Governing Equations

Reducing Soot and NOx Emissions

In HCCI and petrol engines, the fuel and air are mixed before combustion, preventing the soot emissions of diesel engines. Only HCCI engines have multiple ignition points throughout the chamber. This plus their lean burn keeps temperatures low, preventing formation of nitrogen oxides (NOx).

Flame Images

Propagating premixed flame in SI engine

Turbulent diffusion Flame
Diffusion Flames

Video images of ethane jet diffusion flames in quiescent air in 1g and μg. Burner tube inside diameter= 2.87 mm; mean fuel jet velocity=7.5 cm/sec.


Computed Images (from 1 to 200 msec) in terms of temperature field (contours) of a propagating edge diffusion flame in an ethane jet in quasi-quiescent air in 0g. Burner tube diameter= 3 mm; mean fuel jet velocity=6.86 cm/sec.
Counterflow Flame Structure
Conservation Equations Using a Control Volume

Premixed Flame Structure

Conservation Laws Based on Control Volume

Conservation Equation for Property $P$

$$\frac{\partial P}{\partial t} = P_{\text{in}} - P_{\text{out}} + \dot{P}_s$$

Rate of change of $P$ = rate of $P$ flowing in - rate of $P$ flowing out + rate of production of $P$ in the CV

$p$ is the property $P$ per unit mass $p = 1, u_x, e, Y_i$

$$P = \rho p dV = \rho dV, \rho dV, \rho u_x dV, \rho e dV$$

Mixture Mass Conservation

$$\dot{P}_s = 0$$

$$\dot{m}_x = \text{mass flow rate in } x \text{ direction } = (\rho u) dA$$

$$\dot{m}''_x = \text{mass flux in } x \text{ direction } = \rho u$$

$$(P_{\text{in}} - P_{\text{out}})_x = dA[(\rho u)_x - (\rho u)_{x+\Delta x}] = -dx.dy.dz \frac{\partial \rho u}{\partial x}$$

$$\frac{\partial \rho}{\partial t} = - \frac{\partial (\rho u)}{\partial x} = - \frac{\partial \dot{m}''_x}{\partial x} \quad \rightarrow \quad \frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho V)$$

$dV = dx.dy.dz$

$dA = dy.dz$
Species Equation

Conservation of Species Mass (Species Equation)

\[ \frac{\partial \rho_i}{\partial t} = - \frac{\partial (\dot{m}_i^{''})}{\partial x} + \dot{m}_i^{''} \Rightarrow \frac{\partial \rho_i}{\partial t} = - \nabla . (\dot{m}_i^{''}) + \dot{m}_i^{''} \]

\[ \dot{m}_i^{''} = \rho_i \vec{v} + \rho_i \vec{V}_{d,i} = \rho_i \vec{v} - \rho_i D_i \nabla \ln Y_i \]

\[ \dot{m}_i^{''''} = \text{source/sink term due to chemical reactions} \]

- Species mass flux consists of convective mass flux and diffusive mass flux.
- Diffusive mass flux is generally assumed to be due to ordinary or Fickian diffusion.

**Diffusion velocity vector is expressed as:**

\[ V_{d,i} = -D_{im} \nabla \ln Y_i \]

- Dim is the species diffusion coefficient and depends on T and p.
- In addition to the Fickian or concentration gradient diffusion, there is diffusion due to temperature gradient (Soret or thermal diffusion), pressure gradient, and body forces.
- The Soret diffusion causes light species to diffuse from low- to high-temperature regions, and heavy species to diffuse from high- to low-temperature regions, and is expressed as

\[ V_{T,i} = - \frac{D_T^i}{\rho Y_i} \nabla \ln T \]
Species Diffusivity

- In most situations, the Fickian diffusion is the most dominant effect.
- A more general treatment of this diffusion based on kinetic theory can be found in textbooks; see, for example, by Williams (1994) or by Hirschfelder, Curtiss and Bird (1954). Considering multicomponent diffusion, the diffusion velocity can be written as

$$\nabla \ln X_i = \sum_{j=1}^{N} \left( X_j / D_{ij} \right) (V_{d,j} - V_{d,i}) \quad i=1, 2,.. n$$

An alternative form is:

$$V_{d,i} = \frac{1}{X_i M_{mix}} \sum_{j=1}^{N} M_j D_{ij} \nabla X_j$$

Either of these approaches requires the evaluation of $D_{ij}$ which may be written as:

$$D_{ij} = \frac{2(8 m_{ij} k_b T / \pi)^{1/2}}{\pi \sigma_{ij}^2}$$

Here $m_{ij}$ is the reduced molecular mass, $k_b$ the Boltzmann constant, and $\sigma_{ij}$ is the average molecular diameter.

