Combustion and Flame 173 (2016) 57–64

Contents lists available at ScienceDirect

Combustion and Flame

journal homepage: www.elsevier.com/locate/combustflame

Observation of water–gas shift equilibrium in diffusion flames

Wendong Wu[a], Gregory Yablonsky[b], Richard L. Axelbaum[a,*]

[a] Department of Energy, Environmental, and Chemical Engineering, Washington University in St. Louis, One Brookings Drive, Box 1180, Brauer Hall, St. Louis, MO 63130, USA
[b] Saint Louis University, Parks College of Engineering, Aviation & Technology, 3450 Lindell Blvd, St. Louis, MO 63103, USA

ARTICLE INFO

Article history:
Received 25 February 2016
Revised 31 May 2016
Accepted 20 July 2016
Available online 3 September 2016

Keywords:
Water–gas shift
Apparent equilibrium
Diffusion flame
Equilibrium domains

ABSTRACT

The kinetic behavior of the water–gas shift (WGS) sub-system has been studied computationally for hydrocarbon diffusion flames in the counterflow geometry. Of specific interest was the spatial domain in which the reactions in the WGS-complex exhibit characteristics that lead to species concentrations approaching those expected from equilibrium. Two scenarios were observed for WGS equilibrium:

(1) full equilibrium in which every step of the WGS-mechanism is nearly in equilibrium;
(2) “apparent” equilibrium, which is achieved via opposing but coherent shifts away from equilibrium for the two key elementary reactions that constitute the WGS reaction. This interesting phenomenon is caused by the supply of the H radical, which participates in the forward reaction of one step and the reverse reaction of the other. This new form of apparent equilibrium differs from well-known “quasi” equilibrium, which is typically caused by the combination of a fast reversible step and slow irreversible step.

Parametric domains were found in which these two scenarios are observed. For a given fuel type it was shown that the two scenarios can be separated by the location of stoichiometry. On the oxidizer side, the full equilibrium of the overall WGS reaction is achieved, while on the fuel side, apparent equilibrium can occur.

1. Introduction

Detailed kinetic mechanisms for hydrocarbon flames are characterized by high levels of complexity, typically including hundreds of species and many more reactions. Efforts to reduce mechanisms often involve attempts to identify conditions where the water–gas shift (WGS) reaction can be assumed to be in equilibrium, and this assumption is commonly employed [1–6]. The water–gas shift reaction, $CO+H_2O \leftrightharpoons CO_2+H_2$, is slightly exothermic at 41.1 kJ (10 kcal) per mole. As shown in Table 1, the water–gas shift reaction is unique when compared with other important overall reactions within the H_2, H_2O, CO, CO_2 system because of its relatively small enthalpy change, which suggests a reversible nature. As a result, this reaction may achieve equilibrium more rapidly than other important overall reactions.

The water–gas shift reaction can be represented as the sum of elementary reactions from the detailed mechanism. In the simplest case it can be written as:

$$H+H_2O \leftrightharpoons OH+H_2 \tag{R1}$$

$$CO+OH \leftrightharpoons CO_2+H \tag{R2}$$

with the overall reaction being the sum of these two reactions:

$$CO+H_2O \leftrightharpoons CO_2+H_2 \tag{R3}$$

The quotient of the overall reaction is $Q_3=[CO_2][H_2]/[CO][H_2O]$. For reactions (R1) and (R2) the quotients are $Q_1=[OH][H_2]/[H][H_2O]$ and $Q_2=[CO_2][H]/[CO][OH]$, respectively. Equilibrium can be assumed for the WGS reaction when Q_3 approaches the equilibrium constant for (R3) ($K_{eq,3}$).

In addition to the practical benefit of making this assumption, efforts to distinguish the domain of WGS equilibrium are widespread in the literature. Warnatz et al. [1] evaluated experimental and asymptotic results for the premixed H_2–CO system and suggested that at low H_2 or H_2O concentrations equilibrium of (R1) is retarded, and at lower temperatures ($T<1800$ K) equilibrium of (R2) fails. In either case, equilibrium is not achieved for the WGS reaction.

---

* Corresponding author. Fax: +1 314 935 7211.
E-mail address: axelbaum@wustl.edu (R.L. Axelbaum).

http://dx.doi.org/10.1016/j.combustflame.2016.07.025
0010-2180/© 2016 The Combustion Institute. Published by Elsevier Inc. All rights reserved.

Table 1
Enthalpy change for overall reactions.

Reaction	Formula	ΔH (kJ/mol)
Water–gas shift	$CO+H_2O \Rightarrow CO_2+H_2$	−41.1
Hydrogen combustion	$2H_2+O_2 \Rightarrow 2H_2O$	−290
CO combustion	$2CO+O_2 \Rightarrow 2CO_2$	−283
Ethylene pyrolysis	$C_2H_4 \Rightarrow C_2H_2+H_2$	174

