Lecture 5

Stoichiometry

Dimensionless Parameters

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Stoichiometry

Given the reaction

$$\sum_{i=1}^{N} \nu'_i M_i \rightarrow \sum_{i=1}^{N} \nu''_i M_i$$

we have seen that there is a relation between the change in the number of moles of the species; i.e., for any two species $i$ and $j$

$$\frac{dn_i}{\nu''_i - \nu'_i} = \frac{dn_j}{\nu''_j - \nu'_j}$$

or in terms of the partial masses

$$\frac{dm_i}{(\nu''_i - \nu'_i)W_i} = \frac{dm_j}{(\nu''_j - \nu'_j)W_j}$$

Since the total of mass (unlike the total number of moles) in the system is unchanged by chemical reaction, we also have

$$\frac{dY'_i}{(\nu''_i - \nu'_i)W_i} = \frac{dY'_j}{(\nu''_j - \nu'_j)W_j}$$

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Consider a global reaction describing the combustion of a single fuel, for example, the combustion of a hydrocarbon fuel $C_mH_n$:

$$
\nu'_F \, C_mH_n + \nu'_O \, O_2 \rightarrow \nu''_{CO_2} \, CO_2 + \nu''_{H_2O} \, H_2O
$$

with the stoichiometric coefficients

$$
\nu'_F = 1, \quad \nu'_O = m + n/4, \quad \nu''_{CO_2} = m, \quad \nu''_{H_2O} = n/2
$$

where $\nu'_F$ was taken equal to one, arbitrarily.

which may be written as (primes are unnecessary)

$$
\nu_F \, Fuel + \nu_O \, Oxidizer \rightarrow Products
$$

then $\nu_O/\nu_F$ is the ratio of the stoichiometric coefficients, and

$$
\frac{dY_F}{\nu_F W_F} = \frac{dY_O}{\nu_O W_O}
$$

Integrating

$$
\frac{dY_F}{\nu_F W_F} = \frac{dY_O}{\nu_O W_O}
$$

between the initial unburned state (subscript u) and a later state

$$
\frac{Y_F - Y_{Fu}}{\nu_F W_F} = \frac{Y_O - Y_{Ou}}{\nu_O W_O}
$$

A fuel-air mixture is referred to as a stoichiometric mixture, if the fuel-to-oxygen ratio is such that both reactants are entirely consumed; i.e. when combustion to $CO_2$ and $H_2O$ is completed.

$$
\left. \frac{Y_{Ou}}{Y_{Fu}} \right|_{st} = \frac{\nu_O W_O}{\nu_F W_F} \equiv \nu
$$

mass-weighted stoichiometric ratio
In general, the initial state may not be at stoichiometry. A measure of the departure from stoichiometry is given by the equivalent ratio $\phi$

$$\phi = \frac{Y_{F_u}/Y_{O_u}}{Y_{F_u}/Y_{O_u}} = \frac{Y_{F_u}/Y_{O_u}}{\nu_F W_F/\nu_O W_O} = \frac{\nu Y_{F_u}}{Y_{O_u}}$$

$$0 < \phi < \infty$$

$\phi = 1$ stoichiometric mixture  
$\phi < 1$ lean mixture (in fuel)  
$\phi > 1$ rich mixture (in fuel)

for combustion in air, the equivalence ratio is often expressed as the fuel-to-air ratio

$$\phi = \frac{F/Air}{F/Air}_{st}$$

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**Adiabatic Flame Temperature**

If a given combustible mixture is made to approach chemical equilibrium by means of an isobaric, adiabatic process, then the temperature attained by the system is the adiabatic flame temperature $T_a$.

For an adiabatic, isobaric process $dh = 0$. Integrating from the unburned to the burned state

$$h_u = h_b$$

$$\sum_{i=1}^{N} Y_{i_u} h_i = \sum_{i=1}^{N} Y_{i_b} h_i$$

$$\sum_{i=1}^{N} Y_{i_u} h_i^o + \int_{T_u}^{T_b} c_p u \, dT = \sum_{i=1}^{N} Y_{i_b} h_i^o + \int_{T_u}^{T_b} c_p p \, dT$$

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\[ \sum_{i=1}^{N} (Y_{iu} - Y_{ib}) h_i^o = \int_{T_o}^{T_b} c_{p_u} dT - \int_{T_o}^{T_u} c_{p_u} dT \]

where the specific heats are those of the mixture, calculated with the mass fractions of the unburned/burned gas, respectively

\[ c_{p_u} = \sum_{i=1}^{N} Y_{iu} c_{p1}(T), \quad c_{p_b} = \sum_{i=1}^{N} Y_{ib} c_{p1}(T) \]

