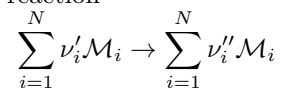


# Lecture 3

## Stoichiometry & Adiabatic Flame Temperature Transport properties

6/26/2011

We have seen that the net production/consumption (moles per unit volume per second) for a global one step reaction



is given by

$$\hat{\omega}_i = (\nu_i'' - \nu_i') \omega = (\nu_i'' - \nu_i') k \prod_{i=1}^N C_i^{\nu_i'} \quad i = 1, 2, \dots, N$$

the term involving the net rate of production of species  $i$  appearing in the energy and species equation,  $\omega_i$ , denotes the time rate of change of the mass of species  $i$  (grams, per unit volume per second). Hence  $\omega_i = W_i \hat{\omega}_i$ , and

$$\omega_i = (\nu_i'' - \nu_i') W_i \omega \quad i = 1, 2, \dots, N$$

---

note that  $\sum_{i=1}^N \omega_i = \omega \sum_{i=1}^N (\nu_i'' - \nu_i') W_i = 0$

6/26/2011

Hence

$$\omega_i = (\nu_i'' - \nu_i') W_i \omega \quad i = 1, 2, \dots, N$$

$$\omega = \mathcal{B} T^\alpha \prod_{i=1}^N \left( \frac{\rho Y_i}{W_i} \right)^{\nu_i'} e^{-E/\mathcal{R}T}$$

with  $\nu_i'$  in the exponents may be replaced with empirical  $n_i$ , as necessary.

and the term appearing in the energy equation becomes

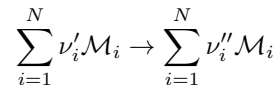
$$\sum_{i=1}^N \omega_i h_i^o = \omega \underbrace{\sum_{i=1}^N (\nu_i'' - \nu_i') W_i h_i^o}_{-Q} = -Q\omega$$

difference between the heat of formation  
of the products and reactants  
(negative for exothermic reactions)  
is the total heat released, or  
**the heat of combustion**

6/26/2011

## Stoichiometry

Given the reaction



we have seen that there is a relation between the change in the number of moles of each 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

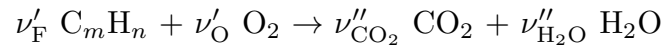
$$\frac{dm_i}{(\nu_i'' - \nu_i') W_i} = \frac{dm_j}{(\nu_j'' - \nu_j') W_j}$$

since the total of mass (unlike the total number of moles) in the system is unchanged by chemical reaction

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

6/26/2011

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



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)



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

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

6/26/2011

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 called stoichiometry, if the fuel-to-oxygen ratio is such that both reactants are entirely consumed 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

6/26/2011

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

$$\phi = \frac{Y_{F_u}/Y_{O_u}}{Y_{F_u}/Y_{O_u}|_{st}} = \frac{Y_F/Y_O}{\nu_F W_F/\nu_O W_O} = \frac{\nu Y_{F_u}}{Y_{O_u}}$$

$$0 < \phi < \infty$$

$\phi = 1$  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

6/26/2011

## 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

$$h_u = h_b$$

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

$$\sum_{i=1}^N Y_{i_u} h_i^o + \int_{T^o}^{T_b} c_{p_b} dT = \sum_{i=1}^N Y_{i_b} h_i^o + \int_{T^o}^{T_u} c_{p_u} dT$$

6/26/2011

$$\sum_{i=1}^N (Y_{i_u} - Y_{i_b}) h_i^o = \int_{T^o}^{T_b} c_{p_b} dT - \int_{T^o}^{T_u} c_{p_u} dT$$

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

$$c_{p_u} = \sum_{i=1}^N Y_{i_u} c_{p_i}(T), \quad c_{p_b} = \sum_{i=1}^N Y_{i_b} c_{p_i}(T)$$

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

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

can be integrated to give

$$Y_{i_u} - Y_{i_b} = (Y_{F_b} - Y_{F_u}) \frac{(\nu_i'' - \nu_i')W_i}{\nu_F W_F}$$

