

Published in final edited form as:

Combust Sci Technol. 2017 ; 189(12): . doi:10.1080/00102202.2017.1347162.

Flame Inhibition by Potassium-Containing Compounds¹

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Abstract

A kinetic model of inhibition by the potassium-containing compound potassium bicarbonate is suggested. The model is based on the previous work concerning kinetic studies of suppression of secondary flashes, inhibition by alkali metals and the emission of sulfates and chlorides during biomass combustion. The kinetic model includes reactions with the following gas-phase potassium-containing species: K, KO, KO₂, KO₃, KH, KOH, K₂O, K₂O₂, (KOH)₂, K₂CO₃, KHCO₃ and KCO₃. Flame equilibrium calculations demonstrate that the main potassium-containing species in the combustion products are K and KOH. The main inhibition reactions, which comprise the radical termination inhibition cycle are KOH+H=K+H₂O and K+OH+M=KOH+M with the overall termination effect: H+OH=H₂O. Numerically predicted burning velocities for stoichiometric methane/air flames with added KHCO₃ demonstrate reasonable agreement with available experimental data. A strong saturation effect is observed for potassium compounds: approximately 0.1% volume fraction of KHCO₃ is required to decrease burning velocity by a factor of 2, however an additional 0.6% volume fraction is required to reach a burning velocity of 5 cm/s. Analysis of the calculation results indicates that addition of the potassium compound quickly reduces the radical super-equilibrium down to equilibrium levels, so that further addition of the potassium compound has little effect on the flame radicals.

Keywords

potassium-containing fire suppressant; potassium bicarbonate; flame inhibition; kinetic model; saturation effect

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1. Introduction

Experimental data have shown that for addition at low volume fraction, compounds containing alkali metals (K, Na) are highly effective flame inhibitors (Birchall, 1970; Friedman and Levy, 1963; Rosser et al., 1963; Hastie, 1973; Iya et al., 1974; Baratov et al., 1991; Hoffmann, 1971; Tapscott et al., 2001; Chatrathi and Going, 2000; Linteris et al., 2008; Hoorelbeke, 2011), about an order of magnitude more effective than CF_3Br on a molar basis. This performance is approaching that of Fe-, Pb- and Cr-containing compounds (Babushok and Tsang, 2000). While potassium-containing compounds have been found to be very effective at reducing burning velocity (Rosser et al., 1963; Hoffmann, 1971; Hoorelbeke, 2011), much of the research has aimed to determine the concentration of agent required to extinguish a flame, using a variety of configurations (e.g., opposed-flow diffusion, cup-burner, liquid pan flame) and for different fuels (methane, propane, heptane, hydrogen) (Ewing et al., 1989; Baratov and Korol'chenko, 1990; Chattaway et al., 1995; Reed et al., 1997a; Chatrathi and Going, 2000; Hoorelbeke, 2011). Because of their proven effectiveness, potassium compounds are the primary constituents of several commercial dry chemical fire suppression compositions, e.g. Monnex, Purple K, Super K.

The mechanism of flame inhibition by potassium was analyzed in several works (Birchall, 1970; Hastie, 1973; McHale, 1975; Jensen et al., 1979; Hastie et al., 1986; Heimerl, 1984; Slack et al., 1989; Baratov et al., 1991). It was suggested that the main radical scavenging reactions (chain carrier termination reactions) are the termolecular recombination reaction $\text{OH} + \text{K} + \text{M} = \text{KOH} + \text{M}$ and the radical scavenging reactions of hydrogen atom and hydroxyl radical with potassium hydroxide, which regenerates the potassium atom: $\text{H} + \text{KOH} = \text{H}_2\text{O} + \text{K}$, and $\text{OH} + \text{KOH} = \text{KO} + \text{H}_2\text{O}$ with further reactions of KO with radicals $\text{KO} + (\text{H}, \text{O}, \text{OH}) = \text{K} + (\text{OH}, \text{O}_2, \text{HO}_2)$. Kinetic models of the behavior of potassium containing species in combustion processes were suggested for the analysis of secondary flash suppression (Heimerl, 1984; Slack et al., 1989) and for the analysis of sulfur and chlorine partitioning with potassium salts in the products of biomass combustion (Hindlyarti et al., 2006; Li et al., 2013).

The purpose of the present work is to develop a detailed gas-phase kinetic model of inhibition of hydrocarbon-air flames by potassium compounds. To this end we present the thermochemistry of K-containing species relevant to the combustion environment, using data in literature when available. When data are absent the thermochemistry is estimated. The kinetic model was compiled from the data available in literature and additional reactions were considered. Using the suggested model, we analyzed the inhibition mechanism of potassium bicarbonate in methane-air flames.

2. Kinetic model. Modeling procedure

Table 1 lists the potassium-containing species considered in the kinetic model, as well as their enthalpy of formation H , standard entropy S , and specific heat at constant pressure C_p (all at 298.15 K). Reactions for most of these species were discussed in previous studies of combustion processes with added potassium compounds (Heimerl, 1984; Slack et al., 1989; Baratov et al., 1991; Glarborg and Marshall, 2005; Hindlyarti et al., 2006). Data have been

added for several species in a condensed phase and for the potassium dimer (Table 1). The Supplemental Materials include the data in the format of the Chemkin suite of programs (Kee et al., 1986, 1989, 1991), which were used for the present simulations.

The kinetic model consists of two sets of reactions. The first is for hydrocarbon combustion, for which Grimech-3.0 is adopted (Smith et al., 2000), and the second is for the reactions of potassium-containing species with the species of the hydrocarbon system. Table 2 shows the reactions of potassium-containing species, consisting of 85 reactions of 12 species (K, KH, KO, KO₂, KO₃, K₂O, K₂O₂, KOH, (KOH)₂, K₂CO₃, KCO₃ and KHCO₃). The set of reactions with K-containing species includes reactions considered in the literature along with their rate parameters. Additional reactions were also added from the analysis of plausible reactions based on thermochemical considerations, with their rates estimated by analogy or using empirical correlations. Note that the kinetic mechanism for the behavior of potassium-containing species was analyzed in several works for different environments (Hastie, 1973; Hastie et al., 1986; Jensen et al., 1979; Slack et al., 1989; Baratov et al., 1991; Benilov et al., 1994; Glarborg and Marshall, 2005; Hindlyarti et al., 2006; Plane et al., 2014).

There are very few experimental data on the influence of potassium compounds on the burning velocity of hydrocarbon systems. For comparison with model predictions we have used experimental data of Rosser et al. (1963) and Hoffmann (1971) on the influence of KHCO₃ on burning velocity of a stoichiometric methane-air flame. Note that KHCO₃ is added to the flames as solid particles, for two ranges of diameter: 2.2 μm (Rosser et al., 1963) and 32–40 μm (Hoffmann, 1971). The experimental data demonstrate that small particles (i.e., those with diameter less than roughly 5–25 μm) provide the maximum inhibition effect (Rosser et al., 1963; Ewing et al., 1989; Ewing et al., 1992); whereas larger particles have lower inhibition effectiveness. This is likely due to the slower evaporation of the larger particles, leading to lower gas-phase potassium species volume fractions in the reactions zone. Experimental studies on the effect of large size KHCO₃ particles on burning velocity of propane were conducted by Hoorelbeke and van Wingerden (2009) and Hoorelbeke (2011). The present comparison of modeling results with experimental data assumes complete evaporation of KHCO₃ particles in the flame reaction zone. Note that in the simulations, although the species KHCO₃ is added as a solid, all references to its concentration in the flames are listed as the volume fraction of the gasphase species that it evaporates to. This facilitates the comparisons with other agents, for which the volume basis (i.e., molar) is the most tractable. Figure 1 shows the measured and numerically predicted normalized burning velocity of premixed stoichiometric methane-air flames as a function of the KHCO₃ volume fraction (added as solid particles); the agreement is reasonable.

3. Results and discussion

Figure 2 shows equilibrium volume fractions of potassium containing species in methane-air flames with added KHCO₃(s) (volume fraction 0.25%) as a function of the fuel-air equivalence ratio. For comparison purposes, Figure 3 provides similar results for sodium bicarbonate (solid). Despite the differences in the absolute level of the equilibrium concentrations, the alkali metal atom and the corresponding hydroxide (KOH and NaOH)

are the major species in the combustion products. For very lean mixtures, KO_2 and KO become significant species. For sodium, low temperature combustion products contain rather large equilibrium concentrations of Na_2CO_3 . These calculations indicate that the main alkali metal-containing species in a flame reaction zone are potassium and sodium atoms and their hydroxides. Note that compounds of potassium in a condensed phase were not considered in flame equilibrium calculations except of initial agent KHCO_3 .

Using the above mechanism, simulations for a stoichiometric methane-air flame with added inhibitor (KHCO_3 , NaHCO_3 , and CF_3Br) are shown in Figure 4. For comparison purposes, calculations are also performed for NaHCO_3 , using the model of Babushok et al. (2003), and for CF_3Br , using the model from Babushok et al. (2015). For KHCO_3 or NaHCO_3 addition, it is assumed that the particles are small and that they rapidly evaporate and decompose. The simulations indicate that KHCO_3 is a more effective inhibitor than sodium bicarbonate, and is a significantly more effective inhibitor than CF_3Br (by a factor of 21, for achieving a 10% reduction in burning velocity), which is consistent with previous experimental results (Babushok and Tsang, 2000).

Figure 5 illustrates the flame structure of a stoichiometric methane-air flame inhibited by KHCO_3 . The main potassium-containing species in the flame zone are potassium atom and potassium hydroxide. A relatively large concentration of KO_2 is observed in a low temperature range as a result of relatively fast formation through the termolecular reaction $\text{K} + \text{O}_2 + \text{M} = \text{KO}_2 + \text{M}$. The KO_2 concentration decreases, and its contribution to the flame inhibition decreases, nearer to the high temperature region of the flame. A relatively large concentration of $(\text{KOH})_2$ is observed in the low temperature region of the flame, as a result of association reaction $\text{KOH} + \text{KOH} = (\text{KOH})_2$. Nonetheless, in the higher temperature regions of the flame, the concentration of $(\text{KOH})_2$ is low and its reactions are not important for flame inhibition (hence it is not shown in Figure 5).

