Methane Oxidation Reactions

\[
\begin{align*}
\text{Total Oxidation (Combustion)} & : & \text{CH}_4 + 2 \text{O}_2 & \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O} \\
\text{Partial Oxidation} & : & \text{CH}_4 + 0.5 \text{O}_2 & \rightarrow \text{CO} + 2 \text{H}_2 \\
\text{CO Oxidation} & : & \text{CO} + 0.5 \text{O}_2 & \rightarrow \text{CO}_2 \\
\text{Hydrogen Oxidation} & : & \text{H}_2 + 0.5 \text{O}_2 & \rightarrow \text{H}_2\text{O} \\
\text{Steam Reforming} & : & \text{CH}_4 + \text{H}_2\text{O} & \rightarrow \text{CO} + 3 \text{H}_2 \\
\text{CO}_2 (‘Dry’) Reforming & : & \text{CH}_4 + \text{CO}_2 & \rightarrow 2 \text{CO} + 2 \text{H}_2 \\
\text{Water Gas Shift (WGS)} & : & \text{CO} + \text{H}_2\text{O} & \rightarrow \text{CO}_2 + \text{H}_2 \\
\end{align*}
\]

...and that’s not even yet a complete list of all possible reactions!
A (fairly) complete chemistry...

Many 'tailored' kinetics in the literature. However, let's look at the whole complex spectrum of possible reactions, using (once again...):

**the GRI-Mechanism**

- compilation of **325 elementary chemical reactions** and associated rate coefficient expressions
- **53 species** and corresponding thermochemical parameters
- The conditions for which GRI-Mech 3.0 was optimized: 1000 to 2500 K, 10 Torr to 10 atm, and equivalence ratio from 0.1 to 5.
- “Cautious use of GRI-Mech 3.0 outside the optimization and validation ranges is not unreasonable, essentially because the elementary reactions, which include all steps thought to be important for describing natural gas ignition and flame propagation (including NO formation and reduction) are described by rate parameters that reflect current understanding of elementary reaction rate theory.
- GRI-Mech has been optimized for methane and natural gas as fuel. However, soot formation not included!
Synthesis Gas Formation

The dominant process for syngas formation is (by far) **steam reforming of methane (SRM)**:

\[ \text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3 \text{H}_2, \quad \Delta H_R = +206 \text{ kJ/mol} \]

The reaction is strongly endothermal and hence energy needs to be supplied to the system, making SRM a major energy consumer.

An alternative process is **partial oxidation of methane**, which can proceed catalytically or as a purely homogeneous process (Texaco-Shell):

\[ \text{CH}_4 + 0.5 \text{O}_2 \leftrightarrow \text{CO} + 2 \text{H}_2, \quad \Delta H_R = -37 \text{ kJ/mol} \]

The (mild) exothermicity of this reaction is one of the major advantages of this process alternative.
Explain!

Chemkin Solution

![Graph showing equilibrium temperature (K) vs. initial temperature (K)]
Setting up the problem: CSTR

1. Define reactor set-up: CSTR with inlet
2. Define working directory
   (any directory with write-permission)
3. Define chemistry
   (GRI-mech 3.0 w/ thermo & transport database)
4. Run pre-processor

1. Define isothermal reactor problem
2. Reactor length: 1 m (fast reaction!)
3. Reactor diameter: 1 ft
4. T,P = 1000K, 1 atm
5. Stoichiometric feed

1. Volumetric inlet flow rate: 1 m³/s
2. T,P = 1000K, 1 atm
3. Stoichiometric feed
Solution...
Setting up the problem: PFR

1. Define reactor set-up: PFR with inlet
2. Define working directory
   (any directory with write-permission)
3. Define chemistry
   (GRI-mech 3.0 w/thermo & transport database)
4. Run pre-processor

1. Define isothermal reactor problem
2. Reactor length: 1 m (fast reaction!)
3. Reactor diameter: 1 ft
4. T,P = 1000K, 1 atm

1. Feed stream with axial velocity of 0.1 m/s
2. Stoichiometric feed for POM

1. Create input file
2. Run model
3. Check result. (’View Results…’)
4. Create graph (’Run Post Processor’)
Concentration Profiles

CHEMKIN Solution

- Mole_fraction_H2
- Mole_fraction_O2
- Mole_fraction_H2O
- Mole_fraction_CH4
- Mole_fraction_CO
- Mole_fraction_CO2

Distance (cm)