



**Question 2** (50 pts).

Asymptotic expansions of the Boltzmann equation indicate that the diffusion velocities  $\mathbf{V}_i$  of species  $i$  in a multicomponent mixture of  $N$  species can be calculated from the equation

$$\begin{aligned} \nabla X_i = & \sum_{j=1}^N \left( \frac{X_i X_j}{D_{ij}} \right) (\mathbf{V}_j - \mathbf{V}_i) + (Y_i - X_i) \left( \frac{\nabla P}{P} \right) + \frac{\rho}{P} \sum_{j=1}^N Y_i Y_j (\mathbf{f}_i - \mathbf{f}_j) \\ & + \sum_{j=1}^N \left( \frac{X_i X_j}{\rho D_{ij}} \right) \left( \frac{D_{T,j}}{Y_j} - \frac{D_{T,i}}{Y_i} \right) \left( \frac{\nabla T}{T} \right) \end{aligned}$$

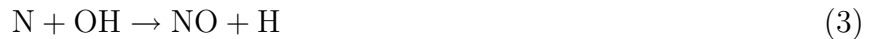
(see for instance, “Molecular theory of gases and liquids” by Hirschfelder, Curtiss and Bird, 1964) where  $\rho$  is the density,  $P$  is the pressure,  $T$  is the temperature,  $X_i$  is the molar fraction of species  $i$ ,  $Y_i$  is the mass fraction of species  $i$ ,  $D_{ij}$  is the binary diffusion coefficient and  $D_{T,i}$  is the Soret coefficient of species  $i$ .

- a) Give a qualitative description of the four different terms; in what conditions are each of them negligible?
- b) Show that this equation reduces to the Fick's law  $\mathbf{V}_i Y_i = -D_{ij} \nabla Y_i$  if all the following conditions are satisfied simultaneously: i) the mixture is binary, ii) the thermal diffusion is negligible, iii) the pressure gradients are small compared to the pressure itself, and iv) the body forces acting on each species are equal.

**Problem 1** (50 pts)

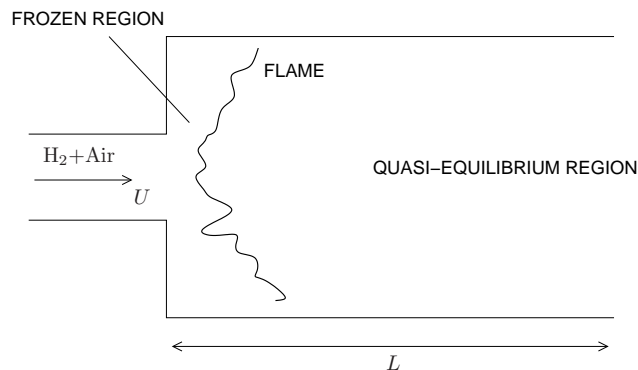
In the design of turbulent-combustion chambers for gas turbines, a careful consideration of pollutant emissions is of particular importance for compliance with current regulations.

Consider a combustion chamber in which a lean mixture of hydrogen  $H_2$  and air is burnt to generate high enthalpy gases that will be sent to the turbine stage. The mixture is injected at a temperature  $T_u = 298$  K and the chamber operates at atmospheric pressure. In this combustor, all the NO is produced by the Zel'dovich mechanism, which is given by the set of chemical reactions



The Zel'dovich mechanism (1)-(4) describes the production of NO by the high-temperature dissociation of the  $N_2$  found in the air premixed with the  $H_2$ . Other NO production mechanisms - such as the Fenimore mechanism for prompt NO formation by hydrocarbon radical action upon  $N_2$ , or mechanisms of NO formation from fuel-bound nitrogen - are irrelevant here since the fuel is pure hydrogen.

