Exercise 8: Sensitivity and path flux analysis for methane-air combustion in Cantera

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1. Introduction & Problem

Sensitivity and path flux analysis are critical tools in combustion research for understanding and improving chemical kinetic mechanisms. These analyses provide fundamental insights into the complex network of chemical reactions that govern combustion processes.

Sensitivity analysis is a method used to examine how changes in input parameters of a model affect its outputs. It helps determine which inputs have the most significant influence on the model's results, allowing for future examination and elimination of uncertainties in models. In the case of laminar flame speed, sensitivity analysis determines which individual elementary reaction rates have the biggest effect on the overall speed of propagation.

Path flux analysis (PFA) is a computational method used to simplify complex chemical kinetic mechanisms by identifying and removing less important reaction pathways. It focuses on analyzing the formation and consumption rates of species at different reaction stages to pinpoint crucial pathways.

These methods allow us to focus our attention on improving the model's kinetics around the most influential reactions to ensure a more accurate model.This report will use both of these methods to analyze methane-air combustion in Cantera. The two cases examined will be:

- Perform laminar flame speed sensitivity analysis for methane-air combustion at initial pressures of 1 atm and 20 atm, unburnt gas temperature 298 K, and equivalence ratio 1. All reactions with sensitivity values within -0.03 to 0.03 are plotted and analyzed to identify differences in sensitive reactions between pressure conditions.
- Generate a path flux diagram for methane-air combustion following the conversion of carbon at pressure 1 bar, temperature range 1500-1800 K, and equivalence ratio 1.

2. Theory and Method

2.1 Laminar Flame Speed Sensitivity

Cantera's methods to calculate flame speed sensitivity is through the Normalized flame speed sensitivity s_i. s_i of each reaction in the mechanism is determined with respect to changes in the reaction rate k_i. See equation 1. s_i is calculated with changes in the flame speed S_L when the reaction rate constant k_i changes. The values are normalized through the normalisation factor (denominator in equation) which makes the sensitivities dimensionless and comparable for future analysis.

$$s_i = \frac{\frac{\partial S_L}{\partial k_i}}{\frac{S_L}{k_i}} = \frac{\partial(\ln S_L)}{\partial(\ln k_i)} = \frac{k_i}{S_L}\frac{dS_L}{dk_i} \tag{1}$$

where, s_i - normalized sensitivity value, k_i - rate coefficient, S_L - flame speed

The sensitivity analysis S_i for each reaction is compared to each other to determine the most influential reaction. Positive sensitivity values indicate that increasing the reaction rate enhances flame propagation, while negative values suggest that the reaction inhibits flame speed. Sensitivity values of zero, also called Zero sensitivity, shows that the flame speed is unaffected by the reaction, and thus should not be focused on to improve the model.

Cantera calculates these values through the inbuilt command `get_flame_speed_reaction_sensitivities()`.

2.2 Path Flux Diagram

Cantera uses the open source graph graph visualization software, Graphviz. Graph visualization is a way of representing structural information as diagrams of abstract graphs and networks. It's used in networking, bioinformatics, software engineering, database and web design, machine learning, and in visual interfaces for other technical domains.

Graphviz layout programs take description of graphs in a simple text language, dot. See figure 1 for structure of DOT language and generated plot from it.

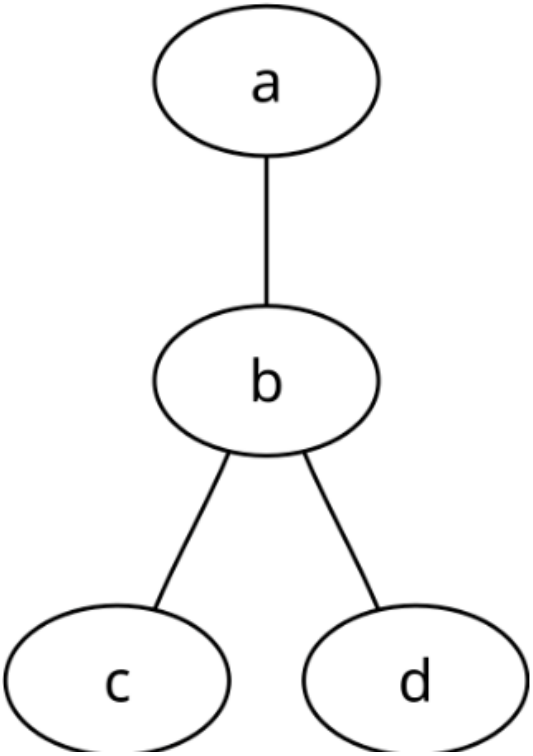

Figure 1: Example of DOT language structure showing undirected and graph representations.

```
// The graph name and the semicolons are optional
graph graphname {
    a -- b -- c;
    b -- d;
}
```

Cantera generates the reaction pathway diagram in dot language, which Graphviz interprets through dot to generate the actual diagram. Cantera's inbuilt function `ct.ReactionPathDiagram(gas, element)`. This creates the reaction path diagram object by analyzing the current gas state and calculating fluxes for the specified element. This is still only saved in the memory. `diagram.write_dot(dot_file)` has to be used to export the analyzed data from memory into a DOT language text file that contains the instructions for Graphviz. `os.system('dot {0} -Tpng -o{1} -Gdpi=300'.format(dot_file, img_file))` is lastly called to generate the the path flux diagram in chosen file type (-Tpng = .png format).

