PROJECT ASSIGNMENT #1: COMBUSTION THERMODYNAMICS

General Information:

- Due date: Thursday, September 21, 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: P1_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 thermodynamics data

To perform some calculations, you will need numerical values for the enthalpy. Most reference books do not provide values at sufficiently high temperatures for combustion. A well-known source in such situations is the work of McBride et al. from the NASA Glenn Research Center (on MyCourses) where the specific heat at constant pressure, cp(T), the enthalpy, h(T) and the entropy, s(T), have been least-square fitted to polynomials using 9 coefficients.

To make you comfortable with the widely used NASA format for thermodynamics data, use the report of McBride et al. to:

1. Write a code to extract the enthalpy (kJ/mol), $h^0(T)$, and the entropy (kJ/mol-K), $s^0(T)$, at given temperatures for:
    O_2
    N_2
    CO_2
    H_2O
    CO
    H_2
    NO – warning, you have to call for 'xNO' to find the properties of NO.
    C

To find these values at another temperature than 298.15K, it requires to be calculated following the coefficients given in Appendix C (page 51). To ease your work, the data for a selection of molecules and atoms have been coded in the following file "thermoDataNASA-9.yaml", and the algorithm to calculate the thermodynamics properties in the file "ThermoPropertiesNASA.ipynb" and "ThermoPropertiesNASA.py", for JN users and Spyder users respectively. The files can be found in the project section of MyCourses and should be downloaded on the same root than your project to be callable. Pay attention to the comments let in the codes to guide you.

2. Provide, without discussion, these data in a single table with proper units.

Part II – Equilibrium constant

When complete combustion is not reached, the equilibrium constant can be used to assess the composition of a chemical system. Kp is also a good indicator of the behavior of a reaction with temperature. Consider the three following reactions:

- $H_2 + {}^1\!/_2\, O_2 \leftrightarrow H_2O$
- ${}^1\!/_2\, N_2 + {}^1\!/_2\, O_2 \leftrightarrow NO$
- $CO + H_2O \leftrightarrow H_2 + CO_2$

and using the standard-state Gibbs change function: $\Delta G_T^0 = c\bar{g}_{C,T}^0 + d\bar{g}_{D,T}^0 - a\bar{g}_{A,T}^0 - b\bar{g}_{B,T}^0 = -R_u T ln(K_p)$,

and the Gibbs function of formation: $\overline{g_{f,\iota}^\circ}(T) = \overline{h_{f,\iota}^\circ}(T) - T \cdot \overline{s_\iota^\circ}(T) - \sum_{j\ elements} v_j'[-T \cdot \overline{s_j^\circ}(T)]$

1. Calculate the equilibrium constant Kp(T) for temperatures from 300K to 3000K in steps of 100K.
   - Hint: you might want to develop a code to calculate $\overline{g_{f,\iota}^\circ}(T)$ for each specie from the data extracted in Part I. To do so, you will need to know how each specie was formed, and their stoichiometric coefficients:
     ➢ $H_2 + {}^1\!/_2\, O_2 \to H_2O$
     ➢ ${}^1\!/_2\, N_2 + {}^1\!/_2\, O_2 \to NO$
     ➢ $C + {}^1\!/_2\, O_2 \to CO$
     ➢ $C + O_2 \to CO_2$
     ➢ Recall that $\overline{h_{f,\iota}^\circ}(T)$ and $\overline{g_{f,\iota}^\circ}(T)$ are 0 for H_2, O_2 and N_2
2. Plot Kp (in log-scale) versus 1000/T, for the three reactions, on the same graph.
3. What do these behaviours indicate for each reaction?
4. Using Kp, calculate X_{NO} for $N_2 + O_2 \leftrightarrow 2NO$, for normal air composition.
5. Plot X_{NO} versus T. Comment.

Part III – Incomplete combustion

By using the assumption of complete combustion, a first estimation of a combustion process can be made by assuming that the reaction goes until the limiting reactant is completely transformed into products. In the case of hydrocarbon combustion at stoichiometry, this means that all the C and H atoms are transformed into CO_2 and H_2O respectively. However, when stoichiometry is not achieved, we need to assume incomplete combustion.