Figures 6 (a,b) show the reaction rate profiles of the main reactions for consumption of H and OH radicals, and Figure 6c shows the main reactions for the formation and consumption of potassium atom in the main reaction zone of the flame. As can be seen, for potassium species reactions, the main H atom scavenging reaction is $\text{KOH} + \text{H} = \text{H}_2\text{O} + \text{K}$, and the OH radical termination reaction is $\text{OH} + \text{K} + \text{M} = \text{KOH} + \text{M}$. For a KHCO_3 additive mole fraction of 0.05% (corresponding to a burning velocity decrease about 45%), the rate of the reaction $\text{KOH} + \text{H}$ is about 30% of the rate of the chain-branching reaction $\text{H} + \text{O}_2 = \text{OH} + \text{H}$.

Thus, the main radical scavenging reactions of potassium-containing species are $\text{K} + \text{OH} + \text{M} = \text{KOH} + \text{M}$ and $\text{KOH} + \text{H} = \text{K} + \text{H}_2\text{O}$. The sequence of these reactions represents a relatively simple radical recombination cycle: potassium atom recombines mostly with hydroxyl radical with formation of potassium hydroxide. The further reaction of potassium hydroxide with hydrogen atom regenerates the potassium atom and completes the inhibition cycle with the overall radical recombination: $\text{OH} + \text{H} = \text{H}_2\text{O}$. This radical recombination cycle was considered in earlier work studying potassium-compound flame inhibition (Birchall, 1970; Hastie, 1973; Jensen et al., 1979) and suppression of secondary combustion (Hastie et al., 1986; Heimerl, 1984). Comparison with the inhibition mechanism of sodium compounds: $\text{Na} + \text{OH} + \text{M} = \text{NaOH} + \text{M}$ and $\text{H} + \text{NaOH} = \text{Na} + \text{H}_2\text{O}$, indicates that the potassium

radical recombination cycle is similar, in agreement with earlier studies (Hastie, 1973; Jensen and Jones, 1982; Williams and Fleming, 1999; Babushok et al., 2003).

Additional reactions of KO and KO₂ may also be important (Hindlyarti et al., 2006; Friedman and Levy, 1963). Hindlyarti et al. (2006) studied the influence of potassium chloride on the CO oxidation by water vapor in nitrogen diluted mixtures in a flow reactor at 773–1373 K. The reaction $\text{KOH} + \text{OH} = \text{KO} + \text{H}_2\text{O}$ was included in the model as the reverse reaction, and they concluded that it is the main reaction for KOH removal for their experimental conditions. The H atom concentration was very low at these conditions (unlike flame conditions, for which H-atom concentration is relatively high, comparable to that of OH). For the estimate of the rate constant for the reverse process (KO+H₂O), Hindiyarti et al (2006) used 1.3×10^{14} (cm³/mole/s) with zero activation energy. We have used the rate constant of Slack et al. (1989), which at flame temperatures is roughly comparable with the data of Hindiyarti et al (2006).

For addition of KHCO₃ to premixed methane-air flames ($\phi=0.7, 1.0, \text{ and } 1.34$), the calculations show a strong decrease in the reduction in burning velocity with increasing addition of agent (Figure 4). This saturation in the inhibition effect is pronounced for gas-phase KHCO₃ volume fractions in the range 0.001 to 0.002, and appears to occur at lower agent loadings for initially richer flames. The inhibition at low loading is also less for richer premixed CH₄-air flames, as was also found in experimental studies (Hoorelbeke, 2011; Hoorelbeke and van Wingerden, 2009), and has been shown for iron (Reinelt and Linteris, 1996; Rumminger et al, 1999), phosphorus (Babushok et al., 2016), HBr (Westbrook, 1980), and Br₂ (Rosser et al, 1958). Figure 7 shows the maximum (solid lines) and equilibrium (dotted lines) concentrations of hydroxyl radical as a function of KHCO₃ concentration. It can be seen that the radical overshoot (the difference between maximum radical concentration and the equilibrium concentration) is decreasing with inhibitor concentration. At a gas-phase volume fraction of KHCO₃ around 0.1 % the OH radical overshoot is disappearing, meaning that the maximum radical concentration does not occur in the main reaction zone of the flame. This can be interpreted as the suppression of chain-branching processes in a flame, as discussed in the work (Noto et al., 1998). Since the burning velocity is generally correlated with radical concentrations (Tanford and Pease, 1947), further reduction in burning velocity would require an inhibitor with some physical effect to lower flame temperature. Figure 8 shows the hydroxyl radical profiles in a methane/air stoichiometric flame at different inhibitor volume fractions. Again, it can be seen that at a KHCO₃ volume fraction of about 0.1%, the radical overshoot disappears, and the maximum hydroxyl concentration is the flame equilibrium concentration. The further addition of agent leads to a decrease of equilibrium concentration as a result of decrease in the equilibrium temperature.

Addition of potassium compounds to a flame accelerates combustion in some regions, and retards it in others. Figure 9a shows the temperature profiles corresponding to the OH profiles of Fig. 8, for the early parts of the flames, while Fig. 9b shows the latter parts. As discussed by Dixon-Lewis and Simpson (1976), addition of the inhibitor decreases the reaction rate in the flame reaction zone (the initial tangent of temperature increase), due to reduced rates of buildup of the chain branching radical pool. Of course, the adiabatic

combustion temperature is reduced with addition of potassium bicarbonate due to its endothermic decomposition and release of the relatively inert CO_2 which acts as a diluent. Nonetheless, as shown in Figure 9b, downstream of the main reaction zone of the flame, the presence of the potassium compound leads to a higher rate of temperature increase towards the equilibrium value. Examination of the reaction fluxes in the downstream region shows that this is due to CO conversion to CO_2 via: $\text{KO} + \text{CO} = \text{K} + \text{CO}_2$, which does not occur in the flames without KHCO_3 .

It is of interest to compare available experimental data on suppression concentrations of KHCO_3 with modeling predictions based on the suggestion that a burning velocity of 5 cm/s roughly corresponds to the flammability limits, although of course this is a very approximate estimation (Egerton and Thabet, 1952; Westbrook, 1983). The calculations (Figure 4) demonstrate that a KHCO_3 volume fraction of 0.7 % is required to reach the burning velocity of 5 cm/s burning velocity for a stoichiometric mixture. For NaHCO_3 (Babushok et al., 2003), a volume fraction of about 2 % is required. Experimental data demonstrate the following suppression gas-phase volume fractions for KHCO_3 : 0.57 % (premixed methane flame, (Ewing et al., 1984)), 0.78% (diffusion flame, heptane, (Ewing et al., 1992)) and 0.61% (pan fire, heptane, Purple-K, (Chattaway et al., 1995)), which reasonably corresponds to the 0.7 % estimate above. For sodium compounds, experimental data generally show about twice as much required (on a mass basis) as compared to potassium, consistent with the above simulations (Birchall, 1970; Fischer and Leonard, 1995; Reed et al., 1997b).

4. Conclusions

A detailed kinetic model of influence of potassium-containing compounds on hydrocarbon-air flames has been developed, and includes 85 reactions of 12 potassium-containing species (K , KO , KO_2 , KO_3 , K_2O , KH , KOH , KCO_3 , KHCO_3 , K_2CO_3 , K_2O_2 , $(\text{KOH})_2$). Simulations employing the mechanism to model premixed methane-air flames inhibited by potassium bicarbonate, have indicated the following:

1. The calculated burning velocity of premixed CH_4 -air flames with added KHCO_3 agrees reasonably well with available experimental data assuming fast evaporation of inhibitor particles in a flame reaction zone.
2. Flame equilibrium calculations demonstrate that the main K-containing species in the combustion products are potassium hydroxide and potassium atom. The species KO and KO_2 are always more than an order of magnitude lower in volume fraction than K and KOH , over a range of equivalence ratios. For very lean conditions (ϕ less than about 0.6) concentrations of KO , KO_2 and $(\text{KOH})_2$ become comparable with K , but are still substantially less than that of KOH .
3. For CH_4 /air flames, the main inhibition reactions are $\text{K} + \text{OH} + \text{M} = \text{KOH} + \text{M}$ and $\text{H} + \text{KOH} = \text{K} + \text{H}_2\text{O}$.
4. The marginal effect of added KHCO_3 to lower the burning velocity in near-stoichiometric CH_4 -air flames is reduced greatly above volume fractions from 0.1 % to 0.2 %. At these loadings, the peak OH radical volume fraction is lowered to equilibrium values, and the burning velocity is about 10 cm/s. Further

decrease in the burning velocity (down to suppression level) is likely the result of reductions in the radical concentrations due to lower temperatures from thermal effects of agent addition.

5. The inhibition effectiveness of KHCO_3 is higher in lean mixtures than in rich fuel mixtures.

Acknowledgements

The work of VB was supported by Total Refining & Chemicals.

