4A13 Examples

Oussama Chaib

April 2022

1 Basic questions

– **Definitions – physical and chemical** :

- Laminar burning velocity (**2015:Q1**).

- Flammability limits (**2015:Q1, 2014:Q1**).

- Quenching distance (**2015:Q1, 2018:Q1**).

- Flame blow-off (**2015:Q1**).

– **Concepts** :

- NOx types, generation mechanisms, and solutions (**2015:Q1, 2018:Q1**).

- Main pollutants, their formation, and solutions (**2018:Q1**).

- Types of elementary reactions (order) + Examples (**2017:Q1**).

- Types of chain reactions, their properties, the difference between gas shift vs. wall termination + Examples (**2017:Q1, 2012:Q1**).

- Where does each chain reaction occur within a laminar premixed flame and why? (**2017:Q1**).

- Criterion for finite concentration, criterion for explosion (**2012:Q1, 2011:Q2**).

- Does pressure affect product composition? (**2019:Q1**).

- How to increase H_2 yield? (**2019:Q1**).

- Thermal equilibrium vs. steady state.

- High pressure vs. low pressure limit effect on decay and collisional reactions (**2016:Q1**).

- Reaction rate of a species present in both reactants and products.

– **Graphs** :

- Ignition graph – energy gain and loss term vs T (**2018:Q1**).

- Blow-off graph – heat conduction and heat generation terms vs. T **(2015:Q1, 2014:Q1)**.

- S_L as a function of ϕ, T_R p (3 cases as a function of order of reaction n) **(2014:Q2, 2017:Q1, 2012:Q2)**.

- T, Y_f, Y_{ox}, Y_p in a freely propagating laminar premixed flame **(2017:Q1)**.

  – **Derivations** :

- Ignition time τ_{ign} **(2018:Q1)**.

- Extinction equation **(2014:Q1)**.

- Laminar flame speed S_L **(2012:Q2, 2010:Q1)**.

- δ_L and S_L as a function of w **(2012:Q2, 2017:Q1)**.

- Quenching distance d **(2014:Q2)**.

2   Chapter 1: Intro

- **Write the balanced combustion reaction of X fuel with air with equivalence ratio ϕ and the molar/mass coefficients of reactants/products**

  1. Write the equation for stoichiometry ($\phi = 1$).
  2. Calculate or derive an expression for a:

  $$a(O_2 + \beta N_2)$$

  Most of the time, $a = x + \frac{y}{4}$, but always check.

  3. Write the real equation.

     (a) $\phi < 1$: Add excess air to the products with its coefficient:

     $$a_5 = a \frac{1 - \phi}{\phi}$$

     (b) $\phi > 1$: Add H_2 and CO. Their stoichiometric coefficients have to be found from the K_p table.

  $$K_p = \frac{\left(P_{H_2}/p^\circ\right)\left(P_{CO_2}/p^\circ\right)}{\left(P_{CO_2}/p^\circ\right)\left(P_{H_2O}/p^\circ\right)} = \frac{(d/n)(a/n)}{(b/n)(c/n)} \frac{(P/p^\circ)(P/p^\circ)}{(P/p^\circ)(P/p^\circ)}$$

  P: total pressure
  p°: 1 bar
  n = a + b + c + d + e

- **Does the composition of products vary with pressure?**
  It doesn't vary with pressure if:
  $$\sum \nu_i = 0$$
  in the associated stoichiometric equation of the products in the K_p section of the databook.

- **How to improve the conversion efficiency (produce more H_2)**

  1. Increase K_p by decreasing temperatures.
  2. Water injection (water will make use of the heat to dissociate the H_2O molecules into H_2). The water gas shift reaction (below) will shift towards the right (Le Chatelier's principle: When H_2O goes up, H_2 goes up).

  $$CO_2 + H_2 = H_2O + CO$$
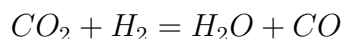
- **Would you expect thermodynamic equilibrium everywhere in the combustion chamber?**
  Not in the flame because kinetics dominate there. The products will slowly approach thermodynamic equilibrium.