For a one-step global reaction, where we consider \( j = 1 \) to be the fuel, denoted by \( F \), the equation

\[ \frac{dY_i}{(\nu_i'' - \nu_i')W_i} = \frac{dY_j}{(\nu_j'' - \nu_j')W_j} \]

\[ \frac{dY_i}{(\nu_i'' - \nu_i')W_i} = -\frac{dY_F}{\nu_F W_F} \]

can be integrated to give

\[ Y_{iu} - Y_{ib} = (Y_{Fb} - Y_{Fu}) \frac{(\nu_i'' - \nu_i')W_i}{\nu_F W_F} \]

Using this last relation in the conservation of energy equation:

\[ \sum_{i=1}^{N} (Y_{iu} - Y_{ib}) h_i^o = \int_{T_o}^{T_b} c_{p_u} dT - \int_{T_o}^{T_u} c_{p_u} dT \]

\[ \frac{Y_{Fb} - Y_{Fu}}{\nu_F W_F} \sum_{i=1}^{N} (\nu_i'' - \nu_i')W_i h_i^o \]

\[ \int_{T_o}^{T_b} c_{p_u} dT - \int_{T_o}^{T_u} c_{p_u} dT = \frac{Y_{Fb} - Y_{Fu}}{\nu_F W_F} Q \]

If the reference temperature \( T_o = T_u \), for complete combustion of fuel \( (Y_{Fb} = 0) \) the adiabatic flame temperature \( T_a \) is calculated from

\[ \int_{T_o}^{T_u} c_{p_u} dT = \frac{Y_{Fu}}{\nu_F W_F} Q \]
It’s convenient to rewrite this relation using the molar heat capacities $C_{p_i}$.

$$\int_{T_u}^{T_a} C_{p_i} \, dT = \frac{Y_{F_u}}{\nu F} \, Q \quad \Rightarrow \quad \int_{T_u}^{T_a} C_{p_i} \, dT = Q$$

Example:

$\text{CH}_4 + 15 (0.21 \, \text{O}_2 + 0.79 \, \text{N}_2) \rightarrow b_1 \, \text{CO}_2 + b_2 \, \text{H}_2\text{O} + b_3 \, \text{N}_2 + b_4 \, \text{O}_2$

atom conservation $\Rightarrow b_1 = 1 \quad b_2 = 2 \quad b_3 = 11.85 \quad b_4 = 1.15$

$$\int_{T_u}^{T_a} C_{p_i} \, dT = Q$$

Let $T_u = 298 \, \text{K}$ $Q = h^0_{\text{CH}_4} - h^0_{\text{CO}_2} - 2h^0_{\text{H}_2\text{O}} = 191.755 \, \text{kcal}$

$$\int_{T_u}^{T_a} [C_{p_1} + 2C_{p_2} + 11.85C_{p_3} + 1.15C_{p_4}] \, dT = 191.755 \, \text{kcal}$$

use an iterative procedure

for $T_a = 2000 \, \text{K}$, LHS = 231.904

for $T_a = 1700 \, \text{K}$, LHS = 187.019

$\Rightarrow \quad T_a = 1732 \, \text{K}$

this is not accurate because we did not account for product dissociation.

With product dissociation

$\text{CH}_4 + 15 (0.21 \, \text{O}_2 + 0.79 \, \text{N}_2) \rightarrow \text{CO}_2, \, \text{H}_2\text{O}, \, \text{N}_2, \, \text{O}_2, \, \text{NO}, \, \text{H}, \, \text{OH}, \, \text{O}, \, \text{N}, \, \text{CO}, \, \text{O}_3, \, \text{NO}^+, \, \text{etc.}$

and the determination of the final compositions requires, in addition to the atom conservation equations, chemical equilibrium equations.