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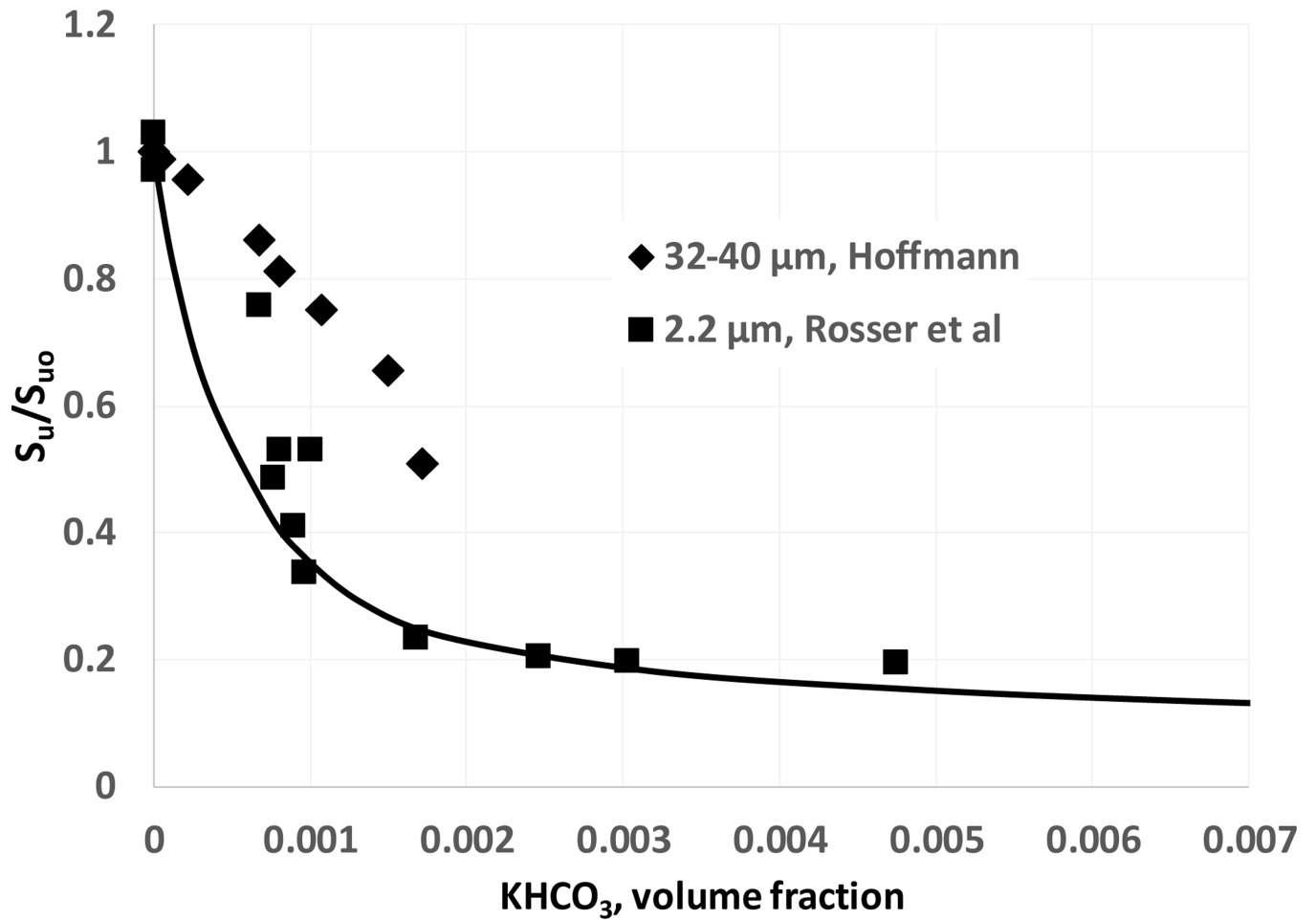


Figure 1. Dependence of burning velocity S_u normalized by the uninhibited burning velocity S_{u0} on KHCO_3 volume fraction for stoichiometric methane-air flame (line: calculations; symbols: experimental data; initial conditions: 298 K, 101.33 kPa).

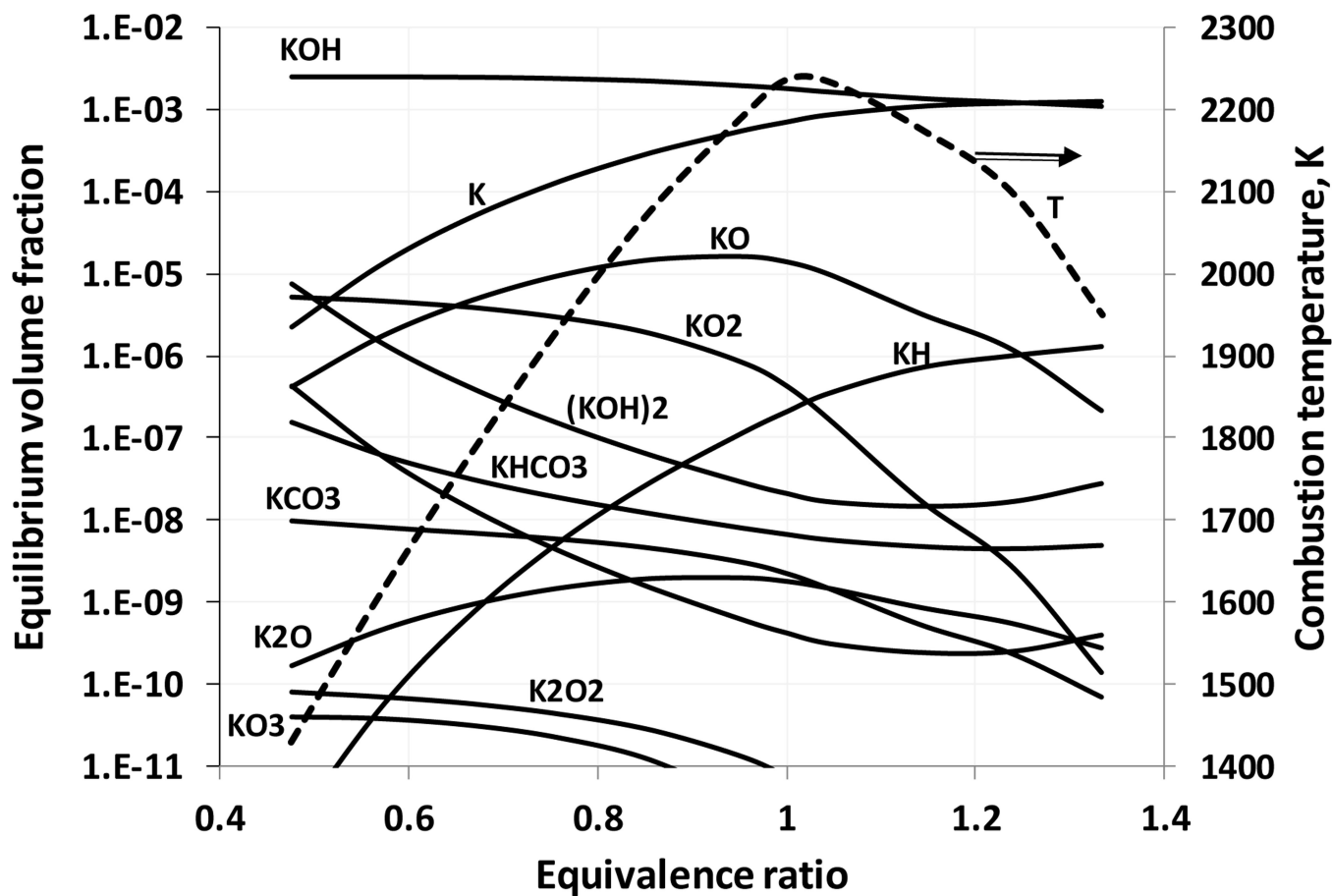


Figure 2. Equilibrium volume fraction of potassium-containing species in the combustion products of a methane-air flame as a function of equivalence ratio (initial conditions: 298 K, 101.33 kPa, $\text{KHCO}_3(\text{s})$ mole fraction of 0.25%).

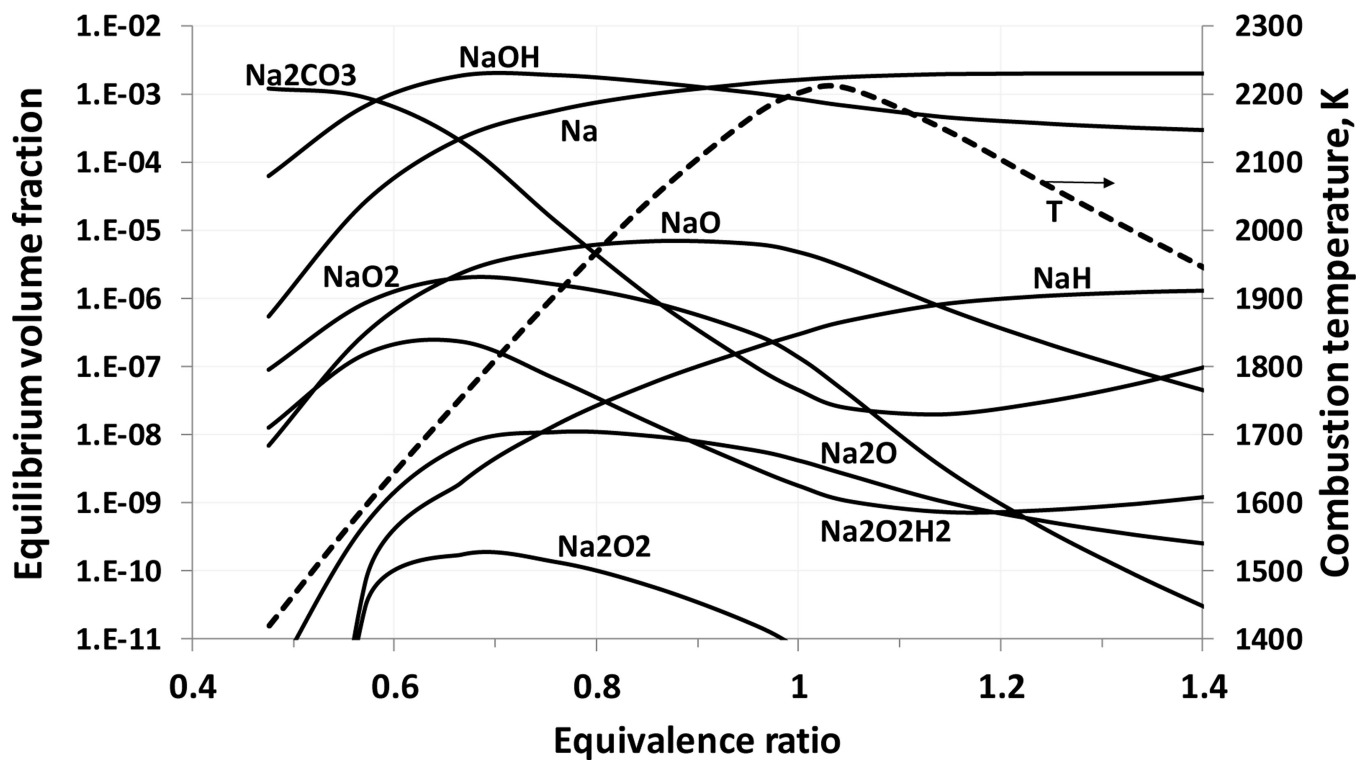


Figure 3. Equilibrium volume fraction of sodium-containing species in the combustion products of a methane-air flame as a function of equivalence ratio (initial conditions: 298 K, 101.33 kPa, NaHCO₃(s) mole fraction of 0.25%).