3 Chapters 2-3: Kinetics, dissociation

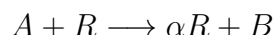- **What type of reaction is X?** (2011:Q2, 2012:Q1)

  1. **Chain initiating:**
  $$A + M \longrightarrow B + R$$
  where R is a radical.
     - Production of a radical.
     - Requires high activation energies.

  2. **Chain branching:**
  $$A + R \longrightarrow \alpha R + B$$
  with $\alpha > 1$.
     - More radicals in products than in reactants.
     - Fast.
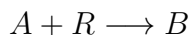   - Low activation energy.
     - Behind explosions.

  3. **Chain propagating:**
  $$A + R \longrightarrow R + B$$
  with $\alpha = 1$.
     - Radicals can change identity but their number in either side is the same.

  4. **Chain terminating:**
  $$A + R \longrightarrow B$$
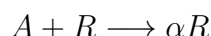 with $\alpha = 0$.
     - Consumption of all radicals.

- **Write the reaction rate of species X in the following reaction:** (2011:Q2, 2012:Q1, 2016:Q1)
  $$A + R \longrightarrow \alpha R$$
  In this case, we write:
  $$\frac{d[R]}{dt} = -k[A][R] + k[A]\alpha[R]$$
  $$\frac{d[R]}{dt} = k(\alpha - 1)[A][R]$$
  Careful with α since it will only appear when calculating the reaction rate of R. In other words:
  $$\frac{d[A]}{dt} = -k[A][R]$$
  Notice there is no *alpha* in this equation.

- **Explosion limits** (2011:Q2, 2012:Q1)

  - Explosions are facilitated by **chain-branching** reactions.
  - Explosions happen when the reaction rate is very high and approaches infinity. Typically, this means the **denominator** of $d[A]/dt$ is very close to zero.

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- **Steady-state vs chemical equilibrium**

  - Species N is in steady-state:
    $$\frac{dN}{dt} = 0$$

  - The elementary reaction is in equilibrium:

    $$A + B \longrightarrow C + D$$

    $$k_f[A][B] = k_b[C][D]$$

- **Other miscellaneous questions**

  - Pressure and T balance into dT/dt as a function of reaction rate (2011:Q2).
  - Types of chain termination (wall vs gas phase) (2012:Q1).
    * Wall: no collision partner required.
    * Gas phase: collision partner required.
  - Show that the rate of formation of P is first order in the high pressure limit and second order in the low pressure limit.
    * Probably has to do with Le Chatelier's principle.
    * At high pressure: more collisions so $k_{collision}$ should be higher.

4 Chapter 4: Autoignition

5 Chapter 5: Extinction

- **Quenching $\neq$ Extinction**

  - The term quenching is used to separate "chemical" extinction (real extinction) due to high inflow of reactants from "physical/thermal" extinction due to heat losses to the cold walls (quenching).

- /!\ **Key equation to memorise**

$$Conductive\ heat\ flux = Reactive\ heat\ flux$$

$$\lambda \frac{dT}{dx} A = Q w_f V$$

$$\lambda \frac{dT}{dx} = Q w_f \delta$$

$$\lambda \frac{\Delta T}{\delta} = (c_p \Delta T) \left(\frac{\rho_0 S_L}{\delta} \right) \delta$$

- /!\ **Quenching distance :** Find an expression for δ as a function of the pipe or flame arrestor diameter d

$$Conductive\ heat\ loss\ at\ walls = Reactive\ heat\ flux$$

$$\lambda \left(\frac{dT}{dx}|_{wall} \right) A = Q w_f V$$

$$\lambda \left(\frac{T_f - T_w}{d/2} \right) \pi d \delta = (c_p (T_f - T_0)) \left(\frac{\rho_0 S_L}{\delta} \right) \left(\frac{\pi d^2}{4} \delta \right)$$

6 Chapter 6: Premixed flames

- **Derivation of S$_\mathbf{L}$**

    1. Derive an expression for $dT/dx|_{x=x_i}$ by combining expressions from the pre-heat zone (only diffusion and advection) and the reaction zone (only diffusion and reaction, taking into consideration their boundary conditions.