In a diffusion flame, the WGS reaction on the oxidizer side is difficult to analyze experimentally because the concentrations of H_2 and CO are too low to measure accurately. Thus, experimental investigations of equilibrium for the WGS reaction have been mainly conducted on the fuel side. Drake et al. [2] found that in a syngas counterflow diffusion flame, (R2) is slower than (R1), and the WGS reaction achieves partial equilibrium only at low strain rates and for temperatures above 1900 K. In a methane–air diffusion flame, Bilger [3] found that the WGS reaction is equilibrated for a range of mixture fractions from 0.033 to 0.047, while the H_2–O_2 system is far from equilibrium. They concluded that since (R2) dominates CO consumption, the consumption of hydrogen is the factor controlling the oxidation of CO in the oxidizer side of the flame; thus, (R1) and (R2) are coupled. Mitchell et al. [4] compared the quotient with the equilibrium constant of the WGS reaction calculated from the measured major species profiles in a methane–air diffusion flame. Their results suggested that the WGS-reaction is approximately equilibrated in a zone encompassing the flame front, where the local equivalence ratio is about unity. On the fuel-rich side, the partial-equilibrium condition breaks down at a local equivalence ratio of approximately 2.5, corresponding to a temperature of 1500 K. Barlow et al. [5] concluded, through numerical studies, that WGS equilibrium is easier to achieve under the equal diffusivity assumption than with full molecular transport. They found that the relative importance of molecular diffusion and turbulent transport can be revealed by the behavior of WGS equilibrium.

Additional results concerning the role of the WGS-reaction in flame processes are summarized in Table 2. Though the WGS reaction has been studied both experimentally and numerically, most analyses have been conducted for simple fuels like syngas and methane, not for higher hydrocarbons. The equilibrium domain for the WGS-subsystem will be significantly influenced by the composition of the chemical mixture, and thus, it is important to identify these domains for a range of hydrocarbons and to study the underlying chemistry in detail. Moreover, the mechanisms responsible for the WGS-equilibrium may differ among fuels. Thus, in this paper the WGS reaction was studied numerically for syngas and a number of hydrocarbon diffusion flames; the equilibrium domains were systematically analyzed under varying strain rate, and the effects of strain rate on this domain were investigated.

2. Methods

The WGS reaction was studied numerically in the counterflow diffusion flame geometry for a variety of fuels and as a function of strain rate. The flames were modeled using the OPPDIF flame code. A total of 143 species and 938 reactions were included in the mechanism, which is a combination of the mechanism by Appel et al. [11] and USC Mech Version II, with chemistry up to pyrene from Wang and Frenklach [12].

The kinetic ratio of the overall reaction, Q/K_{eq}, was employed to quantitatively assess the validity of the WGS equilibrium [11,19] and to determine its parametric domain. The quotient was calculated from the numerical results, and the equilibrium constant was obtained from the CHEMKIN database [20]. WGS equilibrium was considered to be valid if $0.9 < Q/K_{eq} < 1.1$, in other words, when the deviation from equilibrium was less than 10% [5,13].

The concentration and temperature profiles were numerically determined as functions of physical location (*i.e.*, in 'physical space'). However, for utility of interpretation the modeling results will be presented in both mixture fraction space and C/O space. Recent studies have demonstrated that the C/O atomic ratio is a particularly useful variable to analyze diffusion flames [14]. The C/O atomic ratio (or C/O ratio) identifies the ratio of carbon atoms to oxygen atoms locally, and can be expressed as

$$C/O = \sum_i x * \chi^i_{C_xH_yO_z} \Big/ \sum_i z * \chi^i_{C_xH_yO_z}$$

where $\chi^i_{C_xH_yO_z}$ is the local mole fraction of the ith species in the flame, and x, y and z are the number of atoms of C, H and O in the substance, respectively. In C/O space, not only is the flame location independent of the boundary concentrations and strain rate, but the locations of critical zones, *e.g.*, the domains for radical depletion and precursor formation, are independent as well. In contradiction, these locations and domains are strongly dependent on boundary conditions in mixture fraction space.

Boundary conditions for the simulations are shown in Table 3. Here $V_{F,0}$ and $V_{O,0}$ are the inlet velocities at the fuel and oxidizer boundaries, respectively. All strain rates presented in this study will be global.

Table 2
Previous studies of the WGS-reaction in flame processes.

Author	Year	System	Approach and/or key findings
Warnatz [1]	1979	Syngas–air premixed flame	The low temperature and low H_2/H_2O concentrations determine the equilibrium break-down for (R1) and (R2), respectively.
Mitchell [4]	1980	Methane–air diffusion flame	The WGS equilibrium was used to determine whether (R1) and (R2) are co-equilibrated.
Drake and Blint [2]	1988	Syngas–air counterflow diffusion flame	(R2) is slower than (R1).The WGS reaction achieves partial equilibrium only under low strain rates and for temperatures above 1900 K.
Smyth [6,7]	1990	Methane–air diffusion flame	Partial equilibrium for (R1) and (R2) was examined by measuring the OH concentration experimentally.
Chung and Williams [8]	1990	Syngas–air diffusion flame	The region of WGS equilibrium is broad, bounded on the oxidizer side by a thin zone of hydrogen oxidation and on the fuel side by a thin zone of sudden WGS freezing.
Barlow [9]	2000	Syngas–air turbulent diffusion	Unlike for laminar flames, partial equilibrium for the WGS reaction is not a good approximation for turbulent jet flames.
Barlow [5]	2005	Methane–air turbulent diffusion flame	The relative importance of molecular diffusion and turbulent transport can be revealed by the behavior of WGS equilibrium.
Hsu [10]	2011	Syngas–air counterflow flame (numerical)	The decrease in the CO to H_2 ratio of the syngas composition shifts the dominating reaction from (R2) to (R1).