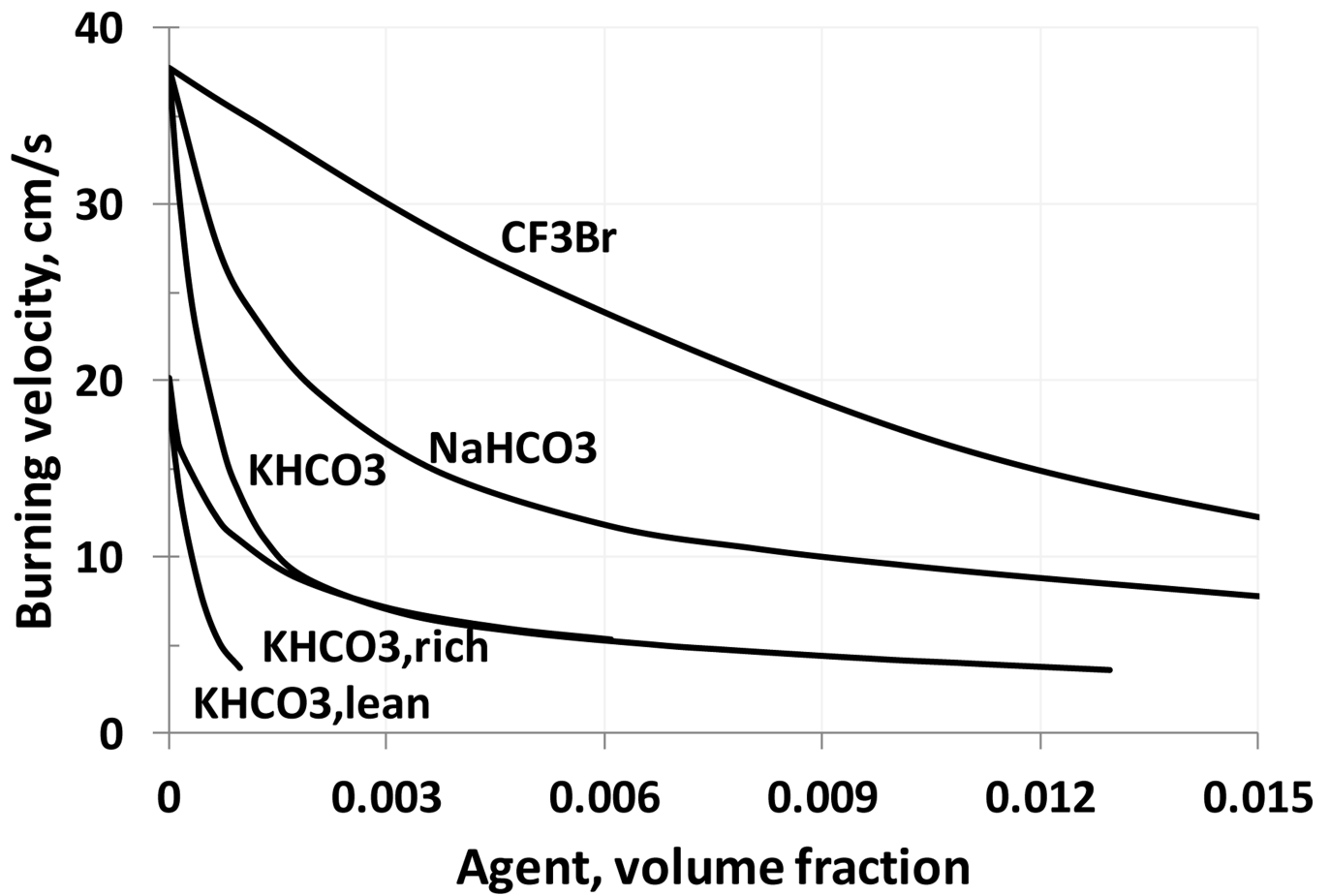


Figure 4. Dependence of burning velocity on inhibitor mole fraction for added CF_3Br , NaHCO_3 , and KHCO_3 (initial conditions: methane-air, 298 K, 101.33 kPa; stoichiometric, lean and rich mixtures, $\phi=0.7, 1.0,$ and 1.34).

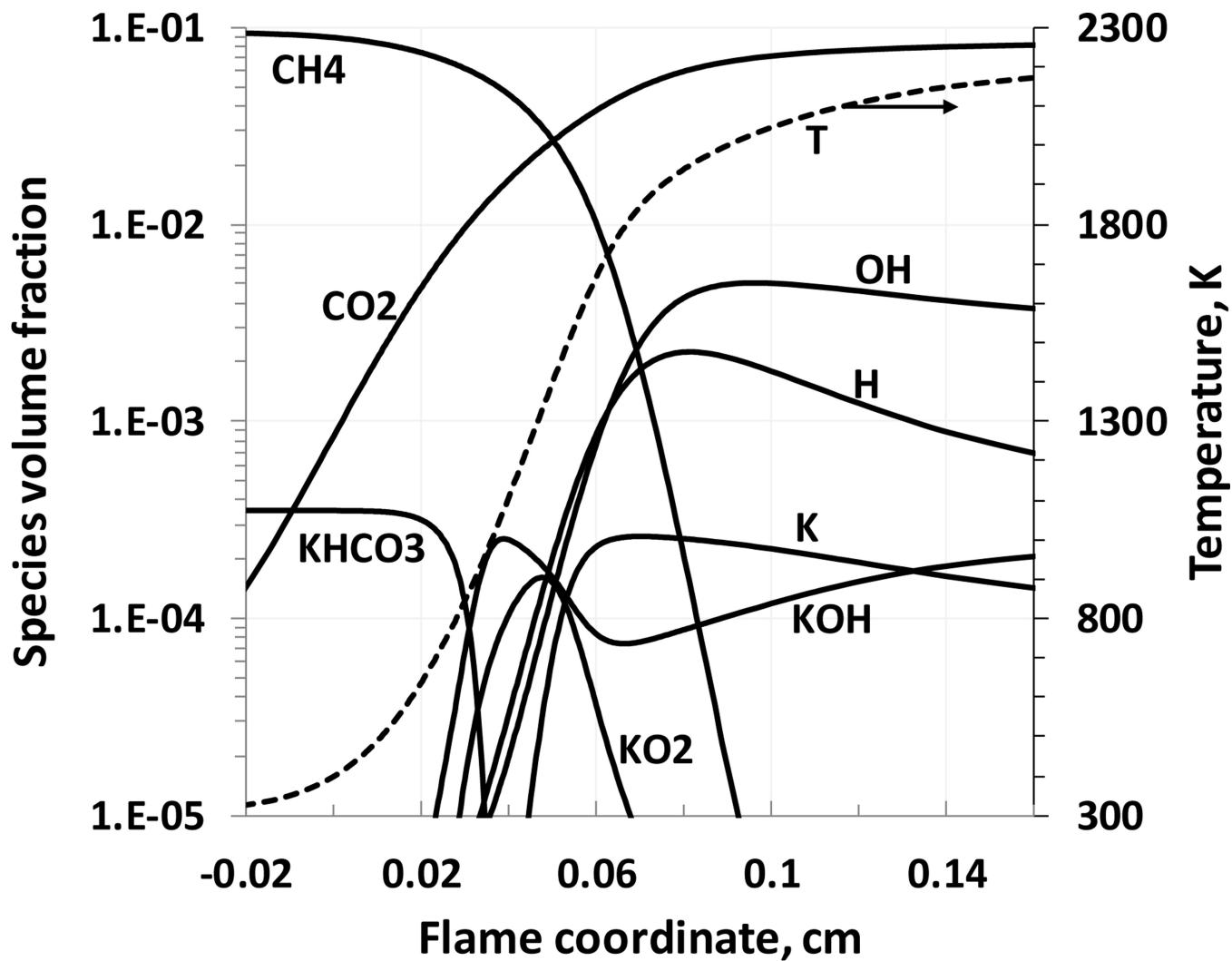
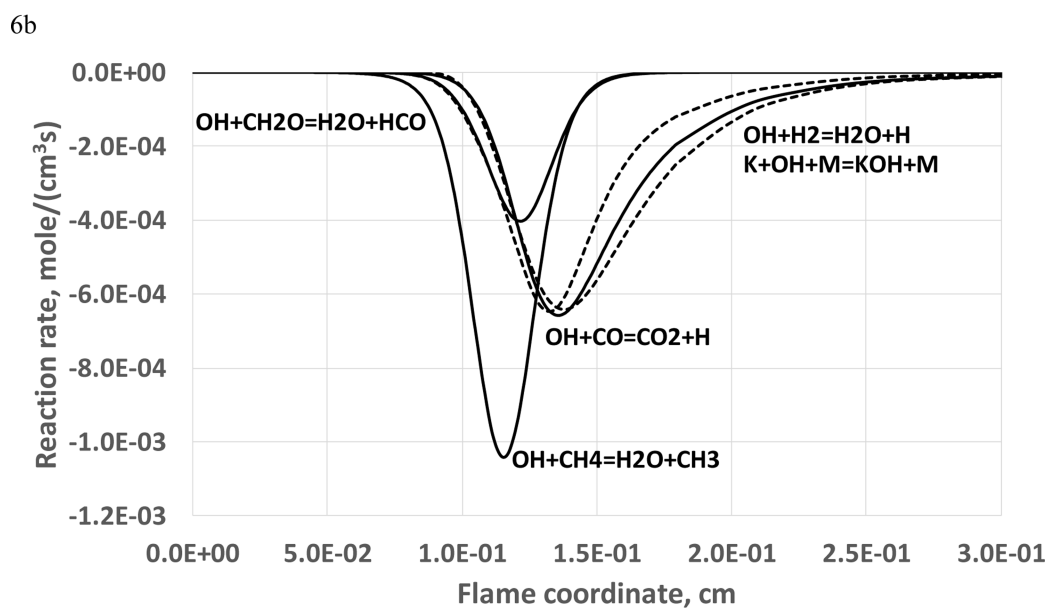
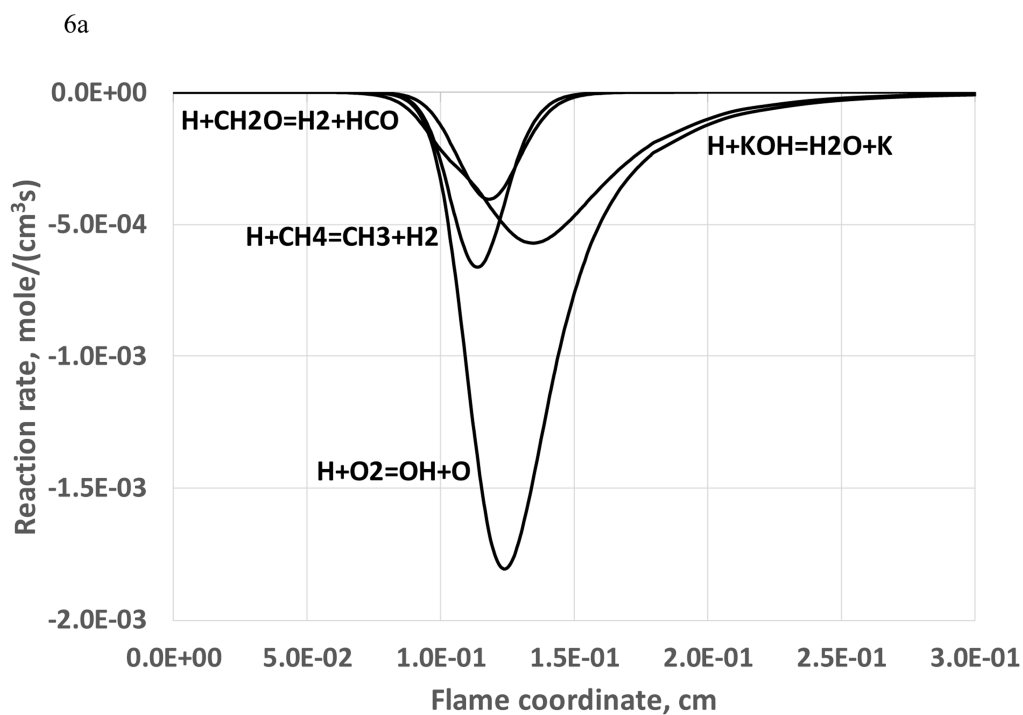