3. Results

From Cantera's calculation and inbuilt commands in the specific two cases, following results were generated.

For the laminar flame speed sensitivity analysis, figure 2 compares the two sensitivity conditions for pressure at 1 atm and 20 atm. The generated laminar flame speed was 37.68 cm/s and 9.86 cm/s for 1 and 20 atm respectively. 1 atm generated 16 sensitive reactions and 20 atm generated 12 that fulfilled the conditions of sensitivity values within -0.03 to 0.03, presented in table 1. Of these reactions, 7 were only found at 1 atm and 2 only at 20 atm, presented in table 2.

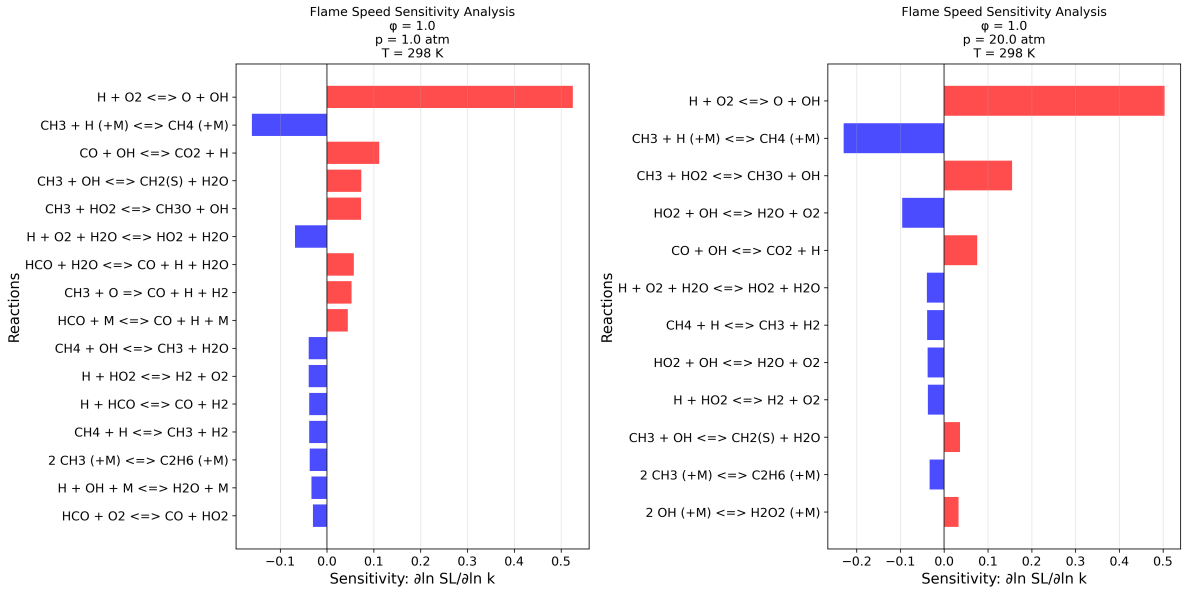

Figure 2: Laminar Flame Speed sensitivity analysis performed for methane-air combustion at initial pressures of 1 atm and 20 atm, unburnt gas temperature 298 K, and equivalence ratio 1. Red shows the reactions with positive sensitivity and blue for negative sensitivity.