A more rigorous treatment yields (see Law, 2006):

$$D_{ij} = \frac{3}{16} \frac{(2\pi (k_b T)^3 / m_{ij})^{1/2}}{\pi p \sigma_{ij}^2 \Omega_{ij}^{1,1}}$$
Mass Diffusivity

A more rigorous treatment yields (see Law, 2006):

\[ D_{ij} = \frac{3}{16} \frac{(2\pi (k_b T)^3 / m_{ij})^{1/2}}{\pi p \sigma_{ij}^2 \Omega_{ij}^{1,1}} \]

Here \( p \) is pressure, and \( \Omega \) is the collision integral representing the transport flux resulting from the interactions between various molecules. Collision integrals for many species are available in the literature.

A simplified treatment for the diffusion velocity is based on an effective binary diffusion coefficient for species \( i \) with respect to the mixture \( m \), \( D_{im} \):

\[ \bar{V}_{d,i} = -D_{im} \bar{\nabla} \ln Y_i \quad i=1, 2,.. N-1 \]

Then the diffusion velocity for the Nth species is obtained from the condition:

\[ \sum_{i=1}^{N} \rho Y_i V_{d,i} = 0 \quad \Rightarrow \quad V_{d,N} = -\frac{1}{Y_N} \sum_{i=1}^{N-1} Y_i V_{d,i} \]

N is taken as the species in excess, which is generally nitrogen. Also \( D_{im} \) is often calculated from:

\[ D_{im} = \frac{1 - X_i}{\sum_{j \neq i} X_j / D_{ij}} \]

When one of the species (such as \( N_2 \)) is in excess, a commonly used simplification is:

\[ D_{im} = D_{iN} \]

This requires the calculation of only N-1 binary diffusion coefficients.
Momentum Conservation

Vector form:
\[
\frac{\partial (\rho \vec{v})}{\partial t} + \nabla (\rho \vec{v} \cdot \vec{v}) = -\nabla p + \nabla \tau + \vec{f}
\]

\[
\frac{\partial (\rho v_i)}{\partial t} + \frac{\partial (\rho v_j v_i)}{\partial x_j} = - \frac{\partial p}{\partial x_i} + \frac{\partial \tau_{ji}}{\partial x_j} + f_i
\]

Non-conservation form:
\[
\rho \frac{\partial v_i}{\partial t} + \rho v_j \frac{\partial v_i}{\partial x_j} = - \frac{\partial p}{\partial x_i} + \frac{\partial \tau_{ji}}{\partial x_j} + f_i
\]

Stress tensor:
\[
\tau_{ji} = \mu \left( \frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right) - \frac{2}{3} \mu \frac{\partial v_k}{\partial x_k}
\]

2-D Momentum Equations

\[
\frac{\partial (\rho v_y)}{\partial t} + \frac{\partial (\rho v_y v_y)}{\partial y} + \frac{\partial (\rho v_y v_y)}{\partial y} = - \frac{\partial p}{\partial y} + \frac{\partial \tau_{xy}}{\partial x} + \frac{\partial \tau_{yy}}{\partial y}
\]

\[
\frac{\partial (\rho v_x)}{\partial t} + \frac{\partial (\rho v_x v_x)}{\partial x} + \frac{\partial (\rho v_y v_x)}{\partial y} = - \frac{\partial p}{\partial x} + \frac{\partial \tau_{xx}}{\partial x} + \frac{\partial \tau_{yx}}{\partial y}
\]
Energy Conservation

Conservation Equation for Property P

\[
\frac{\partial P}{\partial t} = P_{\text{in}} - P_{\text{out}} + \dot{P}_s
\]

\[
P = \rho eV \quad p = e = u + \frac{V^2}{2}
\]

\[
\dot{m}_x = \text{mass flow rate in } x \text{ direction} = (\rho u)dA
\]

\[
\dot{m}'_x = \text{mass flux in } x \text{ direction} = \rho u
\]

Convective energy flux in x direction\((\rho u)e\)

Energy flux also occurs due to heat transfer through conduction, species diffusion and radiation

\[
\bar{q} = -\lambda \nabla T + \rho \sum_{i=1}^{N} Y_i h_i \bar{V}_{d,i} + Q_{rad}
\]

\[
q_x = -\lambda \frac{\partial T}{\partial x} + \rho \sum_{i=1}^{N} Y_i h_i \bar{V}_{d,i,x} + Q_{rad}
\]

\[
dA = dy.dz
\]
Energy Conservation

\[ P_{in} = E_{in} = dA \left[ (\rho u e)_x + q_x \right] \quad \Rightarrow \quad (E_{in} - E_{out})_x = -dx. dy. dz \left[ \frac{\partial (\rho u e)}{\partial x} + \frac{\partial q_x}{\partial x} \right] \]

\[ \frac{\partial (\rho e)}{\partial t} = - \frac{\partial (\rho u e)}{\partial x} - \frac{\partial q_x}{\partial x} + \dot{e}_s \]