Figure 5.
Flame structure of KHCO_3 -inhibited stoichiometric methane flame (initial conditions: 298 K, 101.33 kPa, $\text{KHCO}_3(\text{s})$ mole fraction of 0.036%).



6c

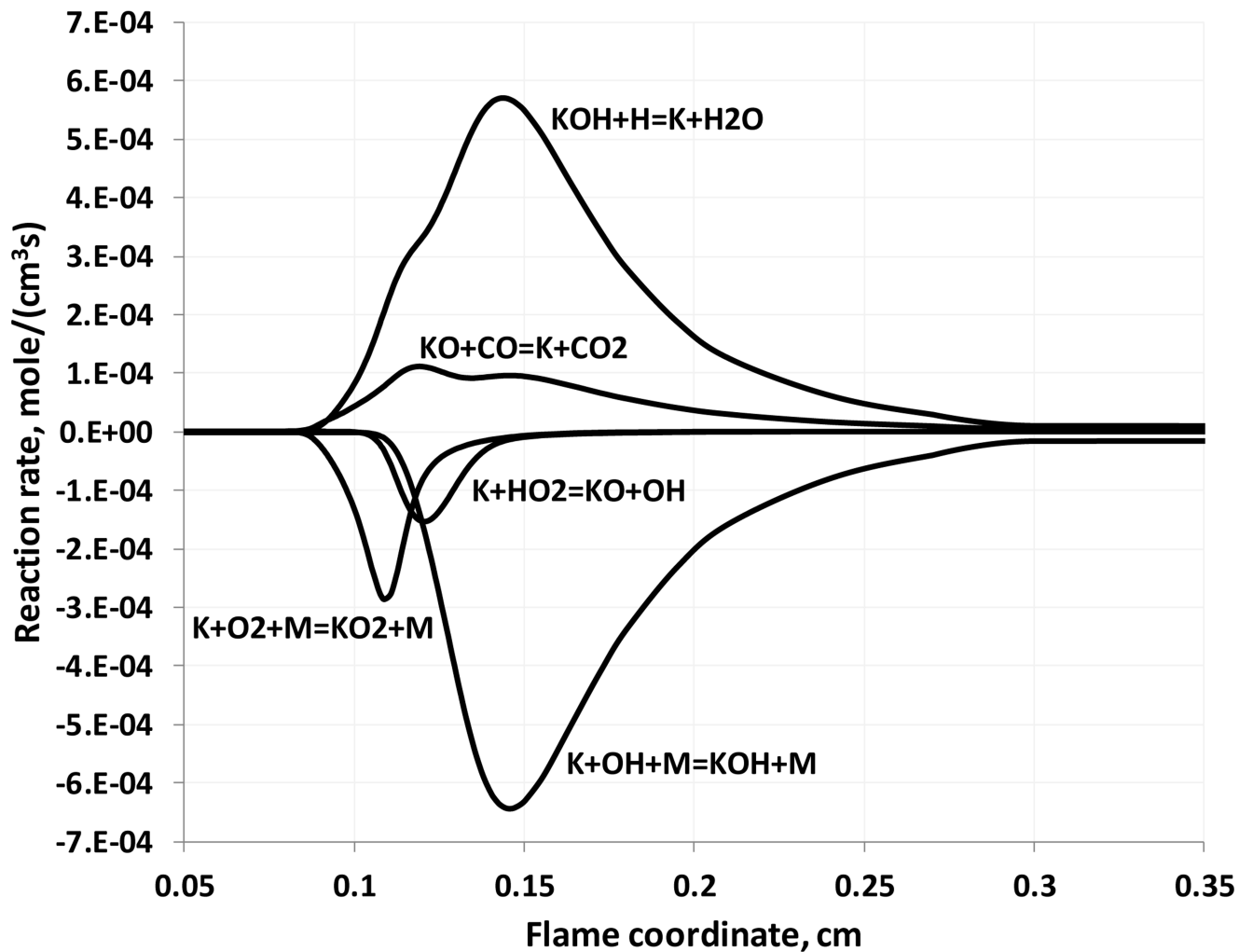


Figure 6.

Reaction fluxes as a function of position in the flame, for the main reactions of: (a) H atom consumption atom (rates of $\text{H} + \text{CH}_2\text{O}$ and $\text{H} + \text{KOH}$ – dotted lines); (b) OH radical consumption (rates of $\text{OH} + \text{H}_2$ and $\text{K} + \text{OH} + \text{M}$ – dotted lines); (c) formation and consumption of potassium atom (stoichiometric methane-air flame, 298 K, 101.33 kPa, $\text{KHCO}_3(\text{s})$ mole fraction of 0.05%).

