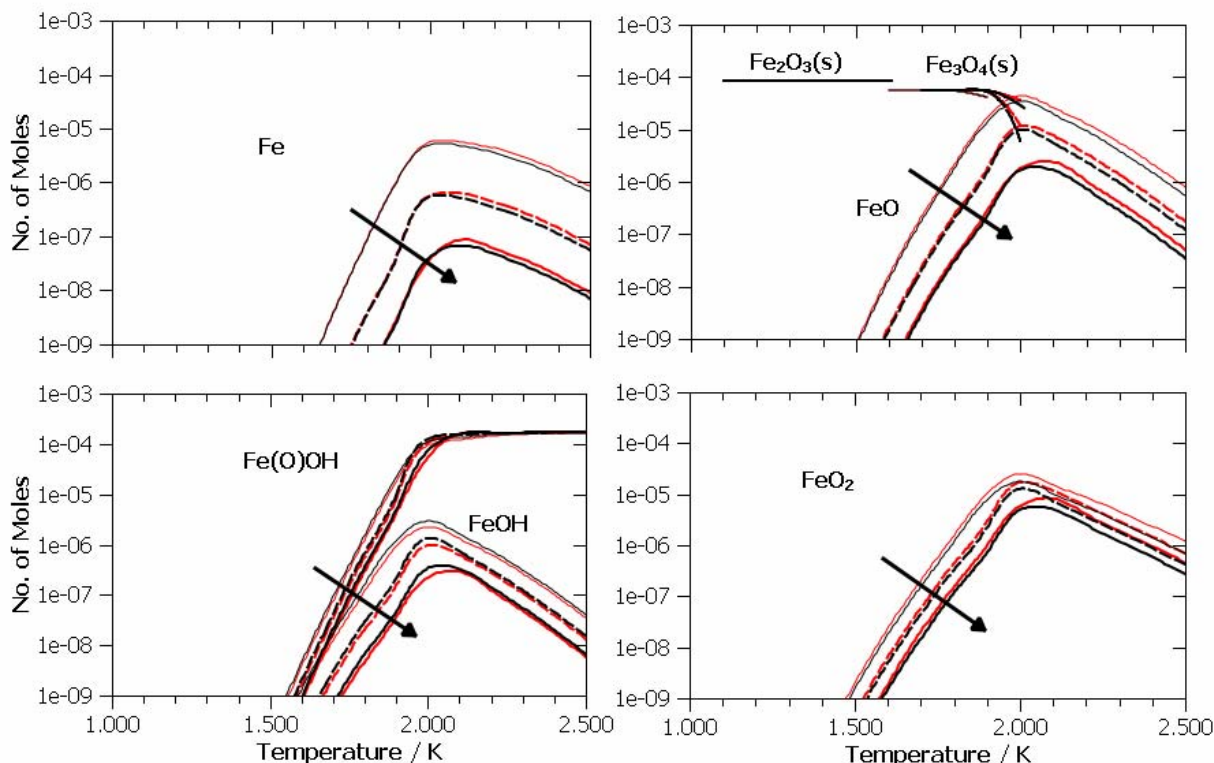


Fig. 3. Effect of fuel and pressure on iron species for lean mixtures ($\phi = 0.37$) (red lines/symbols: C_3H_6 , black lines/symbols: H_2 , thin line/empty symbol: 30 mbar, dashed line: 200 mbar, thick line/solid symbol: 1 bar)

the concentration of the various gas phase iron species for both fuels that were examined. As can be seen, increasing the pressure will shift the curves for atomic iron, iron oxides and FeOH towards higher temperatures. This trend is only reversed for FeO(O)H.

Some difference can be seen when comparing the two fuels investigated, mainly under fuel rich conditions. For the propene, the solid iron phase occurring above $1100^\circ C$ is atomic iron, whereas in the hydrogen system, condensed iron oxide is forming. This effect also explains the difference in the occurrence of gaseous atomic iron at temperatures below 1600 K (at 30 mbar), 1700 K (200 mbar) or 1900 K (1 bar). In the presence of carbon, relatively large amounts of oxygen are bound as carbon dioxide and carbon monoxide. As can be seen from figures 2 and 3, the difference between the two fuels is much less pronounced in stoichiometric and lean mixtures, because more oxygen is available then.