Table 1: Sensitivity Analysis Comparison for Methane-Air Combustion

Reaction	**1 atm**	**20 atm**
$H + O_2 \rightleftharpoons O + OH$	+0.5254	+0.5035
$CH_3 + H\ (+M) \rightleftharpoons CH_4\ (+M)$	-0.1602	-0.2297
$CO + OH \rightleftharpoons CO_2 + H$	+0.1115	+0.0754
$CH_3 + HO_2 \rightleftharpoons CH_3O + OH$	+0.0724	+0.1549
$CH_3 + OH \rightleftharpoons CH_2(S) + H_2O$	+0.0732	+0.0360
$H + O_2 + H_2O \rightleftharpoons HO_2 + H_2O$	-0.0687	-0.0394
$H + HO_2 \rightleftharpoons H_2 + O_2$	-0.0392	-0.0372
$CH_4 + H \rightleftharpoons CH_3 + H_2$	-0.0380	-0.0392
$2\ CH_3\ (+M) \rightleftharpoons C_2H_6\ (+M)$	-0.0370	-0.0331
$HCO + H_2O \rightleftharpoons CO + H + H_2O$	+0.0575	–
$CH_3 + O \Rightarrow CO + H + H_2$	+0.0523	–
$HCO + M \rightleftharpoons CO + H + M$	+0.0447	–
$CH_4 + OH \rightleftharpoons CH_3 + H_2O$	-0.0393	–
$H + HCO \rightleftharpoons CO + H_2$	-0.0383	–
$H + OH + M \rightleftharpoons H_2O + M$	-0.0334	–
$HCO + O_2 \rightleftharpoons CO + HO_2$	-0.0300	–
$HO_2 + OH \rightleftharpoons H_2O + O_2$	–	-0.0959
$2\ OH\ (+M) \rightleftharpoons H_2O_2\ (+M)$	–	+0.0329

Table 2: Pressure-Specific Sensitive Reactions

Only Sensitive at 1 atm	**Only Sensitive at 20 atm**
$CH_3 + O \Rightarrow CO + H + H_2$	$HO_2 + OH \rightleftharpoons H_2O + O_2$
$HCO + M \rightleftharpoons CO + H + M$	$2\ OH\ (+M) \rightleftharpoons H_2O_2\ (+M)$
$H + OH + M \rightleftharpoons H_2O + M$	–
$HCO + H_2O \rightleftharpoons CO + H + H_2O$	–
$CH_4 + OH \rightleftharpoons CH_3 + H_2O$	–
$H + HCO \rightleftharpoons CO + H_2$	–
$HCO + O_2 \rightleftharpoons CO + HO_2$	–

For the Flux path diagram, figure 3 shows the reaction path from our fuel of methane and following the element of carbon. A threshold of 0.02 was chosen to restrict the size of the diagram and still keep the important reactions.