For the reaction of iso-octane and air[1] at initial temperature and pressure of T_{in} = 300K and P_{in} = 1atm :

1. Write down the global reaction for the stoichiometric, the lean, and the rich conditions, as a function of the equivalence ratio φ.
   - Hint: on the rich side, first, C is oxidized into CO, and H into H_2O, and then CO reacts with O_2 to form CO_2. Once there is not enough oxygen, CO reacts with H_2O, and H_2 formation starts in the products through the water-gas shift reaction: $CO + H_2O \leftrightarrow CO_2 + H_2$. However, to make the calculations simpler, we will assume $X_{CO2} = 9 \cdot X_{CO}$ in the products to write down the global reaction for rich combustion.
2. Calculate the lower and higher heating values in kJ/kg$_{C8H18}$ (LHV and HHV) – comment and compare to other values in the literature.
3. Calculate the adiabatic temperature $T_{ad,estimation}$ for φ ranging **from 0.5 to 1.5**, in step of 0.05, by assuming **constant Cp** for the reactants and products Cp = 3.5R, with R = 8314.4621 J/kmol/K. Indicate the maximum temperature, and for which equivalence ratio.
   - Up to this question, this part does not require any computation. The calculation **could** be solved by hand, but I advise you to solve them using a loop.
4. Compute the adiabatic temperature $T_{ad,integration}$ for φ ranging **from 0.5 to 1.5**, in step of 0.05 by iterating the integration of **Cp$_i$(T)**. Indicate the maximum temperature, and for which equivalence ratio.

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[1] For all the projects, unless mentioned otherwise, consider air as a mixture of 21% O_2 and 79% N_2.

- Hint: you will have to write a numerical code to calculate $T_{ad,integration}$. You will have to iterate over T values to find $T_{ad,integration}$, and for that purpose it is strongly suggested to use *fsolve* and *quad* from SciPy package in Python.
5. Plot the result T_{ad} vs. φ for both question 3 and 4 on the same graph.
6. Compare and explain the results.

Part IV – Chemical equilibrium using Cantera

The complete combustion assumption made in section 1 is highly idealized. To obtain more realistic values of flame temperatures, one must consider the dissociation of species. Common equilibrium programs minimize the Gibbs energy to find the equilibrium composition and the corresponding adiabatic flame temperature. In this homework assignment, we won't write an equilibrium program, but instead use Cantera to perform the calculations. Cantera uses a default chemical model "gri30.cti" (or "gri30.yaml" depending on the Cantera version) optimized for the combustion of methane. However, in this work we are using a heavy hydrocarbon that requires the use of a specific model called "Jerzembeck.yaml" which includes the chemistry for iso-octane. It is available on MyCourses and must be downloaded on the same root than your project to be callable by Cantera. In examples where you will see **gas = ct.Solution('gri30.yaml'),** simply replace it by **gas = ct.Solution('Jerzembeck.yaml')**.

⚠ In the Jerzembeck mechanism, iso-octane is defined at IXC8H18 (instead of simply C8H18). Please, ensure you are using the same notation when calling for this molecule within the code. This difference of notation does not impact previous parts of this assignment. It is only applicable when working with the specific mechanism Jerzembeck.

For the same conditions than in Part III, but using Cantera:

1. Calculate and plot $T_{ad,equilibrium}$ for φ ranging from 0.5 to 2 in steps of 0.05.
2. Indicate the maximum temperature and at which equivalence ratio it occurs, explain.
3. Compare $T_{ad,equilibrium}$, $T_{ad,estimation}$, and $T_{ad,integration}$.

Bonus points – Repeating parameters from question IV.1, calculate and plot Tad vs. φ for hydrogen (H_2) combustion. Compare and explain the difference in temperature.