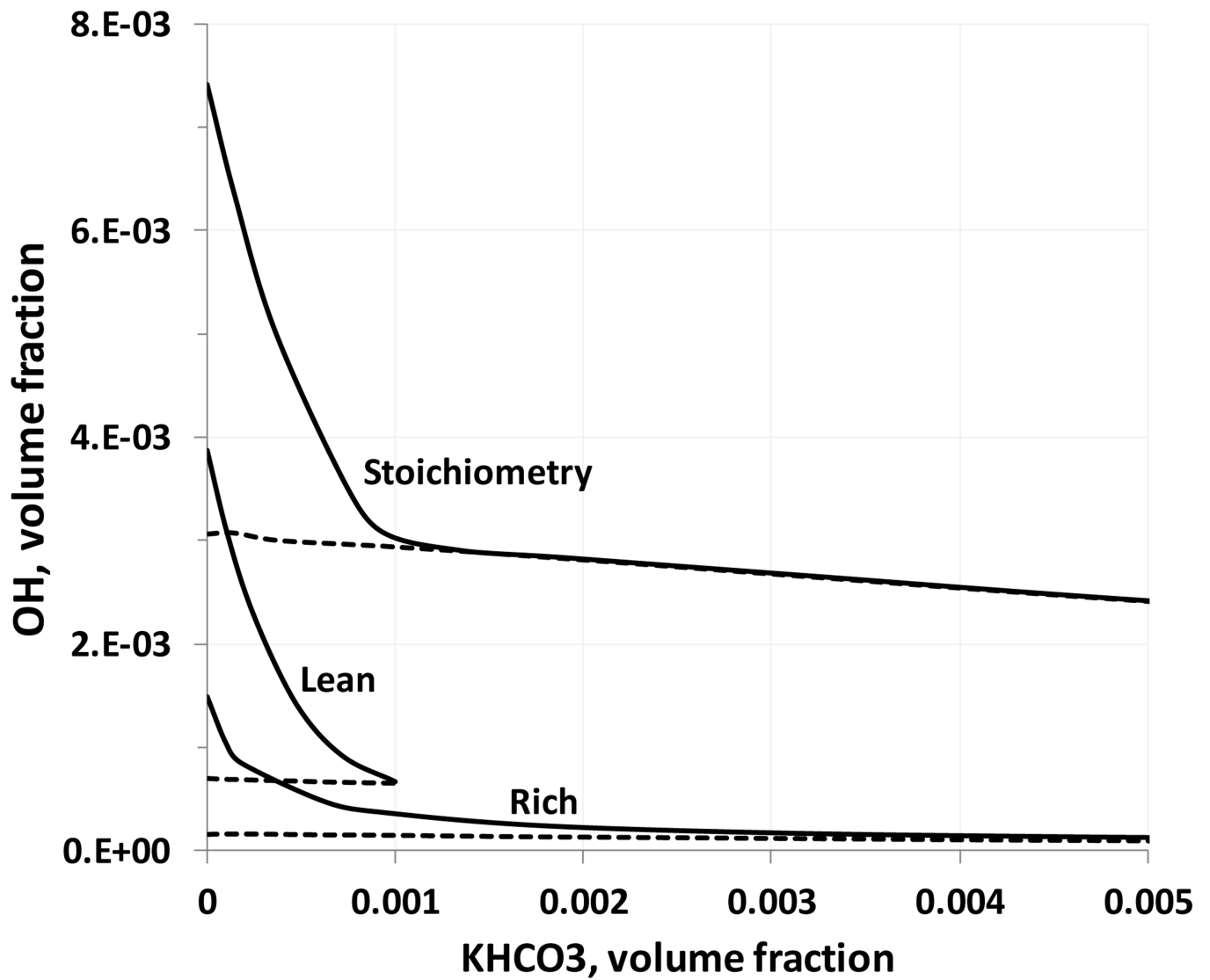


Figure 7. Peak (solid lines) and equilibrium (dotted lines) OH volume fraction as a function of KHCO₃ mole fraction (initial conditions: stoichiometric, lean and rich mixtures, $\phi=0.7, 1.0,$ and 1.34; 298 K, 101.33 kPa).

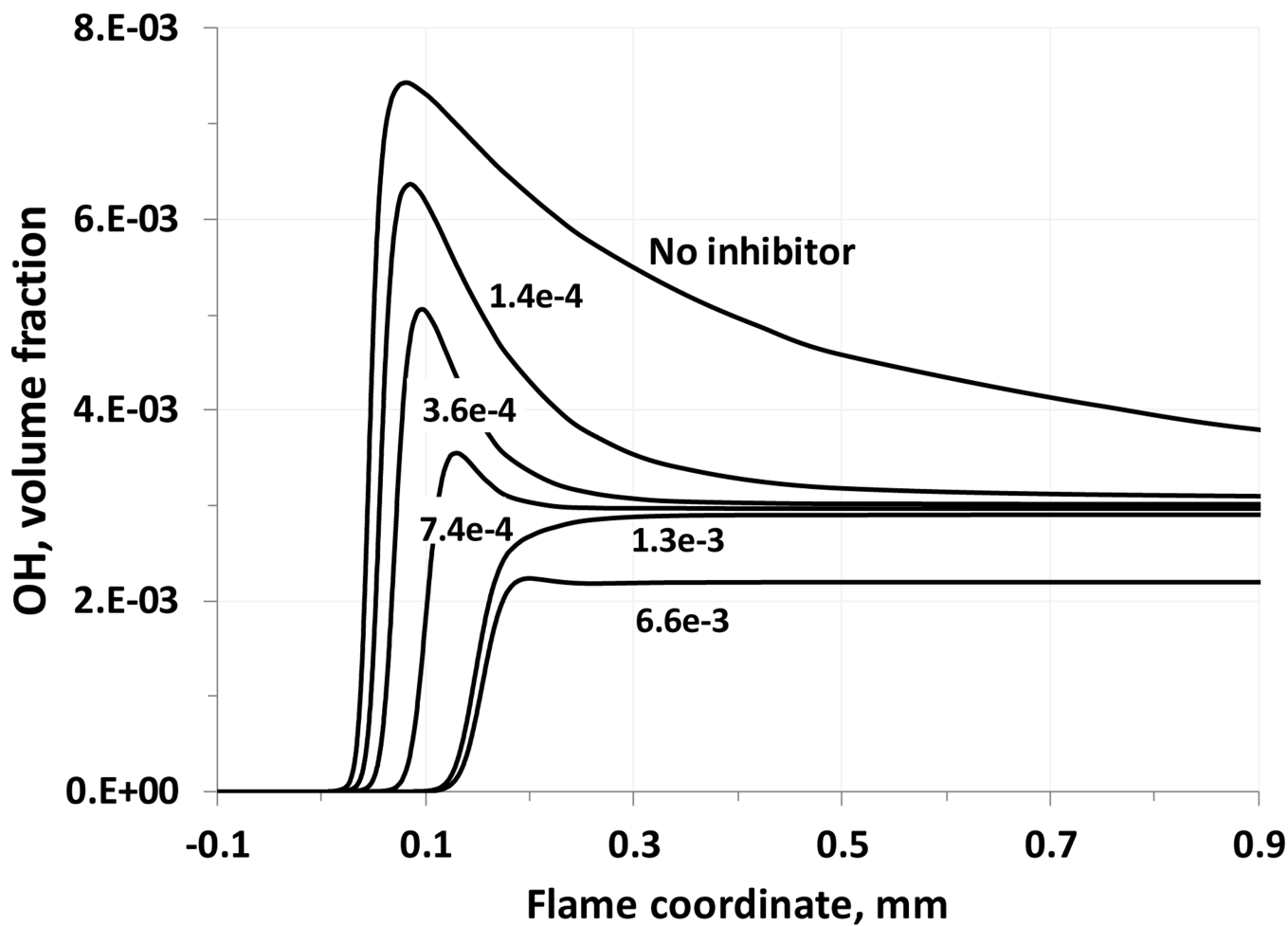
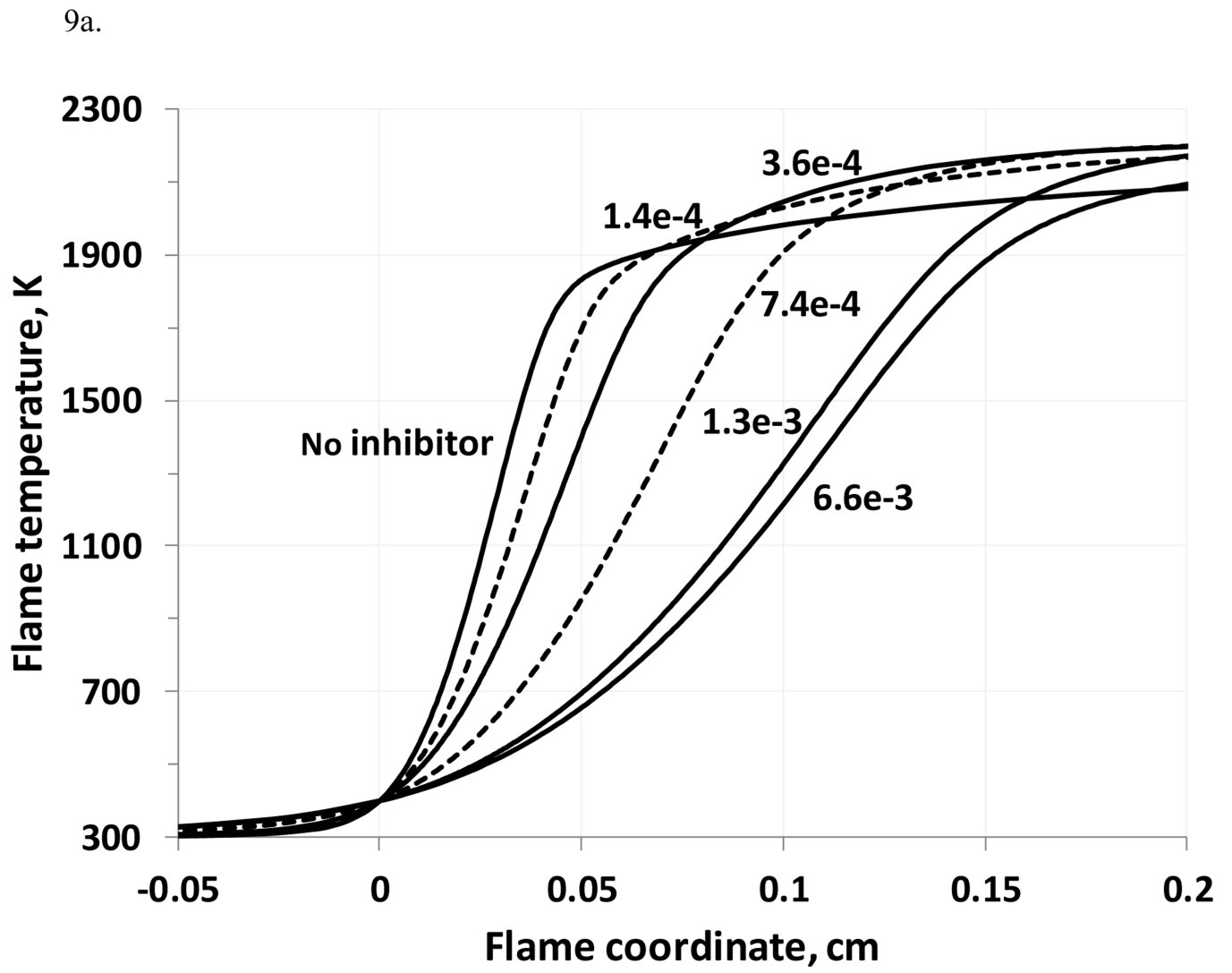


Figure 8.
Flame concentration profiles of hydroxyl radical at different initial $\text{KHCO}_3(\text{s})$ loadings
(stoichiometric methane-air flame, initial conditions: 298 K, 101.33 kPa).



