

Multi-Step / Multi-Species Finite Rate Chemical Reactions

Introduction

The design of hypersonic flight jets, rocket propulsion systems and the space shuttle main engine (SSME) combustion chambers require solving various combustion problems. It is clear that the subject of chemical reaction plays an important role in applications of fluid flows. In general, chemical reactions will occur when the temperature of a fluid is high. The following figure illustrates the temperature ranges for air dissociation and ionization [1].

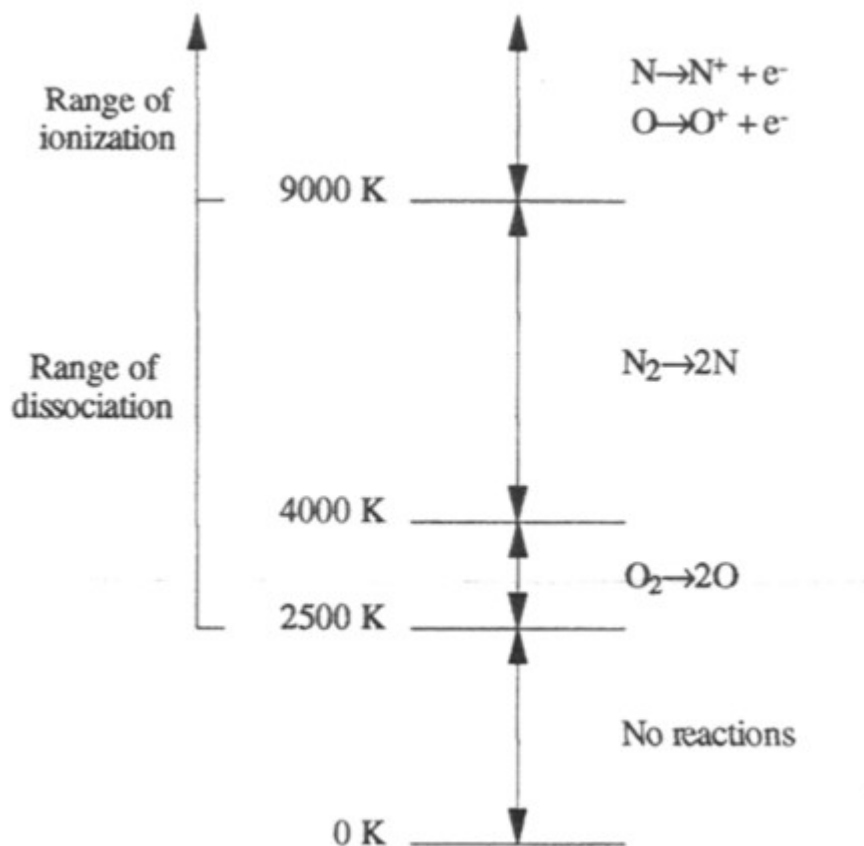


Figure 1. Temperature ranges for air dissociation and ionization (for air at approximately 1 atm).

Thus, high temperature can cause the process in a combustion system to be very complicated. The unknown flow field variables are:

| | |
|-----------|--|
| ρ | Density |
| \vec{V} | Velocity vector |
| h(or e) | Enthalpy (or internal energy) |
| Y_i | ($i = 1, \dots, NS$, NS means components number) Mass fraction |
| T | Temperature |
| p | Pressure |

When simulating a combustion system, multiple characteristic time scales occur:

- (1) The time scale of flow field t_f . It is defined by the time interval that the fluid particles make any small change on the properties such as velocity, Pressure, temperature and density
- (2) The time scale of chemical reaction t_{c_j} ($j=1, \dots, NR$, NR denotes the number of reaction step). They are defined by the serial time integrals that the concentrations of components make any small change in each reaction step

The flow field shows different characteristics with different ratio of time scales. Based on Damkohler's classic analysis [2], the Damkohler number is defined as:

$$D_{lj} = \frac{t_f}{t_{c_j}} \quad j = 1, \dots, NR$$

If the time scale of the flow field is much larger than that of the chemical reaction, that is,

$$D_{lj} = \frac{t_f}{t_{c_j}} \rightarrow 0 \quad j = 1, \dots, NR$$

The chemical reaction takes much more time compared to the time scale of the flow field. Therefore, no reaction takes place. This is called a 'chemically frozen flow'.

