

PROJECT ASSIGNMENT #2: REACTORS

General Information:

- Due date: **Thursday, October 5, 2023 11:59PM**
- Submission on MyCourses
- Write your answer in the word processor of your choice, and upload it as a pdf file in MyCourses. **Don't forget to include your name and your McGill ID number.**
 - Name your file as follow: ProjectNumber_FullName_McGillNumber.pdf
 - For example: P2_JohnSmith_0123456789.pdf
- To perform Cantera calculation, don't hesitate to explore Cantera's documentation examples: <https://cantera.org/examples/index.html> for several applications such as JN, Python, or Matlab, that you can adapt to your software. Make sure to understand what you are using.
- When presenting graphs, do your best to make them readable. Labels for y- and x-axis are required, legend if more than 1 curve, title if needed, consider using log-scale if needed ...

Part I – Introduction to 0D reactors

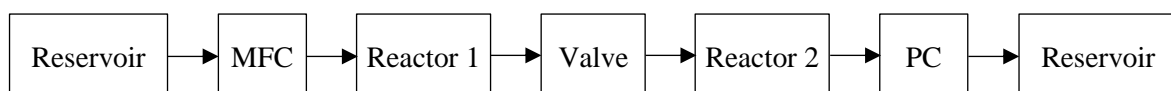
In combustion, it is important to understand and being able to predict the behavior of a mixture when sitting for a long time in a confined space, and through time. In order to model the change of state of a mixture in time, through a constant volume or constant pressure chamber, 0D reactors are used. They allow to model auto-ignition time and the chemistry associated with it, without modeling the flame itself. In this project, several types of reactors will be used to model real-life situations:

- **(Ideal Gas) Reactor:** constant volume, the reacting mixtures is responsible for pressure increase.
- **(Ideal Gas) Constant Pressure Reactor:** constant pressure, the volume of the reactor changes to accommodate a constant pressure as a function of time
- **Flow Reactor:** constant area, steady-state assumption. Time integration follows a fluid element along the length of the reactor.

By default, a simple reactor is considered closed, with fix volume, adiabatic with chemically-inert walls. To change these properties and adapt to a specific problem, it is possible to add components to obtain an opened system, non-adiabatic, with no constant volume etc. These components are:

- **A reservoir:** constant state, does not have any definition of volume or time. Contains a mixture “infinitely” **to be sent to a reactor.**
- **A valve:** Flow device with mass flow rate, function of the pressure drop. Generally, in between reactors to maintain them both at the same pressure.
- **A mass flow controller:** flow device allowing to maintain a mass flow rate through the reactor.
- **A pressure controller:** used in conjunction to an MFC, allows to maintain the flow rate while compensating for pressure difference.
- **A wall:** add heat transfer between two reactors

A typical reactor network with components would look like the following drawing. It is possible to add as many reactors as needed.

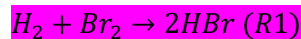


No questions are asked in this part.

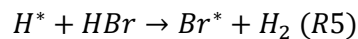
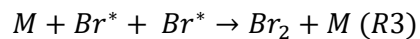
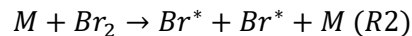
Part II – Identification of reactions and rate calculation

Combustion modelling requires the understanding of the reactions at play in the chemical process. Ultimately, the reaction rates are the limiting factor of the combustion rate, the heat generated, and the pollution formation. Several reaction types are present in combustion modelling and all play a role in different combustion conditions.

Consider the reaction of hydrogen and bromine to form hydrogen bromide:

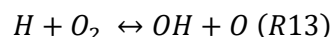
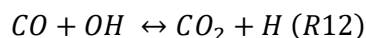
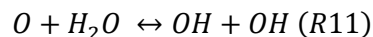
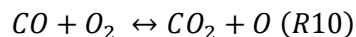


To form HBr, a complex reaction mechanism is at play as the species decompose in intermediate species through the following intermediate reactions:



- For the different reactions (R1-R6), indicate if they are unimolecular, bimolecular or termolecular.
- Definition of molecularity (C.K. Law, p.57): number of molecules that collide within their molecular range. Count is performed on the reactant side. M is including in the count. Two identical molecules reacting together count as 2.
- Indicate the reaction type: global, initiation, propagation, branching, termination.
- Indicate which reaction is pressure dependent.
- Present all your results without discussion.