6/26/2011

$$\underbrace{\sum_{i=1}^N (Y_{i_u} - Y_{i_b}) h_i^o}_{\parallel} = \int_{T^o}^{T_b} c_{p_b} dT - \int_{T^o}^{T_u} c_{p_u} dT$$

$$\frac{Y_{F_b} - Y_{F_u}}{\nu_F W_F} \underbrace{\sum_{i=1}^N (\nu_i'' - \nu_i') W_i h_i^o}_{-Q}$$

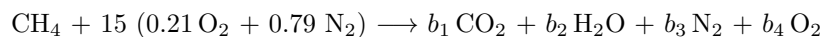
$$\int_{T^o}^{T_b} c_{p_b} dT - \int_{T^o}^{T_u} c_{p_u} dT = \frac{Y_{F_u} - Y_{F_b}}{\nu_F W_F} Q$$

if the reference temperature  $T^o = T_u$ , for complete combustion of fuel ( $Y_{F_b} = 0$ ) the adiabatic flame temperature  $T_a$  is calculated from

$$\int_{T^o}^{T_a} c_{p_b} dT = \frac{Y_{F_u}}{\nu_F W_F} Q$$

6/26/2011

Example: calculate the adiabatic flame temperature for the combustion of methane/air given by  $\text{CH}_4 + 15(0.21 \text{ O}_2 + 0.79 \text{ N}_2)$  at 298 K



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

Using the molar heat capacities  $C_{p_i}$ , the adiabatic flame temperature  $T_a$  is calculated from  $\int_{T^o}^{T_a} C_{p_b} dT = Q$

$$Q = h_{\text{CH}_4}^o - h_{\text{CO}_2}^o - 2h_{\text{H}_2\text{O}}^o = 191.755 \text{ kcal}$$

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

use an iterative procedure

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

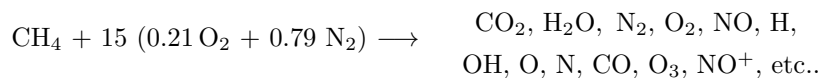
$$\text{for } T_a = 1700 \text{ K, LHS} = 187.019$$

$$\Rightarrow T_a = 1702 \text{ K}$$

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

6/26/2011

With product dissociation



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

6/26/2011

$$\int_{T_o}^{T_a} c_{p_b} dT = \frac{Y_{F_u}}{\nu_F W_F} Q$$

Assume  $c_p$  is nearly constant, the adiabatic temperature for a lean mixture, where the fuel is totally consumed ( $Y_{F_b} = 0$ ) 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 ( $Y_{O_b} = 0$ ), and we obtain in an analogous way

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

6/26/2011

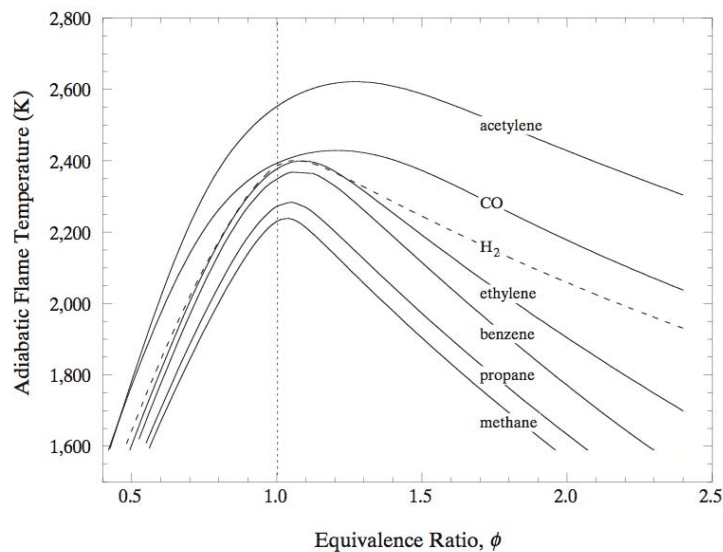


Figure 1.4.3. Adiabatic flame temperature,  $T_{ad}$ , as a function of fuel equivalence ratio,  $\phi$ , for several fuel-air mixtures at STP.