If the time scale of flow field is much less than that of the chemical reaction, that is,

$$D_{ij} = \frac{t_f}{t_{cj}} \rightarrow \infty \quad j = 1, \dots, \text{NR}$$

The species undergoes a chemical reaction immediately. Thus, the chemical reactants and products are always in an equilibrium state. This is called a “chemically equilibrium flow”.

The more common, and difficult, case is when those two time scales are about same order, that is,

$$D_{ij} = \frac{t_f}{t_{cj}} \cong \text{limited value} \quad j = 1, \dots, \text{NR}$$

This is referred to as “finite rate reacting flow”. The numerical method used in computational fluid dynamics faces a major difficulty when solving such finite rate reacting flows. The difficulty is the stiffness of the mathematical models, which describe the transport characteristics of species concentrations.

There are several ways to define a stiff system. A direct definition, however, could be as follows:

If the ratio of the largest time scale T_{cj} to the smallest T_{cj} is very large, that is,

$$\tau = \frac{\max(t_{cj})}{\min(t_{cj})} \gg 1 \quad (j = 1, \dots, \text{NR})$$

for some reactions, then the mathematical description or model of these reactions is termed stiff. The model results in a set of stiff equations, which represent the spatial and temporal variation of species concentrations.

To study the non-equilibrium reaction, i.e., finite rate reaction, the time required for molecular collisions must be taken into account. In order to do this, it is necessary to develop models of chemical reactions based on the theory of chemical kinetics. From a mathematical standpoint, the species conservation is a set of partial differential equations describing the generation, elimination and distribution of species. In such a set of equations, the generation or source

term should be provided by chemical kinetic models, which describe the rate of production of species. The kinetic models cause the equation to become nonlinear and highly stiff, so that special numerical treatments will be needed to solve these species equations [3]. Otherwise, a very small iterative time step should be taken. However, extremely small time steps will expend much computational time for most numerical simulations of reacting flow.

The operator splitting technique, which has been used in the simulation of reacting fluid flows [4,5,6,7,8], provides a tool to solve the stiff reacting flows. This technique divides the procedure of integration of species equations into two steps. The first step is to get effective chemical production terms by integrating a set of ordinary differential equations, which describe the reacting rate of each species in all reaction steps. The second step is to solve partial differential equations of transportation of species to get their distributions in space. This method overcomes the strong stiffness difficulty. The main disadvantage is that the technique will take a little more computing time. Despite the drawback, it is a good method.

Governing Equations

Basic Concepts

For a given multi-component system, define ρ_i as the density of the i^{th} species, which is the mass of i^{th} gas per unit volume. Thus, the density of the gas mixture is:

$$\rho = \sum_{i=1}^{NS} \rho_i$$

Where, NS denotes the total number of species. The pressure of mixture, p , is:

$$p = \sum_{i=1}^{NS} p_i$$

Where, p_i is the i^{th} component pressure. The mass fraction of the i^{th} species is:

$$Y_i = \frac{\rho_i}{\rho}$$

or, mole fraction

$$X_i = \frac{p_i}{p}$$

Usually, if the pressure is not too high and the temperature is not too low, it is assumed that most gases are ideal, obeying the following equation of state:

For the *i*th component:

$$p_i = \rho_i \frac{R_0}{M_i} T$$

For the gas mixture:

$$p = \rho \frac{R_0}{M} T$$

where,

| | |
|-------|---|
| R_0 | universal gas constant $\left(\frac{J}{kmole * K} \right)$; |
| M_i | molecular weight of the <i>i</i> th component; |
| M | molecular weight of gas mixture; |
| T | gas temperature (K) |

It is helpful to define

$$R_i = \frac{R_0}{M_i}$$

as the gas constant of the *i*th component and

$$R = \frac{R_0}{M}$$

as the gas constant of the mixture.