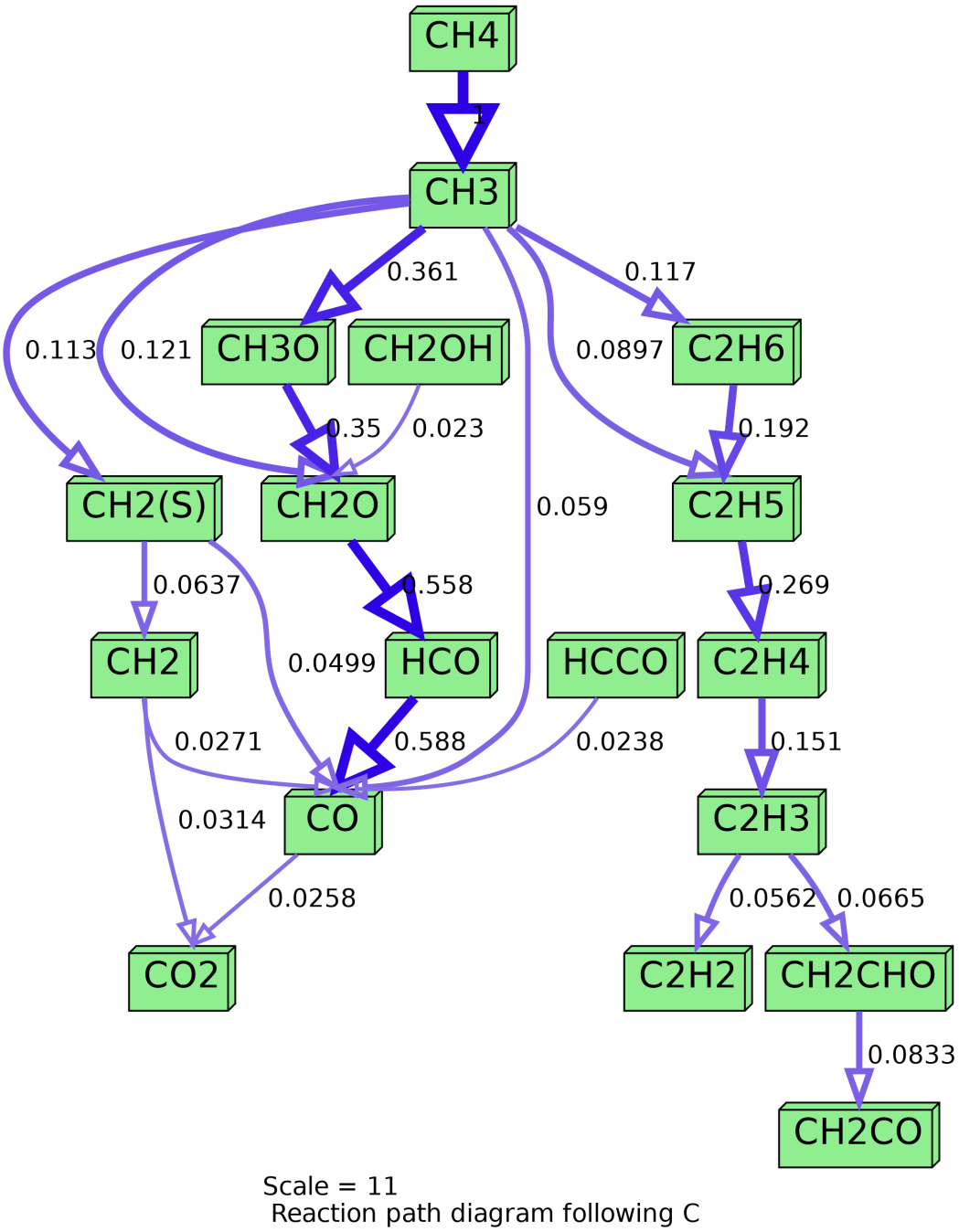

Figure 3: Path flux diagram following Carbon in methane-air combustion carbon at pressure of 1 bar, temperature range 1500-1800 K, and equivalence ratio 1. Green boxes shows the current followed chemical structure and numbers next to arrows show the net flux of the reaction path. All values are normalized against the largest flux.

4. Discussion and Conclusion

From the results we can see several differences between the sensitivity analysis.

Firstly we see that pressure has a large influence on various reaction sensitivities. For example, the reaction CH_3 + H (+M) $\rightleftharpoons$ CH_4 (+M) (see table 1 shows dramatically different sensitivities. -0.1602 at 1 atm versus -0.2297 at 20 atm. This 43% increase in negative sensitivity demonstrates that pressure dependent reactions become more influential at higher pressures because the increased molecular density enhances three-body collision frequencies.

Three-body reactions require a collision partner (M) for energy and momentum transfer during association reactions, with reaction rates following Rate $\propto$ [M]. Thus an increase in pressure results in an increased concentration of the collision partner (M), leading to higher reaction rates for termolecular reactions.

An increase in pressure also changes which radical reactions are dominant. The emergence of HO_2 + OH $\rightleftharpoons$ H_2O + O_2 as a sensitive reaction only at 20 atm (see table 2) illustrates how pressure affects radical reactivity. At higher pressures, HO_2 radicals become more prevalent and reactive as pressure favors the formation of HO_2 in the three body reaction
H + O_2 + (H_2O) $\rightleftharpoons$ HO_2 + H_2O (or the more generlized version H + O_2 + (+M) -$\rightleftharpoons$ HO_2 + (+M). The increased concentration of HO_2 influences the importance of the termination reaction HO_2 + OH $\rightleftharpoons$ H_2O + O_2 resulting in a negative sensitivity and a reduced laminar flame speed.

We also see the clear effect on the laminar flame speed depending on which types of chain reactions are most influential. Branching reactions, such as H + O_2 $\rightleftharpoons$ O + OH, show clear positive sensitivities and termination reactions, such as CH_3 + H (+M) $\rightleftharpoons$ CH_4 (+M) shows clear negative sensitivity. For example the dominant branching reaction (and most sensitive of all reactions) at both pressures, H + O_2 $\rightleftharpoons$ O + OH maintains high positive sensitivity in both cases and therefore is extremely important for model accuracy.

By observing the path flux diagram, we can identify missing important reactions and conclude if we have a relatively good representation of the real reaction pathways. From figure 3, we can identify two important chemicals present which validate the path flux diagram and our choice of tolerance. Firstly, we have a reaction path with several intermediate steps from our fuel CH_4 to CO_2. CO_2 is the final product of combustion and one of the products present in global reaction theory. We also have a reaction path to C_2H_2 (acetylene), which serves as a critical precursor for soot formation in combustion systems. The presence of C_2H_2 and CO_2 in the path flux diagram not only demonstrates the mechanism's capability to predict realistic combustion intermediates but also enhances the reliability of the pathways by showing consistency with well-established combustion theory and established experimental data.

In conclusion, the appearance of 7 unique reactions at 1 atm and 2 unique reactions at 20 atm indicates that pressure significantly alters the chemical pathways controlling flame propagation. The varying sensitivity values as a function of pressure demonstrate the importance of pressure-specific mechanism validation across different operating conditions. This analysis also serves great importance in the accurate formation of path flux diagrams. The identified reactions from the sensitivity analysis indicate which reactions need to be inspected in the reaction mechanism files (.yaml) and updated with correct kinetic values if they are identified as incorrect. Other methods to ensure the accuracy of the path flux diagram include analysis of correct tolerance settings used in path flux creation. A higher tolerance will result in important reaction pathways being filtered out, while too low tolerance will result in an overabundance of reaction paths that may obscure the dominant chemical routes.