Source/sink terms in the energy equation are due to work done by pressure, viscous and body forces. Vector form (3-D) of the energy equation:

\[ \frac{\partial (\rho e)}{\partial t} + \nabla \cdot (\rho \vec{v} e) = -\nabla \cdot \vec{q} - \nabla \cdot (p \vec{v}) + \nabla \cdot (\tau \cdot \vec{v}) + \vec{f} \cdot \vec{v} \quad e = u + \frac{V^2}{2} \]

Scalar product of momentum eq. and velocity vector yields equation for KE:

\[ \frac{\partial (\rho V^2 / 2)}{\partial t} + \nabla \cdot (\rho \vec{v} V^2 / 2) = -\vec{v} \cdot \nabla p + \vec{v} \cdot \nabla \tau + \vec{f} \cdot \vec{v} \]

Subtract the kinetic energy equation from the energy equation:

\[ \frac{\partial (\rho u)}{\partial t} + \nabla \cdot (\rho \vec{v} u) = -\nabla \cdot \vec{q} - p \nabla \cdot \vec{v} + \tau : \nabla \vec{v} \]
Energy Conservation

\[ \frac{\partial(\rho u)}{\partial t} + \nabla \cdot (\rho \nabla u) = -\nabla \cdot \bar{q} - p \nabla \cdot \bar{v} + \tau : \nabla \bar{v} \]

Index notation:

\[ \frac{\partial(\rho u)}{\partial t} + \frac{\partial(\rho uv_j)}{\partial x_j} = - \frac{\partial q_j}{\partial x_j} - p \frac{\partial v_j}{\partial x_j} + \tau_{ji} \frac{\partial v_i}{\partial x_j} \]

Using \( u = h - p / \rho \) →

\[ \frac{\partial(\rho h)}{\partial t} + \nabla \cdot (\rho \nabla h) = -\nabla \cdot \bar{q} + Dp / Dt + \tau : \nabla \bar{v} \]

\[ h = \sum_{i} Y_i h_i = \sum_{i} Y_i \left( h_{fi}^{0} + \int_{T_{\text{ref}}}^{T} c_{pi} dT \right) \quad \bar{q} = -\lambda \nabla T + \rho \sum_{i=1}^{N} Y_i h_i \bar{V}_{d,i} + Q_{\text{rad}} \]

Radiative heat transfer \( (Q_{\text{rad}}) \) is important in reacting flows. However, for convenience, it is not included in the development of sensible energy equation.
Energy Conservation

Species equation:

\[
\frac{\partial \rho Y_i}{\partial t} + \nabla \cdot (\rho Y_i \mathbf{v} + \rho Y_i \mathbf{V}_{d,i}) = \dot{m}_i'''
\]

Multiply this by the enthalpy of formation of species \(i\), and sum over all species:

\[
\frac{\partial}{\partial t} \left( \sum \rho Y_i h_{fi}^o \right) + \nabla \cdot \left( \sum \rho Y_i h_{fi}^o (\mathbf{v} + \mathbf{V}_{d,i}) \right) = \sum h_{fi}^o \dot{m}_i'''
\]

Subtracting it from the enthalpy equation yields the conservation equation for sensible enthalpy:

\[
\frac{\partial (\rho h_s)}{\partial t} + \nabla \cdot (\rho \mathbf{v} h_s) = \nabla \cdot (\lambda \nabla T) - \nabla \cdot (\rho \sum Y_i \mathbf{V}_{d,i} h_{si}) - \sum \dot{m}_i''' h_{fi}^o + \frac{Dp}{Dt} + \tau : \nabla \mathbf{v}
\]

\[
h_s = \sum Y_i h_{si} = \sum_{i=1}^{N} Y_i \int_{T_{ref}}^{T} c_{pi} dT
\]

\[
\dot{m}_i'''' = M_i \omega_i = M_i \sum_{j=1}^{N_R} (\mathbf{v}_{i,j} - \mathbf{v}_{i,j}') k_j \prod_{i}^{N} c_{i}^{v_{i,j}}
\]

\[
c_i = \rho Y_i / M_i
\]