The mass and mole fraction of gas are connected into relations as below:

$$X_i = Y_i \frac{M}{M_i}$$

Where, the molecular weight of mixture is:

$$M = \sum_{i=1}^{NS} X_i M_i$$

or

$$M^{-1} = \sum_{i=1}^{NS} \frac{Y_i}{M_i}$$

Governing Equations

The governing equations in tensor form for gas flow are as follows:

Continuity equation:

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x_i} (\rho U_i) = 0$$

Momentum equation:

$$\frac{\partial \rho U_i}{\partial t} + \frac{\partial}{\partial x_j} (\rho U_i U_j) = - \frac{\partial p}{\partial x_i} + \frac{\partial}{\partial x_j} \left[(\mu + \mu_t) \left(\frac{\partial U_i}{\partial x_j} + \frac{\partial U_j}{\partial x_i} \right) \right] - \frac{2}{3} (\mu + \mu_t) \frac{\partial}{\partial x_i} \left(\frac{\partial U_k}{\partial x_k} \right)$$

Energy equation:

$$\frac{\partial \rho h}{\partial t} + \frac{\partial}{\partial x_j} (\rho h U_j) = \frac{dp}{dt} + \frac{\partial}{\partial x_j} \left[\left(\frac{\mu}{p_r} + \frac{\mu_t}{p_{rt}} \right) \frac{\partial h}{\partial x_j} \right] + \phi$$

Where, ϕ is viscous energy dissipation term and defined as

$$\phi = \left[\mu \left(\frac{\partial U_i}{\partial x_j} + \frac{\partial U_j}{\partial x_i} \right) - \left(\frac{2}{3} \mu \frac{\partial U_j}{\partial x_j} \right) \delta_{ij} \right] \frac{\partial U_j}{\partial x_j}$$

Species conservation:

$$\frac{\partial \rho Y_i}{\partial t} + \frac{\partial}{\partial x_j} (\rho Y_i U_j) = \frac{\partial}{\partial x_j} \left[\left(\frac{\mu}{S_c} + \frac{\mu_t}{S_{ct}} \right) \frac{\partial Y_i}{\partial x_j} \right] + \dot{\omega}_i \quad i=1, \dots, NS$$

Turbulent transport equation for kinetic energy k:

$$\frac{\partial \rho k}{\partial t} + \frac{\partial}{\partial x_j} (\rho k U_j) = \frac{\partial}{\partial x_j} \left[\left(\mu + \frac{\mu_t}{\sigma_k} \right) \frac{\partial k}{\partial x_j} \right] + \mu_t G - \rho \epsilon$$

Turbulent transport equation for dissipation ε

$$\frac{\partial \rho \varepsilon}{\partial t} + \frac{\partial}{\partial x_j} (\rho \varepsilon U_j) = \frac{\partial}{\partial x_j} \left[\left(\mu + \frac{\mu_t}{\sigma_\varepsilon} \right) \frac{\partial \varepsilon}{\partial x_j} \right] + \frac{\varepsilon}{k} (C_1 \mu_t G - C_2 \rho \varepsilon)$$

Equation of state:

$$p = \rho R T$$

where, ρ is the ensemble averaged density of the mixture; U_i is the i th component of the velocity. In the three dimensional space, U_i has three components, $U_i = (U_1, U_2, U_3)$. Each U_i is the component of the vector V in the X , Y and Z direction; H is enthalpy, defined by

$$h = \sum_{i=1}^{NS} Y_i (h_{fi}^0 + \int c_{pi} dT)$$

Y_i ($k=1, \dots, NS$) is mass fraction of the i th species; NS is total species number; h_{fi}^0 is heat of formation of the i th species; c_{pi} is specific heat of the i th species; p is pressure; μ is laminar Viscosity; μ_t is turbulence eddy viscosity, defined by

$$\mu_t = C_\mu \rho \frac{k^2}{\varepsilon}$$

P_r is laminar Prandtl number; P_{rt} is turbulence Prandtl number; S_c is laminar Schmidt number; S_{ct} is turbulence Schmidt number; ω_i is species production rate.

It should be mentioned that the turbulent Reynolds stress and scalar fluxes are modeled from the gradient transport model[9],

$$\overline{\rho u_i' u_j'} = -\mu_t \left(\frac{\partial U_i}{\partial x_j} + \frac{\partial U_j}{\partial x_i} \right) + \frac{2}{3} \delta_{ij} \left(\rho k + \mu \frac{\partial U_k}{\partial x_k} \right)$$

and

$$\overline{\rho u_i' \phi} = -\frac{\mu_t}{\sigma_t} \frac{\partial \phi}{\partial x_i}$$