At all stoichiometries that were examined here, the iron tends to form Fe(O)OH at higher temperatures. The more oxygen is available, the lower the temperature at which almost all iron exists in the form of Fe(O)OH; at $\phi = 0.37$ this is at around 2000 K, whilst for $\phi = 2.31$ it is not until 2500 K. This species may be an interesting candidate for spectroscopic flame studies.

Figure 4 shows the temperatures below which condensed phases of iron species can be expected in equilibrium. As can be seen from the previous figures, this will be in the form of solid atomic iron for the fuel rich propene mixture and iron oxides (FeO , Fe_2O_3 or Fe_3O_4) for the fuel rich hydrogen mixture and the

stoichiometric or lean mixtures of both fuels. Hence, the type of fuel, or more correctly the ratio of hydrogen to carbon in the mixture, only has an effect at the higher equivalence ratio. This shows that of the iron species examined here, pure iron condenses at the lowest temperatures with 1600 K at 30 mbar. The occurrence of solid iron is most likely in oxygen-lean mixtures; as more oxygen is available the iron equilibrium will tend towards iron oxides, which will condense already at higher temperatures (from 1700 K at 30 mbar to 1900 K at atmospheric pressure in the case of FeO, and the other oxides at even higher temperatures).

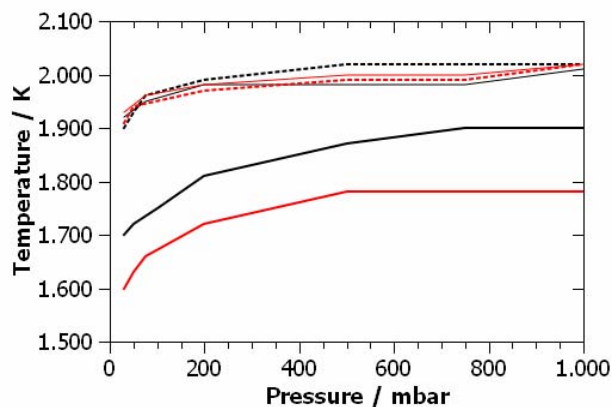


Fig. 4. Maximum temperature of condensed phase iron as a function of pressure, effect of stoichiometry and fuel (red: C_3H_6 , black: H_2 , thick lines: $\phi = 2.31$, dashed: $\phi = 1$, thin: $\phi = 0.37$)

Generally, it can be noted that the temperature below which condensed phases can be expected is reduced as the pressure is reduced.

Since the above observations are based on equilibrium calculations, they are not representative of the mixture composition near the flame front, even at the same temperature and pressure conditions. They can, however, give an indication of the species that could be expected in those regions of the combustion chamber where longer residence times of the gases are possible.

When a nozzle is used for sampling from a flame, for example to produce a molecular beam for gas phase mass spectrometry (e.g. [11]) or particulate sampling (as suggested by Roth [17]), the local temperature can be reduced drastically to well below the condensing temperatures. For quartz nozzles this temperature will be typically below 1400 K, whilst the adiabatic flame temperatures for these mixtures lie between around 2700 K at 30 mbar and around 3200 K at atmospheric pressure in this stoichiometric range. The effect can be the deposition of iron and/or iron oxides on the sampling nozzle, which will lead to a reduced nozzle aperture. By the same token, any iron that condenses on the nozzle can not be detected by any measurement equipment analysing the molecular beam, thus making MBMS not viable measurement technique for iron species under those conditions. Surely this condensation can also take place in part in the gas phase, leading to particle formation, which may deteriorate the measured particle size distribution.

Conclusions

The equilibrium calculations for propene/oxygen/argon and hydrogen/oxygen/argon gas mixtures seeded with 170 ppm iron pentacarbonyl or ferrocene have shown that both pressure and mixture composition have an effect of the iron intermediates that will form. The calculated profiles may aid the design of future laser diagnostics studies by helping to find conditions with relatively high concentrations of iron species in the gas phase, such as Fe, Fe(O)OH or FeO.

For the case of the condensed iron species, lowering the pressure will reduce the temperature below which they can be expected. But even at pressures as low as 30mbar, solid atomic iron may be present until temperatures of 1600K and above. This is well above the temperature of, for example, a sampling nozzle for molecular beam mass spectrometry. Hence, MBMS techniques are probably not viable for the detection of iron and iron intermediates from flames.

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