<table>
<thead>
<tr>
<th>$T_a$</th>
<th>$\text{CO}_2$</th>
<th>$\text{H}_2\text{O}$</th>
<th>$\text{CO}$</th>
<th>$\text{N}$</th>
<th>$\text{NO}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1732.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1731.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1731.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1727.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1725.7</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>

The inclusion of other products such as $\text{O}_3, \, \text{CH}_3, \, \text{HO}_2, \, \text{CH}_2\text{O}, \, \text{C}_2\text{H}_6, \, \text{NO}_2, \, \text{HCO}$ etc., did not change the adiabatic flame temperature.
**Simplified expression**

For complete combustion of fuel \( (Y_{F_b} = 0) \),
the adiabatic flame temperature \( T_a \) is calculated from

\[
\int_{T_u}^{T_a} c_p \, dT = \frac{Y_{F_u}}{\nu_F W_F} Q
\]

Assume \( c_p \) is nearly constant, the adiabatic temperature for a *lean mixture*, where the fuel is totally consumed \( (Y_{F_u} = 0) \) is

\[
T_a = T_u + \frac{(Q/c_p)Y_{F_u}}{\nu_F W_F}
\]

For a rich mixture, the oxidizer is totally consumed \( (Y_{O_u} = 0) \), and we obtain in an analogous way

\[
T_a = T_u + \frac{(Q/c_p)Y_{O_u}}{\nu_O W_O}
\]

The two expressions are identical when \( \phi = 1 \).

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**TABLE 1.2** Approximate Flame Temperatures of Various Stoichiometric Mixtures, Initial Temperature 298 K

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Oxidizer</th>
<th>Pressure (atm)</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetylene</td>
<td>Air</td>
<td>1</td>
<td>2600</td>
</tr>
<tr>
<td>Acetylene</td>
<td>Oxygen</td>
<td>1</td>
<td>3410</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>Air</td>
<td>1</td>
<td>1840</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>Oxygen</td>
<td>1</td>
<td>2400</td>
</tr>
<tr>
<td>Heptane</td>
<td>Air</td>
<td>1</td>
<td>2290</td>
</tr>
<tr>
<td>Heptane</td>
<td>Oxygen</td>
<td>1</td>
<td>3100</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>Air</td>
<td>1</td>
<td>2400</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>Oxygen</td>
<td>1</td>
<td>3080</td>
</tr>
<tr>
<td>Methane</td>
<td>Air</td>
<td>1</td>
<td>2210</td>
</tr>
<tr>
<td>Methane</td>
<td>Air</td>
<td>20</td>
<td>2270</td>
</tr>
<tr>
<td>Methane</td>
<td>Oxygen</td>
<td>1</td>
<td>3010</td>
</tr>
<tr>
<td>Methane</td>
<td>Oxygen</td>
<td>20</td>
<td>3460</td>
</tr>
</tbody>
</table>

*The maximum exists at \( \phi = 1.1 \).
*The maximum exists at \( \phi = 1.7 \).

Glassman & Yetter, 2008
If the reference temperature $T_o = T_u$, for complete combustion of fuel ($Y_{F_u} = 0$) the adiabatic flame temperature $T_a$ is calculated from

$$T_a = T_u + \left( \frac{Q}{c_v} \right) Y_{F_u}$$

Assuming constant specific heats

$$T_b = T_u + \frac{(Q/c_v)Y_{F_u}}{\nu F W_F}$$

and $T_b$ is clearly larger than the adiabatic flame temperature $T_a$. For lean/rich mixtures

$$T_b = T_u + \frac{(Q/c_v)Y_{O_u}}{\nu O W_O}$$
Simplified Model and Dimensionless Equations

In the following the chemistry will be represented by a global one-step (irreversible) reaction

$$\nu_F \text{ Fuel} + \nu_O \text{ Oxidizer} \rightarrow \text{Products}$$

describing the combustion of a single fuel.

The reaction will be assumed of order $n_F, n_O$, with respect to the fuel/oxidizer, and an overall order $n = n_F + n_O$. The reaction rate will be assumed to obey an Arrhenius law

$$\omega = B \left( \frac{\rho Y_F}{W_F} \right)^{n_F} \left( \frac{\rho Y_O}{W_O} \right)^{n_O} e^{-E/RT}$$

with an overall activation energy $E$ and a pre-exponential factor $B$ (treated as constant).
For simplicity, we will treat $\mu, \lambda, \rho D_i$ constants (although some of the theoretical development could accommodate temperature-dependent transport without much difficulty) so that

$$\frac{\partial p}{\partial t} + \nabla \cdot \rho \mathbf{v} = 0$$

$$\rho \frac{D\mathbf{v}}{Dt} = -\nabla p + \mu \left[ \nabla^2 \mathbf{v} + \frac{1}{3} \nabla (\nabla \cdot \mathbf{v}) \right] + \rho g$$

$$\rho \frac{DY_i}{Dt} - \rho D_i \nabla^2 Y_i = -\nu_i W_i \omega, \quad i = F, O$$

$$\frac{\rho c_p DT}{Dt} - \lambda \nabla^2 T = \frac{Dp}{Dt} + \Phi + Q \omega$$

$$p = \rho RT/W$$

$$\omega = B \left( \frac{\rho V_F}{W_F} \right)^{\rho_F} \left( \frac{\rho V_O}{W_O} \right)^{\rho_O} e^{-E/RT}$$