        – Pre-heat zone:
        $$\frac{\partial T}{\partial x}|_{x=x_i} = S_L \frac{T_I - T_0}{\alpha}$$

        – Reaction zone:
        $$\frac{\partial^2 T}{\partial x^2}|_{x=x_i} = 2\frac{Q}{\lambda}(T_f - T_I)\int_{T_I}^{T_f} \dot{w}_{fu}dT$$

        In the above equation, we use a trick to convert the diffusion term $\partial^2 T/\partial x^2$ to an expression involving $(\partial T/\partial x)^2$.

    2. Combine both expressions at $x = x_i$ to get a single expression for $(\partial T/\partial x)$, then derive a first expression for S_L.

        $$\frac{\partial T}{\partial x} = \sqrt{\frac{2Q}{\lambda}RR}$$

        $$S_L = \sqrt{2\alpha \underbrace{\frac{1}{\rho_0\, Y_{fu,0}}}_{reactants} \underbrace{\frac{RR}{T_f - T_0}}_{T_I-T_0 \approx T_f-T_0}}$$

    3. Derive an expression for the integrated reaction rate term RR.

        $$RR = \underbrace{\rho_1^2}_{products} \frac{A}{M_{ox}} \int_{T_I}^{T_f} Y_{fu}Y_{ox}exp\left(\frac{T_a}{T}\right)dT$$

        $$RR = \rho_1^2 \frac{A}{M_{ox}} \int_{T_I}^{T_f} Y_{fu}Y_{ox}exp\left(\frac{T_a}{T}\right)dT$$

    4. Simplify the exponential term by using **high activation energy expansion**.

        $$exp\left(-\frac{T_a}{T}\right) = exp\left(-\frac{T_a}{T_f - \Delta T}\right) = exp\left(-\frac{T_a}{T_f(1 - \underbrace{\Delta T/T_f}_{<<1})}\right)$$

        $$= exp\left(-\frac{T_a}{T_f}(1 + \frac{\Delta T}{T_f})\right)$$

        $$= exp\left(-\frac{T_a}{T_f}\right)\underbrace{exp\left(-\frac{T_a}{T_f^2}(T_f - T)\right)}_{T\,in\,numerator}$$

    5. Plug in the above expression and derive an expression for RR. Some useful assumptions:

- Stoichiometric mixture $Y_{fu,0} = S.Y_{ox,0}$
- Complete combustion $Y_{fu,f} = 0$

6. Perform a change of variable inside the RR integral to introduce the Zeldovich number:

$$\beta = \frac{T_a}{T_f^2}(T_f - T)$$

- The value of β is very high, so $exp(-\beta) << 1$.

7. Derive a final expression for S_L.

- **How does S_L vary with the ratio of O_2 and CO_2 in reactants?**

  - High $O_2\% \longrightarrow NOx$ capture easier (but high T_f, so potentially high thermal NO_x, and need for air separation units).
  - CO_2 dilution $\longrightarrow$ Lower T_f and NO_x.

- **Prove that $\delta_f^2 = \lambda/c_p\dot{\omega}$**
  For a propagating flame, equate the reaction heat flux and conductive heat flux

$$H\dot{\omega}\delta_f = \lambda\frac{dT}{dx}$$

$$c_p\Delta T\dot{\omega}\delta_f = \lambda\frac{\Delta T}{\delta_f}$$

- **Effect of ϕ, $T_{reactants,0}$, and p^n on S_L**

  - ϕ: This is standard. However, the $\dot{\omega}$ expression we use is for lean mixtures, so hard to explain tendencies at $\phi > 1$ using the S_L equation derived.
  - $T_{reactants,0}$: When T of reactants increases, S_L increases but not 100% linearly because the **exponential term** contains T_f which is responsible for the exponential tendency at higher values of $T_{reactants,0}$.
  - p^n: The effect of pressure is seen from the **density** term in the S_L expression. Depending on the value of n (order of reaction), the correlation between p and S_L can be positive ($n > 2$), negative ($n = 1$), or inexistent ($n = 2$).

7 Chapter 8: Pollutants