A strongly corrugated premixed flame is produced as a result of the chemical reactions and the turbulence in the combustor, as depicted in Fig. 1. The flame front separates an entrance region, in which the temperature is low and the chemistry is frozen, from a quasi-equilibrium region, in which the temperature is high and all species concentrations (except NO) reach the values given by chemical equilibrium. The production of NO occurs mainly in this second region because of the slow rate of the NO chemistry and its strong dependence on temperature. To illustrate the influences of the equivalence ratio, consider three different gaseous mixtures at the injection: i) Mixture A with  $Y_{H_2,u} = 0.015$  balanced with air, and ii) Mixture B with  $Y_{H_2,u} = 0.025$  balanced with air.



- a) Obtain the composition of the fresh gases ( $Y_{N_2,u}$ ,  $X_{N_2,u}$ ,  $Y_{O_2,u}$ ,  $X_{O_2,u}$ ,  $Y_{H_2,u}$ ,  $X_{H_2,u}$  and equivalence ratio  $\phi$ ) for the two initial mixtures A and B.

- b) Assuming that the burnt gases only contain  $N_2$ ,  $O_2$  and  $H_2O$  (i.e. the concentration of other species are much smaller), use the conservation of atoms to determine the molar fractions and mass fractions of the products in the quasi-equilibrium zone for the fresh mixtures A and B.
- c) Calculate the adiabatic temperature in the quasi-equilibrium region for the fresh mixtures A and B. To simplify the calculations, assume that the specific heat of the mixture is  $c_p = 1.4 \text{ kJ/kgK}$  for both fresh and burnt gases. Assume  $h_{H_2O}^0 = -13.4 \cdot 10^3 \text{ kJ/kg}$ .
- d) In order to obtain the production rate of NO in the quasi-equilibrium region, use the Zel'dovich mechanism given in the problem statement and follow these steps (show the work):
- i) Assume that the N radical is in steady state, or equivalently, that the rates of the steps 2 and 3 are much faster than the rate of step 1, and therefore  $d[N]/dt = 0$ . In this way, you should be able to write down an equation for the production rate  $\dot{\omega}_{NO}$  that only depends on the concentrations of  $N_2$  and O.
  - ii) Assume that step 4 is in chemical equilibrium, and obtain a relation between the concentrations of O and  $O_2$  in equilibrium. Using this result, write the production rate of NO as a function of  $O_2$  and  $N_2$  concentrations.

After performing successfully steps i) and ii), you would obtain

$$\frac{d[\text{NO}]}{dt} = \dot{\omega}_{\text{NO}} = k[\text{N}_2][\text{O}_2]_{eq}^{1/2} \quad (5)$$

where  $k = 2k_1K_{c4}^{-1/2}$ , where  $k_1$  is the rate constant of reaction (1) and  $K_{c4}$  is the concentration equilibrium constant of reaction (4). You can use this result if you were not able to obtain it using i) and ii) above.

- e) Using equation (5), estimate the molar fraction of NO at the combustor exit for the fresh mixtures A and B if the characteristic injection velocity of the fresh gases is  $U = 10$  m/s and the combustor length is  $L = 10$  cm. Notice that  $\tau \sim L/U$  is a characteristic integral time scale of the problem that can be used in (5) to estimate  $X_{\text{NO}}$ . For solving this part, assume  $k = 1.83 \cdot 10^{15} \left( \frac{\text{cm}^3}{\text{s}^2\text{mol}} \right)^{1/2} \exp \left[ -\frac{567.5\text{kJ/mol}}{R^0T} \right]$ .

- f) If the combustion chamber was sufficiently long, then the residence time in the quasi-equilibrium region would be large and the concentration of NO would reach the equilibrium value. This concentration can be obtained by assuming that the reaction



is in chemical equilibrium. Use the results from part b) and the chemical-equilibrium constraint on reaction (6) to obtain the molar fraction of NO at the combustor exit for mixtures A and B, and compare it to the results obtained from e). For this part, use  $g_{\text{NO}}^0 = 70.15$  kJ/mol at 1600 K and  $g_{\text{NO}}^0 = 58.71$  kJ/mol at 2500 K.

The comparison should indicate that overall chemical equilibrium tends to overestimate the production of NO in typical combustors.