Non-dimensional Equations

Characteristic values:

- the fresh unburned state $p_0, \rho_0, T_0$ (satisfying $p_0 = \rho_0 RT_0/W$) for $p, \rho, T$
- a characteristic speed $v_0$ to be specified
- the diffusion length $l_D \equiv D_{th}/v_0$ for distances, where $D_{th} = \lambda/\rho c_p$ is the mixture thermal diffusivity
- the diffusion time $l_D/v_0$ for $t$

This choice is clearly not unique and there may be other length, time, and velocity scales that, for a given problem, could be more relevant.

We will use the same variables for the dimensionless quantities; i.e. after substituting $\tilde{\mathbf{v}} = \mathbf{v}/v_0$ say, we remove the "$.$
\[
\begin{align*}
\frac{\partial \rho}{\partial t} + \nabla \cdot \rho \mathbf{v} &= 0 \\
\rho \frac{D \mathbf{v}}{Dt} &= -\frac{1}{\gamma M^2} \nabla p + \text{Pr} \left[ \nabla^2 \mathbf{v} + \frac{1}{3} \nabla (\nabla \cdot \mathbf{v}) \right] + \text{Fr}^{-1} \rho \mathbf{e}_g \\
\rho \frac{DY_F}{Dt} - Le_F^{-1} \nabla^2 Y_F &= -\omega \\
\rho \frac{DY_O}{Dt} - Le_O^{-1} \nabla^2 Y_O &= -\nu \omega \\
\rho \frac{DT}{Dt} - \nabla^2 T &= \frac{\gamma - 1}{\gamma} \left( \frac{Dp}{Dt} + \text{Pr} M^2 \Phi \right) + q \omega \\
p &= \rho T \\
\omega &= D \rho^n Y_F^n Y_O^n e^{-\beta_0/T}
\end{align*}
\]

\textbf{Dimensionless Parameters}

\begin{align*}
M &= \frac{v_0}{\sqrt{\gamma p_0/\rho_0}} \quad \text{Mach number} \\
\text{Fr} &= \frac{v_0^2/l_D}{g} \quad \text{Froude number} \\
\text{Pr} &= \frac{\mu c_p}{\lambda} \quad \text{Prandtl number} \\
Le_i &= \frac{\lambda/\rho c_p}{D_i} \quad \text{Lewis number of species } i \\
n &= \frac{Q/\nu F}{cp T_0} \quad \text{heat release parameter} \\
\nu &= \frac{\nu_O W_O}{\nu_F W_F} \quad \text{mass weighted stoichiometric coeff.} \\
D &= \frac{\left( \frac{l_D}{v_0} \right)}{\left[ (\rho_0/W_F)^{-1} (\rho_0/W_O)^{-\nu F} \mathbf{F} \right]^{-1}} = \frac{\text{flow time}}{\text{reaction time}} \quad \text{Damköhler number}
\end{align*}

Note: the units of \( \nu F \mathbf{F} \) like the units of \( t \) is \( \left( \text{[conc]}^{-1} \text{[time]} \right) \) \( \text{[one usually set } \nu F = 1 \text{ in writing the chemical reaction equation].} \)
Low Mach Number Approximation

The propagation speed of ordinary deflagration waves is in the range 1-100 cm/s, namely much smaller than the speed of sound (in air $a_0 = 34,000$ cm/s).

$$M \ll 1$$

momentum equation $\Rightarrow \nabla p = 0$

$$p = P(t) + \gamma M^2 \hat{p}(x,t) + \cdots$$

will all other variables expressed as $v + \gamma M^2 \hat{v} + \cdots$

$$\rho \frac{Dv}{Dt} = -\nabla \hat{p} + Pr \left[ \nabla^2 v + \frac{1}{3} \nabla (\nabla \cdot v) \right] + Fr^{-1} \rho e_g$$

$$\rho \frac{DT}{Dt} - \nabla^2 T = \frac{\gamma - 1}{\gamma} \frac{dP}{dt} + q \omega$$

$$\rho T = P(t)$$

acoustic disturbances travel infinitely fast, and are filtered out.