Part V – Parameters affecting T_{ad}

In gas turbine conditions, the pressure and temperature of the gas are very different from the conditions in Part III and IV. Gas entering the combustion chamber have a temperature of the order of 800K, and a pressure of 30atm. This leads to a different adiabatic temperature, and *in fine*, to a different generated power. In this part, we will identify the parameters affecting the adiabatic temperature, especially in gas turbines conditions.

For the reaction of iso-octane and air, and using results from Part IV as a reference case:

For the species: [$O,CO,CO_2,H_2,H_2O,H,OH,NO$]

2. Keeping P_{in} = 1atm and T_{in} = 300K constant, compute T_{ad} and the equilibrium composition of the specified species for φ ranging from 0.5 to 2 in steps of 0.05
3. Keeping φ = 1 and T_{in} = 300K constant, compute T_{ad} and the equilibrium composition of the specified species for pressures ranging from 1 to 36atm in steps of 5atm
4. Keeping φ = 1 and P_{in} = 1atm constant, find T_{ad} and the equilibrium composition of the specified species for initial temperatures ranging from 300K to 900K in increments of 100K
5. Plot the effects of equivalence ratio, pressure, and initial temperature on T_{ad} and the equilibrium composition of the specified species.
   - Hint: you should have 3 graphs minimum.

- The most compact graph you could have would be for example: x-axis – φ; y-axis-left – T_{ad}; y-axis-right – X_i (log scale, to also observe minor species)
- You can also separate these parameters on 6 different graphs, for example: a graph for x-axis – φ; y-axis-left – T_{ad}; y-axis-right – X_i for major species ($>10^{-5}$), and a graph for x-axis – φ; y-axis-left – T_{ad}; y-axis-right – X_i for minor species ($<10^{-5}$)
- You can also do 9 graphs…

6. Comment on the effect of the initial temperature, pressure, and equivalence ratio on T_{ad} and the equilibrium composition.

Part VI – For graduate students (undergrads – bonus points) - Effect of dilution on T_{ad} - Exhaust Gas Recirculation (EGR)

Any combustion with air will lead to the emission of Nitrogen Oxides (NO_x), an important combustion pollutant which reacts to form smog and acid rain and results in ground-level ozone that has a very negative effects on the respiratory system. N_2 from air, dissociates and reacts with oxygen to form NO_x (mainly composed of NO and NO_2). However, due to the strong triple covalent bond of N_2 that needs to be broken, such reactions only occur at high temperature (higher than about 1800K for NO_x production to be significant). Therefore, one of the main sources of NO_x in combustion processes is the, so called, thermal NO_x which is highly temperature dependent.

Sometimes, it is desirable to limit the flame temperature by diluting the inlet mixture with gases such as helium (He), argon (Ar), nitrogen (N_2) and carbon dioxide (CO_2). This is particularly the case in fundamental research, the flame temperature has a strong impact on the formation of pollutants and the laminar flame speed, as we will see in subsequent lectures. Therefore, in order to compare fuels only on the basis of their chemistry (i.e. remove the effect of flame temperature), and to control the formation of some compounds, researchers use different levels of dilution to control T_{ad}.

In practice, the exhaust gas (which is mainly composed of CO_2) is recirculated back to the engine to control the temperature and stabilize the flame. EGR is a feature of advanced low-emission gas turbine engines. In this section, we will simulate EGR through Cantera by using dilution:

For the reaction of iso-octane and air:

1. For fixed values of $\varphi = 0.9$, Pin = 30atm, and Tin = 800K, vary the mole fraction of CO_2 in the reactant mixture from 0 to 0.95, in steps of 0.05. Compute and plot T_{ad} and X_{NO}, X_{NO2}, X_{CO}, and X_{CO2}. How and why are these parameters affected by increasing dilution of CO_2? What would happen if we were to increase CO_2 dilution to 100%?
2. Repeat the process with H_2O, instead of CO_2. Comment on the difference between the two gases.
3. What would happen if we were to remove N_2 from air in the combustion of iso-octane and air ?
4. Repeat question V.1 with the dilution of an inert Ar and explain your results.