COMBUSTION

Doctoral Qualifying Examination, May 2016

Mechanical Engineering Department, Columbia University

Problem 1

In hydrogen combustion at sufficiently high pressures that HO_2 is no longer considered unreactive, competition between the reactions

$$H + O_2 = OH + O \qquad (R1)$$

$$H + O_2 + M = HO_2 + M \quad (R2)$$

which govern the second explosion limit, $2k_1 = k_{2,o}[M]$, continue to play a significant role in terms of characteristic timescales.

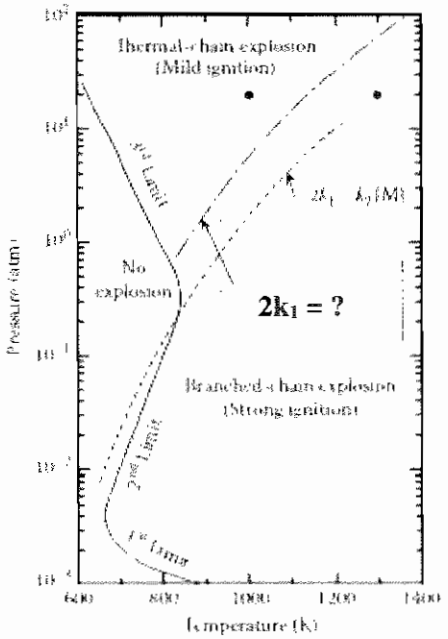
Notably, it has been observed that an "extended second limit" governed by R1 and R2 along with

$$H + HO_2 = H_2 + O_2 \qquad (R5)$$

$$H + HO_2 = OH + OH \quad (R6)$$

demarcates regions of slow and rapid ignition.

Under the assumption of O, OH, and HO_2 as quasi-steady state species and all reactions proceeding predominantly in the forward direction, find an expression for the second explosion limit, $2k_1 = ?$, in terms of k_2, k_5, k_6, and [M].



(Figure adapted from Chaos et al. 2010)

List of relevant H_2/O_2 reactions

(R1) $H + O_2 = OH + O$

(R2) $H + O_2 + M = HO_2 + M$

(R3) $O + H_2 = OH + H$

(R4) $OH + H_2 = H_2O + H$

(R5) $H + HO_2 = H_2 + O_2$

(R6) $H + HO_2 = OH + OH$

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Problem 2

Starting from the non-dimensionalized governing equations

$$\frac{\partial(\rho\tilde{T})}{\partial t}+\frac{\partial}{\partial x}\left(\rho u\tilde{T}-\lambda/c_p\frac{\partial\tilde{T}}{\partial x}\right)=-\omega_F$$

$$\frac{\partial(\rho\tilde{Y}_i)}{\partial t}+\frac{\partial}{\partial x}\left(\rho u\tilde{Y}_i-\rho D_i\frac{\partial\tilde{Y}_i}{\partial x}\right)=\omega_F$$

derive the jump relations across a reaction sheet relating values and fluxes of $\tilde{Y}_i$, $\tilde{Y}_{j\neq i}$ and $\tilde{T}$. Explain each step and declare all necessary assumptions during the derivation from the equations above. Your jump relations should work for a non-equidiffusive system ($\rho D_F \neq \rho D_O \neq \lambda/c_p$), i.e. do not assume the system is equidiffusive.

Problem 3

Consider a steady-state, one-dimensional chamber flame with a constant convective mass flux, $f = \rho u$, from a porous wall at $x = 0$ to a porous wall at $x = l$. The porous wall at $x = 0$ maintains a constant temperature, T_0, constant fuel mass fraction, $Y_{F,c}$, and zero mass fractions of oxidizer and products. The porous wall at $x = l$ maintains a constant temperature, T_l, constant oxidizer mass fraction, $Y_{O,l}$, and zero mass fractions of fuel and products. You can use the non-dimensionalized governing equations from Problem 2 above in your solution and apply the reaction sheet assumption. Assuming constant thermal conductivity, constant specific heats, and constant diffusivities, find the functions describing $\tilde{Y}_F(\tilde{x})$ and $\tilde{Y}_O(\tilde{x})$ in terms of $\tilde{x}_f$ and the functions describing $\tilde{T}(\tilde{x})$ in terms of $\tilde{x}_f$ and $\tilde{T}_f$, and then plot them for a non-equidiffusive system where $\rho D_F > \rho D_O > \lambda/c_p$. Additionally, describe all necessary steps (but do not implement them) for solving for the flame location, $\tilde{x}_f$, and flame temperature, $\tilde{T}_f$.