Unless $P(t)$ is specified, we are missing an equation, since $p$ has been replaced by two variables $P$ and $\hat{p}$. An equation in bounded problems can be obtained as follows:

$$\rho \frac{\partial T}{\partial t} + \rho v \cdot \nabla T - \nabla^2 T = \frac{\gamma - 1}{\gamma} \frac{dP}{dt} + q \omega$$

$$\frac{\partial p}{\partial t} + \nabla \cdot \rho v = 0 \quad / T$$

$$\frac{\partial (\rho T)}{\partial t} + \nabla \cdot (\rho v T) - \nabla^2 T = \frac{\gamma - 1}{\gamma} \frac{dP}{dt} + q \omega$$

$$\frac{1}{\gamma} \frac{dP}{dt} = -\nabla \cdot (P v - \nabla T) + q \omega$$

$$\frac{1}{\gamma} \int \frac{dP}{dt} dV = -\int_S (P v - \nabla T) \cdot n dS + q \int \omega dV$$

on the surface $S$, $v \cdot n = 0$ and for adiabatic conditions $\partial T/\partial n = 0$. 

$$\frac{dP}{dt} = \frac{\gamma q}{V} \int \omega dV$$
The low Mach number equations are (with the ”hat” in \( p \) removed), therefore

\[
\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0
\]

\[
\rho \frac{D\mathbf{v}}{Dt} = -\nabla p + Pr \left[ \nabla^2 \mathbf{v} + \frac{1}{3} \nabla (\nabla \cdot \mathbf{v}) \right] + Fr^{-1} \rho e_g
\]

\[
\rho \frac{DY_F}{Dt} - L e_F^{-1} \nabla^2 Y_F = -\omega
\]

\[
\rho \frac{DY_O}{Dt} - L e_O^{-1} \nabla^2 Y_O = -\nu \omega
\]

\[
\rho \frac{DT}{Dt} - \nabla^2 T = \frac{\gamma - 1}{\gamma} \frac{dP}{dt} + q \omega
\]

\[
\rho T = P
\]

and when the underlying pressure does not change in time, \( P = 1 \).

Otherwise, unless it is specified, we need an equation for \( P(t) \) (the pressure \( p \) has been replaced by two variables \( P \) and \( \hat{p} \)), which can be obtained by a global integration across the entire volume (as discussed below).

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Coupling Functions

For unity Lewis numbers the operator on the left hand side of these three equations is the same.

\[
\rho \frac{DY_F}{Dt} - L e_F^{-1} \nabla^2 Y_F = -\omega
\]

\[
\rho \frac{DY_O}{Dt} - L e_O^{-1} \nabla^2 Y_O = -\nu \omega
\]

\[
\rho \frac{DT}{Dt} - \nabla^2 T = q \omega
\]

The combinations \( H_F = T + qY_F \) and \( H_O = T + q Y_O/\nu \) (and hence \( Y_F - Y_O/\nu \)) satisfy reaction-free equations

\[
\rho \frac{DH_i}{Dt} - \nabla^2 H_i = 0
\]

leaving only one equation with the highly nonlinear reaction rate term. This is a great simplification, but as we shall see, small variations of the Lewis numbers from one produce instabilities and nontrivial consequences.

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The constant-density approximation $\rho = 1$
Thermo-Diffusive model

One must abandon the equation of state $\rho T = 1$

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \rho \mathbf{v} = 0$$

$$\rho \frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla) \mathbf{v} = -\nabla p + Pr \left[ \nabla^2 \mathbf{v} + \frac{1}{3} \nabla (\nabla \cdot \mathbf{v}) \right] + Fr^{-1} \rho \mathbf{e}_g$$

solve to determine $\mathbf{v}$

$$\rho \frac{\partial Y_F}{\partial t} + \mathbf{v} \cdot \nabla Y_F - Le_F^{-1} \nabla^2 Y_F = -\omega$$

$$\rho \frac{\partial Y_O}{\partial t} + \mathbf{v} \cdot \nabla Y_O - Le_O^{-1} \nabla^2 Y_O = -\nu \omega$$

$$\rho \frac{\partial T}{\partial t} + \mathbf{v} \cdot T - \nabla^2 T = q$$

Can be derived systematically by assuming that the heat release $q \ll 1$