Consider the following elementary reaction system, where both the forward and reverse reactions are important:



- Write out the rate equation of OH and O; $\frac{d[OH]}{dt}$ and $\frac{d[O]}{dt}$ using the forward and reverse rate ($k_{i,f}$ and $k_{i,b}$) of the reactions R10 to R13.

Part III – Explosion theory

In the design of a combustion chamber for example, it is important to know the limit of explosion of the mixture that will flow through it, in order to orientate the design to avoid any accident. In this part we will consider a mixture of iso-octane and air and simulate the different ignition events that could happen in the combustion chamber that needs to be designed.

Adiabatic ignition

Considering a stoichiometric mixture of iso-octane and air, inside a closed, **adiabatic**, and constant volume reactor, approximated to a sphere, with the following parameters: $r = 37\text{mm}$, $T_{in} = 800\text{K}$, and $P = 1\text{am}$.

Consider using the object `ct.IdealGasReactor`. You can use the code ‘batch_reactor_ignition_delay_NTC.ipynb’ available here: https://cantera.org/examples/jupyter/reactors/batch_reactor_ignition_delay_NTC.ipynb.html to get inspired. If using it, you will need to estimate the ignition delay time of the mixture. For this case, use an estimated ignition delay of 20s (once you obtain ignition, you can vary this number to observe the impact of this guess on your solution). As usual, use Jerzembek mechanism to perform your calculation.

1. Calculate the volume and surface of this reactor
2. Execute the simulation and calculate the heat release at each time step
3. Does the mixture ignite? If so, calculate the required time to auto-ignite the mixture
 - In this case, we can define that a mixture is ignited if the difference of temperature is greater than 500K, or $(T - T_{in} - 500)$ is minimum but not negative
4. Plot the heat release of the reactor versus its temperature
5. Repeat Q2-4 for a lighter fuel, methane. Comment on the difference on ignition time and heat release. You might need to modify your initial guess for the estimated ignition delay.

Semenov theory

Let's consider that the sphere is subject to **heat loss** due to the air surrounding the vessel. Too much heat loss will prevent ignition inside the vessel, while heat brought by the environment might accelerate it. Using the adiabatic case as a reference, we will introduce theoretical heat loss to the reactor, without executing the simulation.

6. Following Cantera's definition of heat loss through a wall, compute the heat loss function, depending on temperature of the adiabatic reactor.
 - For $T_{\text{environment}} = 1000\text{K}$ and $U = 0.1 \text{ MW/m}^2\text{K}$
 - For $T_{\text{environment}} = 1000\text{K}$ and $U = 1.0 \text{ MW/m}^2\text{K}$
 - For $T_{\text{environment}} = 1000\text{K}$ and $U = 2.0 \text{ MW/m}^2\text{K}$
7. Plot these 3 functions on top of the heat release versus temperature plot from Q4.
8. Just using the graph, and for each environmental condition, determine if the mixture will ignite
9. Confirm your theory by computing a reactor with the same heat loss functions than for Q6. Consider emissivity ϵ and the heat flux function $q_0(t)$ to be 0.
10. If it does ignite, calculate the required time to auto-ignite the mixture and compare the value to the adiabatic case. What can you conclude?

Hydrogen S-curve

For this exercise, use the Cantera built-in mechanism ‘gri30.yaml’ to accelerate the processing time.

Using again an **adiabatic** reactor, we will determine the explosivity of hydrogen-air depending on pressure and temperature. By iterating on pressure from 1/1000atm to 10,000atm in step of 10^n , vary the inlet temperature in step of 10K from 650K to 950K until you reach ignition. For this case, use an estimated ignition delay of 10s.

11. Compute the ignition temperature (meaning the initial temperature required to ignite the mixture at this pressure) for each pressure step. Plot these results on a semi-log graph. Comment your results. What reactions are at play?
12. Why is the S-curve not fully described at low pressure?