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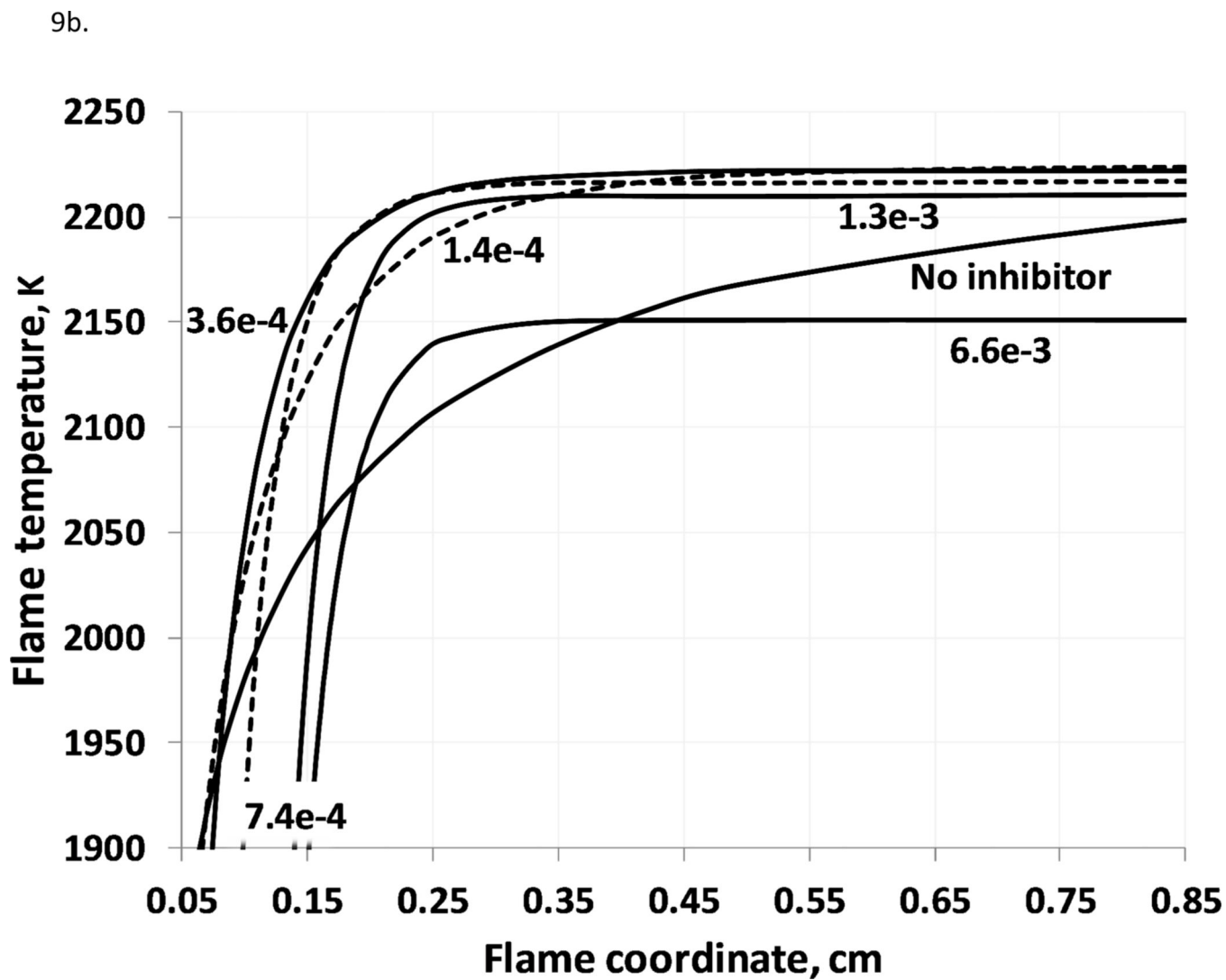


Figure 9.
(a,b). Flame temperature profiles at different $\text{KHCO}_3(\text{s})$ loadings (stoichiometric methane-air flame, initial conditions: 298 K, 101.33 kPa; temperature profiles for $1.4\text{e-}4$ and $7.4\text{e-}4$ – dotted lines).

Table 1.

Thermodynamic data for potassium-containing species (kJ, J, mole, K)

Species	H(298 K)	S(298 K)	C _p (298 K)	Reference *
K	89.0	160.3	20.8	Goos et al., 2012
K(s)	0.0	64.9	29.6	Goos et al., 2012; Gurvich et al., 1993
K ₂	127.1	249.7	37.9	Kee et al., 1990
KH	123.0	197.9	31.0	Kee et al., 1990
KH(s)	-57.7	50.2	37.9	Kee et al., 1990
KO	64.9	241.1	35.4	Gurvich et al., 1993
KO ₂	-86.6	268.6	48.1	Glarborg and Marshall, 2005; Sander et al., 2011
KO ₂ (s)	-284.5	122.6	77.4	Kee et al., 1990
K ₂ O	-74.1	286.6	54.2	Goos et al., 2012
K ₂ O(s)	-363.2	94.1	72.0	est; Kee et al., 1990; Gurvich et al., 1993
K ₂ O ₂	-191.6	306.5	71.0	Goos et al., 2012
K ₂ O ₂ (s)	-495.8	113.4	100.0	Kee et al., 1990
KOH	-231.8	275.7	49.2	Glarborg and Marshall, 2005
KOH(s)	-424.7	79.1	64.9	Gurvich et al., 1993
(KOH) ₂	-638.9	342.7	105.9	Glarborg and Marshall, 2005; Gurvich et al., 1993
K ₂ CO ₃	-811.7	345.5	90.0	Gurvich et al., 1993
K ₂ CO ₃ (s)	-1150.2	155.6	114.2	Kee et al., 1990; Gurvich et al., 1993
KO ₃	-77.0	285.8	64.4	est; Sander et al., 2011; Vasiliu et al., 2010
KHCO ₃	-739.7	315.5	74.5	est; Plane et al., 2014
KHCO ₃ (s)	-963.2	115.5	89.1	est; Meng et al., 1995; Wagman et al., 1982
KCO ₃	-523.0	311.3	68.6	est; Plane et al., 2014

* est – estimate in this work

Table 2.

Kinetic model for potassium-containing species (AT)

	A	b	E	Reference*
K atom reactions				
1. K+O2(+M)=KO2(+M)	3.60E+14	0.0	0.0	(Glarborg and Marshall, 2005, Sorvajarvi et al., 2015)
LOW /2.0e22 -1.55 0./				
H2/2.0/ H2O /6.0/ CH4/2.0/ CO/1.5/ CO2/2.0/ C2H6 /3.0/				
2. K+OH+M=KOH+M	2.18E+21	-1.0	0.0	(Jensen and Jones, 1982),a
H2/2.0/ H2O /6.0/ CH4/2.0/ CO/1.5/ CO2/2.0/ C2H6 /3.0/				
3. K+H+M=KH+M	3.00E+17	-1.0	0.0	(Hindiyarti et al., 2006)
H2/2.0/ H2O /6.0/ CH4/2.0/ CO/1.5/ CO2/2.0/ C2H6 /3.0/				
4. k+o+m=ko+m	1.50E+21	-1.5	0.0	(Glarborg and Marshall, 2005)
H2/2.0/ H2O /6.0/ CH4/2.0/ CO/1.5/ CO2/2.0/ C2H6 /3.0/				
5. K+HCO=KH+CO	3.00E+13	0.0	14.64	(Williams and Fleming, 1999),b
6. K+HO2=KH+O2	2.00E+13	0.0	58.58	b
7. K+HO2=KOH+O	7.00E+12	0.0	31.38	(Baratov et al., 1991),b
8. K+H2O2=KOH+OH	2.50E+13	0.0	0.0	(silver et al., 1984),Na
9. K+H2O2=KO+H2O	1.60E+13	0.0	0.0	(silver et al., 1984),Na
KO reactions				
10. KO+H=K+OH	2.00E+14	0.0	6.28	(Williams and Fleming, 1999),b
11. KO+O=K+O2	1.20E+14	0.0	1.00	(plane et al., 2014)
12. KO+OH=KOH+O	2.00E+13	0.0	0.0	(Glarborg and Marshall, 2005, Williams and Fleming, 1999)
13. KO+OH=K+HO2	3.00E+13	0.0	41.84	b
14. KO+HO2=KOH+O2	5.00E+13	0.0	0.0	(Glarborg and Marshall, 2005, Williams and Fleming, 1999)
15. KO+HO2=KO2+OH	3.00E+12	0.0	16.74	(Heimerl and Keller, 1987),b
16. KO+H2=KOH+H	1.60E+13	0.0	0.0	(williams and Fleming, 1999),Na
17. KO+H2=K+H2O	3.10E+12	0.0	0.0	(Glarborg and Marshall, 2005, Williams and Fleming, 1999),Na
18. KO+H2O=KOH+OH	6.00E+11	0.5	0.0	(Slack et al., 1989)
19. KO+CO=K+CO2	1.00E+14	0.0	0.0	(Heimerl and Keller, 1987)
20. KO+HCO=KOH+CO	3.00E+13	0.0	0.0	(Williams and Fleming, 1999),Na
21. KO+CH4=KOH+CH3	1.20E+12	0.0	14.64	(Baratov et al., 1991)