Problem 4

At high temperatures, formation of the harmful pollutant NO is kinetically limited and its rate of formation is often well approximated by the following expression:

$$\frac{d[NO]}{dt}=2k_{1,f}[O]_{eq}[N_2]$$

where [] indicates the molar concentrations of each species and $k_{1,f}$ is the rate constant for $O + N_2 \rightarrow NO + O$. Estimate time it takes for NO to reach 1 part per million (i.e. a mole fraction, X_{NO}, of 10^6) in post-combustion gases at 2000 K and 1000 kPa from combustion of CH_4/air of equivalence ratio 0.8. You can use the major-minor species model and assume that O and O_2 are in equilibrium. The rate constant $k_{1,f}$ is 8.5×10^5 cm^3 mol^{-1} s^{-1} at 2000 K and the equilibrium constant, $K=\left(\prod X_i^{\nu_i''-\nu_i'}\right)\left(\frac{P}{P_0}\right)^{\sum\nu_i''-\nu_i'}$, for $O_2 = 2O$ with P_0= 100 kPa is 4.47×10^{-7} at 2000 K. For reference, the universal gas constant is 8.314 J mol^{-1} s^{-1}.

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Problem 1

Using the major-minor species model, calculate the adiabatic flame temperature and mole fractions of major products for a CH_4/air mixture of equivalence ratio 1.5 at a constant pressure of 1 atm and 298 K. The equilibrium constant, K_p, for $CO + H_2O = CO_2 + H_2$ is 1.443 at 1000 K, 0.3887 at 1500 K, and 0.22 at 2000 K. Use the table below for any other relevant quantities as necessary.

	Enthalpy of formation kcal/mol	*Heat capacity* cal/mol-K	*Lennard-Jones parameters diameter* Å	*well depth* K
CH_4	-17.8	17.2	3.75	141.0
O_2	0.0	8.3	3.46	107.4
N_2	0.0	7.8	3.62	97.5
CO	-26.4	7.9	3.65	98.1
CO_2	-94.0	13.0	3.76	244.0
H_2	0.0	7.2	2.92	38.0
H_2O (g)	-57.8	9.9	2.61	572.4

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Problem 2

Consider the Lindemann mechanism for the following association reaction:

$$A + B \underset{k_d}{\overset{k_a}{\rightleftharpoons}} C^*$$

$$C^* + M \xrightarrow{k_s} C + M$$

Derive an expression for the association rate constant, k, defined as

$$\frac{d[C]}{dt} = k[A][B]$$

as a function of c_M in terms of k_a, k_d, and k_s using the steady state assumption for C*. Also derive expressions for the association rate constant, k, in the two limiting cases for pressure $\rightarrow 0$ and pressure $\rightarrow \infty$.

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Problem 3

A steady-state flame is situated inside of chamber with constant cross-sectional area and constant pressure. Two porous walls at $x = 0$ and $x = l$ maintain constant concentrations and temperatures of $Y_F = Y_{F,o}$, $Y_O = 0$, $Y_P = 0$, and $T = T_o$ at $x = 0$ and $Y_F = 0$, $Y_O = Y_{O,l}$, $Y_P = 0$, and $T = T_l$ at $x = l$, where Y_i is the mass fraction of the i^{th} species and T is the temperature. Assuming no convection and assuming that the length of the chamber is much larger than the length of the reaction zone, calculate the location of the flame in terms of the chamber length, l, mass diffusivities of the fuel and oxidizer, D_F and D_O, and the boundary conditions.

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Problem 4

A one-dimensional, adiabatic, laminar flat flame is stabilized just after the exit of a tube flowing premixed CH_4 and air at an equivalence ratio of 0.75 at a velocity of 30 cm/s. The unburned gases are at 300 K and the system is at atmospheric pressure. Using any necessary quantities from the table below, estimate the velocity of the burned gases.

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