The turbulent production term is:

$$\mu_t G = \mu_t \left(\frac{\partial U_i}{\partial x_j} + \frac{\partial U_j}{\partial x_i} \right) \frac{\partial U_i}{\partial x_j} - \frac{\mu_t}{\rho^2} \frac{\partial \rho}{\partial x_j} \frac{\partial \rho}{\partial x_j} - \frac{2}{3} \left(\rho k + \mu_t \frac{\partial U_i}{\partial x_i} \right) \frac{\partial U_j}{\partial x_j}$$

All constants in the equations above are listed in the following Tables:

Turbulence model constants

| C_1 | C_2 | C_μ | σ_k | σ_ε | σ_t |
|-------|-------|---------|------------|----------------------|------------|
| 1.45 | 1.92 | 0.09 | 1.0 | 1.3 | 0.9 |

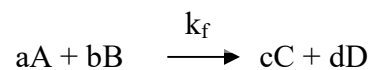
Prandtl and Schmidt numbers

| P_r | P_{rt} | S_c | S_{ct} |
|-------|----------|-------|----------|
| 0.7 | 0.9 | 0.7 | 0.9 |

Finite Rate Reaction

Basic Concepts

If there is a reaction as follows:



Where, a, b, c, and d are the stoichiometric coefficients, A,B,C and D are arbitrary species and k_f is the forward reaction rate. The net decreasing rate of species A and B, based on the law of mass action, are[10]

$$\dot{\omega}_A = \frac{dC_A}{dt} = -a k_f C_A^a C_B^b$$

$$\dot{\omega}_B = \frac{dC_B}{dt} = -b k_f C_A^a C_B^b$$

Also, the net increasing rate of species C and D are

$$\dot{\omega}_C = \frac{dC_C}{dt} = c k_f C_A^a C_B^b$$

$$\dot{\omega}_D = \frac{dC_D}{dt} = d k_f C_A^a C_B^b$$

In the equations above, C_i ($i=A,B,C,D$) means the concentration of species. The forward reaction rate is given by the Arrhenius equation:

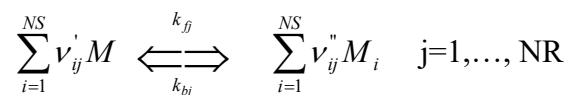
$$k_f = AT^N \exp\left(-\frac{E_a}{R_0 T}\right)$$

where, A, N and E_a are constants. The term $A T^N$ is the collision factor and E_a is called the activation energy. The physical meaning of E_a is that only those molecules which possess an energy greater than E_a will react. The values of A, N and E_a are Not obtained by theory but from experimental or empirical data.

When given initial data of species A, B, C and D, by integrating equations earlier presented, the species concentrations can be calculated at any time. If there are many reactants, numerical integration will be necessary.

Finite Rate Reaction Model

Generally, chemical reactions will not proceed in the forward direction only, they are reversible and proceed in forward and backward directions. A general multi-step chemical reaction equation is



Where, v'_{ij} and v''_{ij} are the stoichiometric coefficients of reactants and products in the jth step; M_i the species formula; NS, the total species number; NR, the total reaction step; k_{fj} the forward reaction rate for the jth step; k_{bj} the backward reaction rate for the jth step.

Based on the law of mass action, the net reaction rate of species I at the jth reaction step is

$$\dot{\omega}_i = \frac{dC_{M_i}}{dt} = (v''_{ij} - v'_{ij}) k_{fj} \prod_{k=1}^{NS} C_{M_k}^{v'_{kj}} + (v'_{ij} - v''_{ij}) k_{bj} \prod_{k=1}^{NS} C_{M_k}^{v''_{kj}}$$

$$i = 1, \dots, NS, \quad j = 1, \dots, NR$$

It is obvious that if the jth reaction step is at thermodynamic equilibrium, then

$$\left(\frac{dC_{M_i}}{dt} \right) = 0 \quad j = 1, \dots, NR$$

This leads to

$$(v''_{ij} - v'_{ij}) k_{fj} \prod_{k=1}^{NS} C_{M_k}^{v'_{kj}} \Big|_{eq} = -(v'_{ij} - v''_{ij}) k_{bj} \prod_{k=1}^{NS} C_{M_k}^{v''_{kj}} \Big|_{eq}$$

which means equilibrium. The new equilibrium constant k_{cj} can be defined as

$$K_{cj} = \left(\frac{k_{fj}}{k_{bj}} \right) = \frac{\prod_{k=1}^{NS} C_{M_k}^{v''_{kj}}}{\prod_{k=1}^{NS} C_{M_k}^{v'_{kj}}} \quad j=1, \dots, NR$$