Part IV – For graduate students (undergrads – bonus points) - Constant pressure ignition

In the case of a constant pressure reactor, the pressure is held constant while the volume is varying. This is the example of the combustion chamber of a gas turbine. Using a constant pressure reactor:

1. For $P = 1\text{ atm}$, calculate the autoignition delay for a stoichiometric mixture of iso-octane and air for a range of temperature from 500K to 1600K, in steps of 50K. Plot the autoignition delay vs T on a semilog plot.
2. Repeat the question but using methane instead.
3. Comment on the differences of the results
4. What would an increase of pressure change to the ignition delay? Explain.

For the next question, a different mechanism, 'seiser.yaml', will be used. Available on MyCourses, remember to save it on the same root than your project. This mechanism has been developed to target n-heptane ignition and extinction modelling, it is therefore better suited for the next question to capture the effect of negative temperature coefficient.

5. For $P = 1\text{ atm}$, using 'seiser.yaml', calculate the autoignition delay for a stoichiometric mixture of n-heptane and air for a range of temperature from 500K to 1600K. Note n-heptane is affected by low temperature chemistry, so you must adapt the T step to capture the negative coefficient region correctly.
 - a. For each initial temperature, plot the temperature profile versus time. Comment on the evolution of the profiles with T .
 - b. Plot the autoignition delay vs $1000/T$ on a semilog graph. Comment on the negative-temperature coefficient region.

Hint: You can use the example `batch_reactor_ignition_delay_NTC.ipynb`

Part IV – Perfectly stirred reactor

Land-based gas turbines are used for a variety of applications including electricity production and natural gas/oil pressurization in pipelines. Two types exist: aero-derivative and light/heavy frame. The former consists of an aircraft engine modified (mostly the combustor) to burn gaseous fuels like natural gas. As such, aero-derivative GT operate at high compression ratios (25-50 atm). The latter are gas turbines designed from scratch for land-based applications, generally larger than aero-derivative ones (in terms of size and power output), and operate at lower compression ratios (10-25 atm).

In industry, the design of a new combustor often starts with first estimations obtained from 0D reactors such as perfectly stirred reactors (PSR). The preliminary goal is to find the best configuration to reduce pollutant formation (e.g. NO_x , CO, unburned hydrocarbons (UHC), etc.). In this homework assignment, we will look at the effect of air admission in the combustor on the pollutant emissions. We will consider an aero-derivative gas turbine with an efficiency of 42% and a power output of 120 MW. The total air flow rate, fixed by the compressor at 240 kg/s, enters the 0.40 m^3 combustor at 30 atm at a temperature of 800K.

1. From the information given above, calculate the required mass flow rate of iso-octane at full load for the above conditions, as well as the overall equivalence ratio, assuming a heating value of 45 MJ/kg.
2. For these conditions (composition, temperature, and pressure), calculate the equilibrium flame temperature, and mole fractions of CO, and NO.
3. Assume the combustor can be simulated using a single PSR with the above cited volume, calculate the concentration of CO and NO. To get started, use the following example:
 - <https://cantera.org/examples/python/reactors/combustor.py.html>
 - You may also wish to review the following links:
 - <https://cantera.org/science/reactors.html>
 - <https://cantera.org/documentation/docs-2.4/sphinx/html/cython/zerodim.html#reactor-networks>
4. What is the residence time for these conditions?
5. How does the PSR concentration values for CO and NO compare with the equilibrium values. Explain the differences between the concentration for these 2 calculations.
6. Explain the difference between the PSR temperature and the equilibrium temperature calculation.

Bonus question: write a script to prove your argumentation for item 5 and 6.

In order to increase the power output of the combustor, the mass flow rate of fuel is increased, as the flow rate of air is generally a fixed parameter tied of the design of the turbine. Thus, an increase of power leads to an increase of equivalence ratio, and a reduction of the residence time.

7. Looping through different power output, from 100MW to 350MW, in steps of 50MW.

- Recalculate the mass flow rate of fuel, equivalence ratio and residence time
- Repeating the PSR simulation, plot the molar fraction of CO_2 , CO , and NO , as well as the temperature, with residence time. Explain the behaviors.