Law, 2006

6/26/2011

## Transport Coefficients

The bulk viscosity is negligible in combustion processes and will be set to zero, i.e.,  $\kappa = 0$ .

The dependence of the binary diffusion coefficients  $\mathcal{D}_i$  (which actually stands for  $\mathcal{D}_{i,N}$ ) on pressure and temperature is

$$\mathcal{D}_i \sim T^\alpha/p \quad 3/2 \leq \alpha \leq 2$$

Typical values at  $p = 1 \text{ atm}$  are in the range  $0.01 - 10 \text{ cm}^2/\text{s}$ .

Although the transport coefficients  $\lambda, \mu$  in a multicomponent mixture depend in general on the concentrations, this dependence is generally ignored and average quantities are used; they remain dependent on pressure and temperature.

Similarly  $W$  is assumed constant.

6/26/2011

The kinematic viscosity  $\mu/\rho$  has the same units and the same pressure and temperature dependence as the binary diffusion coefficients

$$\mu/\rho \sim T^\alpha/p \quad 3/2 \leq \alpha \leq 2$$

Typical values at  $p = 1 \text{ atm}$  are in the range  $0.1 - 1 \text{ cm}^2/\text{s}$ .

The thermal conductivity depends mostly on temperature, and behaves as

$$\lambda \sim T^\alpha/p \quad 1/2 \leq \alpha \leq 1$$

More relevant, however, is the thermal diffusivity  $\lambda/\rho c_p$  which has the same units and the same temperature and pressure dependence as the diffusion coefficients and the kinematic viscosity. In particular

$$\lambda/\rho c_p \sim T^\alpha/p \quad 3/2 \leq \alpha \leq 2$$

Typical values at  $p = 1 \text{ atm}$  are in the range  $0.1 - 1 \text{ cm}^2/\text{s}$ .

6/26/2011



Since  $\lambda/\rho c_p$ ,  $\mu/\rho$ ,  $\mathcal{D}_i$  have the same dependence on temperature, their ratios are nearly constant.

$$\frac{\lambda/\rho c_p}{\mathcal{D}_i} = Le_i \quad \text{Lewis number}$$

$$\frac{\mu/\rho}{\lambda/\rho c_p} = Pr \quad \text{Prandtl number}$$

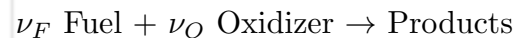
$$\frac{\mu/\rho}{\mathcal{D}_i} = Sc_i \quad \text{Schmidt number}$$

We can write  $\rho \mathcal{D}_i = Le_i^{-1}(\lambda/c_p)$  and  $\mu = Pr(\lambda/c_p)$  with  $\lambda = \lambda(T)$ . A good approximation (Smooke & Giovangigli, 1992) for the latter is

$$\frac{\lambda}{c_p} = 2.58 \cdot 10^{-4} \frac{\text{g}}{\text{cm s}} \left( \frac{T}{298\text{K}} \right)$$

The Prandtl and Lewis numbers are nearly constant;  $Pr = 0.75$  and  $Le$  varies in the range 0.2 – 1.8.

We will be mostly concerned with a global reaction



$$\omega = \mathcal{B} T^\alpha \prod_{\substack{i=1 \\ \text{reactants}}}^N \left( \frac{\rho Y_i}{W_i} \right)^{n_i} e^{-E/\mathcal{R}T} = \mathcal{B} T^\alpha \left( \frac{\rho Y_F}{W_F} \right)^{n_F} \left( \frac{\rho Y_O}{W_O} \right)^{n_O} e^{-E/\mathcal{R}T}$$

with  $\alpha = 0$  (although in the asymptotic treatment one can easily retain this factor with minor modifications).

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

$n = n_F + n_O$  is the (overall) reaction order  
 $n_F, n_O$  are the reaction orders w.r.t. the fuel/oxidizer