The above equation represents a way to calculate the backward reaction rate k_{bj} , if K_{cj} can be determined. Defining the partial pressure equilibrium constant K_{pj} as,

$$K_{pj} = \prod_{i=1}^{NS} P_i^{d_{ni}} = \prod_{i=1}^{NS} P_i^{(v''_{ij} - v'_{ij})}$$

From thermodynamics, we have

$$K_{pj} = \exp \left(-\frac{\Delta G^0}{R_0 T} \right) \quad j=1, \dots, NR$$

Where ΔG^0 is defined as

$$\Delta G^0 = \sum_{i=1}^{NS} v''_{ij} \mu_i^0 \Big|_{\text{products}} - \sum_{i=1}^{NS} v'_{ij} \mu_i^0 \Big|_{\text{react}}$$

$$j = 1, \dots, NR$$

Here, it should be noted that ΔG^0 can be calculated from the Gibbs free energy of the mixture at the reference state ($T, p_o = 1 \text{ atm}$). The equation for K_{pj} shows the relation between the standard free energy change and the equilibrium constant at any arbitrary pressure and temperature. The practical importance of the equilibrium constant K_{pj} results from the fact that it is independent of total pressure and can therefore be listed as a unique function of temperature.

In order to calculate K_{cj} , we note the mixture is at equilibrium and substitute the equation of state into the equation for K_{cj} to get,

$$K_{cj} = \prod_{i=1}^{NS} C_i^{(v''_{ij} - v'_{ij})}$$

or

$$K_{cj} = (R_o' T)^{-(v_{ij}'' - v_{ij}') } K_{pj} \quad j=1, \dots, NR$$

It should be mentioned that R_o and R_o' are universal gas constants but have different units.

So far, a general computational procedure for finite rate chemical reactions in the gas phase has been developed. During any time of reaction, the concentrations of species can be calculated by integrating the equation for the net reaction rate of species, usually, by some numerical procedure. To complete the calculation, the chemical kinetics model should be provided.

Species Predictor Step

In finite rate reacting flows, there are several different time scales: the flow field time scale t_f and the reaction time scale Δt_{cj} ($j=1, \dots, NR$). Usually, Δt_{cj} is less than Δt_f for a large number of reactions, such as hydrogen combustion and air dissociation. Due to very small Δt_{cj} , the reaction goes to completion at very short time interval. This means the reaction rate of species $\dot{\omega}_i$ ($i=1, \dots, NS$) is larger than the effects of convection and diffusion. It is necessary to integrate the equation with very small time steps of less than Δt_f to obtain accurate solutions. This causes the species transport equation to be a stiff set of equations.

To explain the operator splitting procedure in more detail, the species transport equation is written in the following form:

$$\frac{\partial \rho Y_i}{\partial t} + C(Y_i) = D(Y_i) + \dot{\omega}_i \quad i = 1, \dots, NS$$

Where, $C(Y_i)$ is the convection term and $D(Y_i)$ is the diffusion term.

In predictor step, omitting the convection and diffusion terms, the equation becomes:

$$\frac{\partial \rho Y_i}{\partial t} = \dot{\omega}_i \quad i = 1, \dots, NS$$

It is integrated in a fully implicit fashion from time increment t^n to t^{n+1} . In this step, we get an effective source term

$$\left(\frac{\partial \rho Y_i}{\partial t}\right)_{eff} = \dot{\omega}_i \quad i = 1, \dots, NS$$

Species Corrector Step

In the corrector step, the convection and diffusion terms are combined in the transport equations and replace source term $\dot{\omega}_i$ by the effective one $\left(\frac{\partial \rho Y_i}{\partial t}\right)_{eff}$:

$$\frac{\partial \rho Y_i}{\partial t} + C(Y_i) = D(Y_i) + \left(\frac{\partial \rho Y_i}{\partial t}\right)_{eff} \quad i = 1, \dots, NS$$

Solving the equation we get the final species mass fractions Y_i^{n+1} at time level t^{n+1} ,

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