Notes: (1) Radiation term is not included above, (2) Pressure and stress terms are important in detonation and other high speed reacting flows.
Energy Conservation

\[ \frac{\partial (\rho h_s)}{\partial t} + \nabla \cdot (\rho \mathbf{v} h_s) = \nabla \cdot (\lambda \nabla T) - \nabla \cdot (\rho \sum Y_i \mathbf{V}_{d,i} h_{si}) - \sum \dot{m}_i h_{fi}^o \]

Using \[ \mathbf{V}_{d,i} = -D_{im} \nabla \ln Y_i \]

and \[ \nabla h_s = \nabla \left( \sum Y_i \int_{T^o}^T C_p dT \right) = \sum \nabla Y_i \int_{T^o}^T C_p dT + C_p \nabla T \]

\[ \frac{\partial (\rho h_s)}{\partial t} + \nabla \cdot (\rho \mathbf{v} h_s) = \nabla \cdot \left( \frac{\lambda}{C_p} \nabla h_s \right) + \nabla \left[ \left( \frac{\lambda}{C_p} \right) \sum (Le_i^{-1} - 1) h_{si} \nabla Y_i \right] - \sum \dot{m}_i h_{fi}^o \]

**Lewis number:** \[ Le_i = \frac{\lambda}{\rho C_p D_{im}} \]

**Shvab Zeldovich Formulation:** Consider steady state and \( Le=1 \)

\[ \nabla \cdot (\rho \mathbf{v} h_s) = \nabla \cdot \left( \frac{\lambda}{C_p} \nabla h_s \right) - \sum \dot{m}_i h_{fi}^o \]

**Analogy with the species equation:** \[ \nabla \cdot (\rho \mathbf{v} Y_i) = \nabla \cdot (\rho D_{im} \nabla Y_i) + \dot{m}_i^m \]

See Turns: Equations (7.55), (7.61), (7.63), (7.65), (7.66), and (7.67)  
Law: Chapter 5
Governing Equations (Summary)

Mass Conservation: \[
\frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho \mathbf{V})
\]

Species equation: \[
\frac{\partial \rho Y_i}{\partial t} + \nabla \cdot (\rho Y_i \mathbf{v} + \rho Y_i \mathbf{V}_{d,i}) = \dot{m}_i'' - \nabla \cdot \left( \lambda \nabla T \right) - \nabla \cdot \left( \rho Y_i \nabla \phi_i \right)
\]

Momentum equation: \[
\frac{\partial (\rho \mathbf{v})}{\partial t} + \nabla \cdot (\rho \mathbf{v} \mathbf{v}) = -\nabla p + \nabla \tau + \mathbf{f} - \frac{2}{3} \mu \frac{\partial v_k}{\partial x_k}
\]

Energy equation: \[
\frac{\partial (\rho h)}{\partial t} + \nabla \cdot (\rho \mathbf{v} h) = -\nabla . \dot{q} + \frac{Dp}{Dt} + \mathbf{\tau} : \nabla \mathbf{v}
\]

\[
\dot{q} = -\lambda \nabla T + \rho \sum_{i=1}^{N} Y_i h_i \mathbf{V}_{d,i} \quad \frac{\partial (\rho h)}{\partial t} + \nabla \cdot (\rho \mathbf{v} h) = -\nabla . \dot{q}
\]

\[
\frac{\partial (\rho h_s)}{\partial t} + \nabla \cdot (\rho \mathbf{v} h_s) = \nabla \cdot (\lambda \nabla T) - \nabla \cdot \left( \rho \sum_{i=1}^{N} Y_i \mathbf{V}_{d,i} h_s \right) - \sum \dot{m}_i'' h_{f_i}^o
\]

\[
\frac{\partial (\rho h_s)}{\partial t} + \nabla \cdot (\rho \mathbf{v} h_s) = \nabla \cdot \left( \frac{\lambda}{c_p} \nabla h_s \right) + \nabla \cdot \left[ \left( \frac{\lambda}{c_p} \right) \sum (Le_i^{-1} - 1) h_s \mathbf{V}_{Y_i} \right] - \sum \dot{m}_i'' h_{f_i}^o
\]

Shvab Zeldovich Formulation: \[
\nabla \cdot (\rho \mathbf{v} h_s) = \nabla \cdot \left( \frac{\lambda}{c_p} \nabla h_s \right) - \sum \dot{m}_i'' h_{f_i}^o
\]
Well-Stirred Reactor

Species equation:
\[ \frac{\partial \rho Y_i}{\partial t} + \nabla \cdot (\rho Y_i \vec{v} + \rho Y_i \vec{V}_{d,i}) = m_i''' \]