	A	b	E	Reference*
22. $\text{KO}+\text{CH}_2\text{O}=\text{KOH}+\text{HCO}$	1.20E+13	0.0	16.74	b
23. $\text{KO}+\text{KO}=\text{KO}_2+\text{K}$	1.00E+13	0.0	0.0	(Singh and Weaver, 1991)
24. $\text{ko}+\text{h}+\text{m}=\text{koh}+\text{m}$	3.60E+22	-2.0	0.0	(Baratov et al., 1991)
25. $\text{KO}+\text{O}+\text{M}=\text{KO}_2+\text{M}$	1.45E+19	-1.0	0.0	(Baratov et al., 1991)
26. $\text{KO}+\text{CH}_3=\text{K}+\text{CH}_3\text{O}$	2.30E+13	0.0	2.5.10	b
27. $\text{KO}+\text{C}_2\text{H}_6=\text{KOH}+\text{C}_2\text{H}_5$	1.20E+13	0.0	2.5.10	b
28. $\text{KO}+\text{C}_2\text{H}_4=\text{KOH}+\text{C}_2\text{H}_3$	1.50E+13	0.0	33.47	b
29. $\text{KO}+\text{C}_2\text{H}_2=\text{KOH}+\text{C}_2\text{H}$	2.00E+13	0.0	37.66	b
30. $\text{KO}+\text{C}_3\text{H}_8=\text{KOH}+\text{C}_3\text{H}_7$	1.50E+13	0.0	20.92	b
K ₂ O reactions				
31. $\text{KO}_2+\text{H}=\text{K}+\text{HO}_2$	1.90E+12	0.0	0.0	(Singh and Weaver, 1991)
32. $\text{KO}_2+\text{H}=\text{KOH}+\text{O}$	1.00E+13	0.0	0.0	(singh and Weaver, 1991)
33. $\text{KO}_2+\text{H}=\text{KO}+\text{OH}$	5.00E+13	0.0	29.29	(Babushok et al., 2003),Na
34. $\text{KO}_2+\text{O}=\text{KO}+\text{O}_2$	1.30E+13	0.0	0.0	(DeMore et al., 1997, Glarborg and Marshall, 2005),Na
35. $\text{KO}_2+\text{CO}=\text{KO}+\text{CO}_2$	6.00E+13	0.0	96.23	(Baratov et al., 1991)
36. $\text{KO}_2+\text{OH}=\text{KOH}+\text{O}_2$	1.20E+13	0.0	0.0	(Baratov et al., 1991)
37. $\text{KO}_2+\text{H}_2=\text{KOH}+\text{OH}$	1.80E+12	0.0	83.14	(Baratov et al., 1991)
38. $\text{KO}_2+\text{HCO}=\text{KOH}+\text{CO}_2$	6.00E+12	0.0	0.0	(Baratov et al., 1991)
39. $\text{KO}_2+\text{CH}_3=\text{KOH}+\text{CH}_2\text{O}$	6.00E+12	0.0	0.0	(Baratov et al., 1991)
KOH reactions				
40. $\text{KOH}+\text{H}=\text{K}+\text{H}_2\text{O}$	2.20E+12	0.5	0.0	(Slack et al., 1989)
41. $\text{KOH}+\text{CH}_3=\text{K}+\text{CH}_3\text{OH}$	3.50E+12	0.0	41.84	b
42. $\text{KOH}+\text{HO}_2=\text{KO}_2+\text{H}_2\text{O}$	6.00E+12	0.0	22.18	(Baratov et al., 1991)
43. $\text{KOH}+\text{KOH}=(\text{KOH})_2$	8.00E+13	0.0	0.0	(Glarborg and Marshall, 2005)
KH reactions				
44. $\text{KH}+\text{H}=\text{K}+\text{H}_2$	1.00E+14	0.0	0.0	(Hindlyarti et al., 2006)
45. $\text{KH}+\text{O}=\text{K}+\text{OH}$	5.00E+13	0.0	0.0	(Hindlyarti et al., 2006)
46. $\text{KH}+\text{O}=\text{KO}+\text{H}$	6.00E+12	0.0	29.29	b
47. $\text{KH}+\text{OH}=\text{K}+\text{H}_2\text{O}$	1.00E+14	0.0	0.0	(Heimerl and Keller, 1987)
48. $\text{KH}+\text{OH}=\text{KOH}+\text{H}$	1.00E+13	0.0	0.0	(Heimerl and Keller, 1987)
49. $\text{KH}+\text{HCO}=\text{K}+\text{CH}_2\text{O}$	2.00E+13	0.0	0.0	b

	A	b	E	Reference*
50. KH+CH3=CH4+K	1.00E+14	0.0	0.0	(Babushok et al., 2003),Na
51. KH+CH3O=K+CH3OH	2.00E+13	0.0	0.0	b
52. KH+KO=K+KOH	1.00E+14	0.0	0.0	(Heimerl and Keller, 1987)
K2O reactions				
53. KO+K+M=K2O+M	1.00E+16	0.0	0.0	b
54. K2O+H=K+KOH	5.00E+12	0.0	12.55	(Babushok et al., 2003),Na
55. K2O+O=K2O2	1.00E+14	0.0	0.0	b
56. K2O+O=KO+KO	1.00E+13	0.0	41.84	b
57. K2O+OH=KO+KOH	1.00E+13	0.0	20.92	b
K2O2 reactions				
58. KO+KO=K2O2	1.00E+14	0.0	0.0	b
59. K2O2+H=KOH+KO	1.50E+13	0.0	4.18	(Babushok et al., 2003), Na
60. K2O2+O=K2O+KO	1.00E+13	0.0	33.47	b
61. K2O2+OH=KOH+K2O	1.00E+13	0.0	12.55	b
KO3 reactions				
62. KO2+O+M=KO3+M	1.45E+19	-1.0	0.0	(Baratov et al., 1991.)
H2/2.0/ H2O /6.0/ CH4/2.0/ CO/1.5/ CO2/2.0/ C2H6 /3.0/				
63. H+KO3=KO2+OH	2.00E+13	0.0	0.0	b
64. O+KO3=KO2+O2	2.00E+13	0.0	0.0	b
65. OH+KO3=KO2+HO2	1.00E+13	0.0	37.66	b
66. CH3+KO3=CH3O+K2O	1.00E+13	0.0	20.92	b
67. KO+O2(+M)=KO3(+M)	3.40E+14	0.0	0.0	(DeMore et al., 1997), Na
LOW /1.1e23 -2.0 0.0/				
H2/2.0/ H2O /6.0/ CH4/2.0/ CO/1.5/ CO2/2.0/ C2H6 /3.0/				
KHCO3, KCO3, K2CO3 reactions				
68. KOH+CO2(+M)=KHCO3(+M)	4.09E+14	0.0	0.0	(DeMore et al., 1997),Na (Plane et al., 2014)
LOW /1.25e30 -4.21 0. /				
H2/2.0/ H2O /6.0/ CH4/2.0/ CO/1.5/ CO2/2.0/ C2H6 /3.0/				
69. KO+CO2(+M)=KCO3(+M)	3.90E+14	0.0	0.0	(DeMore et al., 1997),Na
LOW /3.8e2 5 -2.0 0.0/				
H2/2.0/ H2O /6.0/ CH4/2.0/ CO/1.5/ CO2/2.0/ C2H6 /3.0/				

	A	b	E	Reference*
70. $\text{KCO}_3+\text{H}+\text{M}=\text{KHCO}_3+\text{M}$	$2.00\text{E}+16$	0.0	0.0	b
$\text{H}_2/2.0/ \text{H}_2\text{O} /6.0/ \text{CH}_4/2.0/ \text{CO}/1.5/ \text{CO}_2/2.0/ \text{C}_2\text{H}_6 /3.0/$				
71. $\text{K}_2\text{O}+\text{CO}+\text{M}=\text{K}_2\text{CO}_3+\text{M}$	$3.00\text{E}+16$	0.0	0.0	(DeMore et al., 1997),Na
72. $\text{K}+\text{KCO}_3+\text{M}=\text{K}_2\text{CO}_3+\text{M}$	$2.00\text{E}+18$	0.0	0.0	b
$\text{H}_2/2.0/ \text{H}_2\text{O} /6.0/ \text{CH}_4/2.0/ \text{CO}/1.5/ \text{CO}_2/2.0/ \text{C}_2\text{H}_6 /3.0/$				
73. $\text{KHCO}_3+\text{H}=\text{K}+\text{CO}_2+\text{H}_2\text{O}$	$2.70\text{E}+13$	0.0	29.83	(Plane et al., 2014)
74. $\text{KHCO}_3+\text{H}=\text{KCO}_3+\text{H}_2$	$1.50\text{E}+13$	0.0	41.84	b
75. $\text{KHCO}_3+\text{O}=\text{KCO}_3+\text{OH}$	$1.00\text{E}+13$	0.0	52.30	b
76. $\text{KHCO}_3+\text{OH}=\text{KCO}_3+\text{H}_2\text{O}$	$2.00\text{E}+13$	0.0	31.38	b
77. $\text{KCO}_3+\text{H}=\text{KOH}+\text{CO}_2$	$3.00\text{E}+12$	0.0	16.74	b
78. $\text{KCO}_3+\text{O}=\text{K}_2\text{O}+\text{CO}_2$	$5.00\text{E}+12$	0.0	12.55	b
79. $\text{KHCO}_3+\text{KO}=\text{K}_2\text{CO}_3+\text{OH}$	$6.00\text{E}+12$	0.0	29.29	b
80. $\text{KHCO}_3+\text{KOH}=\text{K}_2\text{CO}_3+\text{H}_2\text{O}$	$3.00\text{E}+12$	0.0	37.66	b
81. $\text{KCO}_3+\text{KO}=\text{K}_2\text{CO}_3+\text{O}$	$7.00\text{E}+12$	0.0	20.92	b
82. $\text{KCO}_3+\text{KO}_2=\text{K}_2\text{CO}_3+\text{O}_2$	$1.00\text{E}+13$	0.0	12.55	b
83. $\text{K}_2\text{CO}_3+\text{M}=\text{K}_2\text{O}+\text{CO}_2+\text{M}$	$5.00\text{E}+16$	0.0	338.9_0	b
84. $\text{K}_2\text{CO}_3+\text{OH}=\text{KCO}_3+\text{KOH}$	$3.00\text{E}+14$	0.0	46.02	b
85. $\text{K}_2\text{CO}_3+\text{O}=\text{K}_2\text{O}_2+\text{CO}_2$	$3.00\text{E}+14$	0.0	29.29	b

* a-Na, increased 20%; b-estimation by analogy or using empirical correlations