Assumptions: (1) Steady State, (2) No gradients, (3) Momentum equation: \( \frac{dp}{dx} = 0 \)

\[ \nabla \cdot (\rho Y_i \vec{v}) = m_i''' \quad \Rightarrow \quad \dot{m}(Y_{i,\text{out}} - Y_{i,\text{in}}) = \dot{w}_i M_i V \quad \quad \dot{m} = \rho v A \]

Energy equation:
\[ \frac{\partial (\rho h)}{\partial t} + \nabla \cdot (\rho \vec{v} h) = -\nabla \cdot \vec{q} \quad \Rightarrow \quad \dot{m}(h_{\text{out}} - h_{\text{in}}) = \dot{Q} \quad (\text{J/s}) \]

\[ h = \sum Y_i h_i = \sum Y_i (h_{fi}^o + \int_{T_{\text{ref}}}^T c_{pi} dT) \quad \dot{m} = (\rho V) / t_r \]

Residence time \( (t_r) \) is specified or calculated from the given mass flow rate and reactor volume \( (V) \)
1-D Equations Used in Chemkin

\[ \frac{\partial \rho}{\partial t} + \nabla \cdot (\dot{m}^\prime) = 0 \quad \Rightarrow \quad \frac{d\dot{m}^\prime}{dx} = 0 \quad \dot{m}^\prime = \rho v \]

\[ \frac{d\dot{m}_i^\prime}{dx} = \dot{m}_i^\prime \quad \Rightarrow \quad \dot{m}_i^\prime \frac{dY_i}{dx} + \frac{d}{dx} \left( \rho Y_i V_{d,i} \right) = \dot{\omega}_i M_i \quad Y_{d,i} = -D_{im} \frac{dY_i}{dx} \]

\[ \frac{dp}{dx} = 0 \]

\[ \frac{\partial (\rho h)}{\partial t} + \nabla \cdot (\rho \dot{v} h) = -\nabla \cdot \vec{q} + Dp / Dt + \tau : \nabla \dot{v} \quad \Rightarrow \quad \frac{d}{dx} (\rho uh) = -\frac{dq}{dx} \]

\[ q = -\lambda \frac{dT}{dx} + \rho \sum_{i=1}^{N} Y_i h_i V_{d,i} \quad \dot{m}^\prime \frac{dh}{dx} - \frac{d}{dx} \left( \lambda \frac{dT}{dx} \right) + \frac{d}{dx} \left( \sum \rho Y_i V_{d,i} h_i \right) = 0 \]

\[ \frac{dh}{dx} = \sum Y_i c_{pi} \frac{dT}{dx} + \sum h_i \frac{dY_i}{dx} \quad \frac{d}{dx} \left( \sum \rho Y_i V_{d,i} h_i \right) = \sum h_i \frac{d}{dx} (\rho Y_i V_{d,i}) + \sum \rho Y_i V_{d,i} c_{pi} \frac{dT}{dx} \]

Using \[ \dot{m}^\prime \sum h_i \frac{dY_i}{dx} + \sum h_i \frac{d}{dx} (\rho Y_i V_{d,i}) = \sum h_i \dot{\omega}_i M_i \] yields

\[ \dot{m}^\prime c_p \frac{dT}{dx} - \frac{d}{dx} \left( \lambda \frac{dT}{dx} \right) + \sum \rho Y_i V_{d,i} c_{pi} \frac{dT}{dx} = -\sum h_i \dot{\omega} M_i \]
Thermodynamic and Transport Data

Solution of the conservation equations requires thermodynamic and transport data:

\[ h_i, \ c_{pi}, \ V_{di}, \ \mu, \ \lambda \]

\[ h_i = h_{fi}^o + \int_{T_{ref}}^{T} c_{pi}dT = h_{fi}^o + h_{s,i} \]

\[ h_{s,i}(T) \text{ and } c_{pi}(T) \text{ are expressed as } 4^{th} \text{ degree polynomials:} \]

\[ c_{pi} = \sum_{m=1}^{5} a_{mi} T^{m-1} \]

Approaches for computing \( V_{d,i} \) have been discussed earlier. For instance

\[ V_{d,i} = -D_{im} \nabla \ln Y_i \quad \text{i=1, 2,.. N-1} \]

Viscosity of species i

\[ \mu_i = \frac{5}{16} \frac{(\pi m_i k_b T)^{1/2}}{\pi \sigma_i^2 \Omega^{2,2}} \]

Mixture viscosity may be calculated using the mixture averaging

\[ \mu = \sum_{i=1}^{N} \frac{X_i \mu_i}{\sum_{j=1}^{N} X_j \phi_{ij}} \]

Mixture conductivity is calculated in a similar way. See Law’s book or CHEMKIN manual for details