Aerospace Combustion

Lecture 4:

Combustion: Basic Definitions and Equations Part 1

Content

- Basics Definitions and Equations
- Equation of State (EOS)
- NASA Polynominals
- Fluid Properties
- Global and Elementary Reactions
- Adiabatic Flame Temperature

Basics

Basic Definitions and Equations

(1/3)

- Conservation of Mass and Elements (however, species will be consumed, others formed)

- Avogadro number $\mathbf{N_A} = 6.0236 \times 10^{23}$ molecules are defined as one mole

- Number of moles of species ***i***: n_i

- Total number of moles in the system: $n_s = \sum_{i=1}^{k} n_i$

- Mole fraction of species ***i***: $X_i = \frac{n_i}{n_s}, \quad i = 1, 2, \ldots, k$

- Mass of all molecules of species ***i***: $m_i = W_i n_i$ with W_i molecular weight of species i

- Total mass of molecules in the system: $m = \sum_{i=1}^{k} m_i$

Basics

Basic Definitions and Equations

(2/3)

- Mass fraction of species ***i***: $$Y_i = \frac{m_i}{m}, \quad i = 1, 2, \ldots., k$$
- Mean molecular weight ***W***: $$W = \sum_{i=1}^{k} W_i X_i$$
- Number of atoms of element ***j*** in a molecule of species ***i*** : a_{ij}
- Mass of all atoms ***j*** in the system: $$m_j = \sum_{i=1}^{k} \frac{\mathrm{a}_{\mathrm{ij}} W_j}{W_i} m_i; \quad j = 1, 2, \ldots.. k_e$$

  with k_e the total number of elements in the system
- Element ***j*** mass fraction: $$Z_j = \frac{m_j}{m} = \sum_{i=1}^{k} \frac{a_{ij} W_j}{W_i} Y_i = \frac{W_j}{W_i} k \sum_{i=1}^{k} a_{ij} X_i; \quad j = 1, 2, \ldots.. k_e$$

Basics

Basic Definitions and Equations (3/3)

$$\Longrightarrow \quad \sum_{i=1}^{k} X_i = 1, \qquad \sum_{i=1}^{k} Y_i = 1, \qquad \sum_{j=1}^{k_e} Z_j = 1$$

- Number of moles of species ***i*** per volume: $[X_i] = \frac{n_i}{V}, \quad i = 1,2,\ldots,k$
- Total molar density of the system: $\frac{n_s}{V} = \sum_{i=1}^{k} [X_i]$
- Partial molar density of species ***i***: $\rho_i = \frac{m_i}{V} = \rho Y_i$
- Density of system: $\rho = \frac{m}{V}$

Basics

Basic Thermodynamic Definitions and Equations

- Specific enthalpy: $h = u + pv$
- Specific enthalpy (ideal gas) $h = u + \frac{RT}{M}$
- Energy balance for a closed system $du = \delta q + \delta w$

- Specific internal energy and specific enthalpy of mixtures $u = \sum_{i=1}^{k} Y_i u_i ; \quad h = \sum_{i=1}^{k} Y_i h_i$
- Relation between single species enthalpy and internal energy $h_i = u_i + \frac{RT}{M_i}$

Only for an ideal gas are enthalpy and internal energy temperature dependent only

Basics

Example:

Mixture of Methane 10% (mass) and Air (21%); Air consists of 21% O2 and 79% N2 (vol.) and we are looking for mole fractions and element mass fractions

Mole masses: M_{O2} ~ 32 g/mol, M_{N2} ~ 28 g/mol, M_{CH4} ~ 16 g/mol

Mole fractions in air: $$X_{O_2} = \frac{n_{O_2}}{n_{O_2} + n_{N_2}} = \frac{0.21}{1} = 0.21; \quad X_{N_2} = 1 - X_{O_2} = 0.79$$

Mass fractions in air: $$Y_{O_2,air} = \frac{M_{O_2} X_{O_2,air}}{M_{O_2} X_{O_2,air} + M_{N_2} X_{N_2,air}} = 0.232, \quad Y_{N_{2,air}} = 1 - Y_{O_2,air} = 0.768$$

Mass fractions in mixture: $$Y_{O_2,m} = 0.9 \cdot Y_{O_2,air} \sim 0.209, \quad Y_{N_{2,air}} = 0.9 \cdot Y_{N_2,air} \sim 0.691; Y_{CH_4} = 0.1$$

Basics

Example:

Mixture of Methane 10% (mass) and Air (21%); Air consists of 21% O2 and 79% N2 (vol.) and we are looking for mole fractions and element mass fractions

Mean molar mass:

$$M=\left(\sum_{i=1}^{3} Y_i/M_i\right)^{-1}=27.5\ g/mol$$

Mole fractions in mixture:

$$X_i=\frac{M}{M_i}Y_i;\Rightarrow X_{O_2}\sim 0.17; X_{N_2}\sim 0.66; X_{CH_4}=\sim 0.17$$

Molar mass of elements: M_O ~ 16 g/mol, M_N ~ 14 g/mol, M_C ~ 12 g/mol; M_H ~ 11 g/mol,

Element mass fractions:

$$Z_j=\left(\sum_{i=1}^{3}\frac{a_{ij}M_j}{M_i}Y_i\right)\Rightarrow Z_H=0.025; Z_C=0.075; Z_N=0.69, Z_O=0{,}21$$

Basic Thermodynamics

Definitions and Equations

- Partial specific enthalpy (ideal gas):

$$h_i = h_{i,ref} + \int_{T_{ref}}^{T} c_{p_i} dT ; i = 1,2,\ldots k$$

- Partial molar enthalpy (ideal gas):

$$h_{i,m} = h_{i,m,ref} + \int_{T_{ref}}^{T} c_{p_i,m} dT ; i = 1,2,\ldots k$$

$$c_{p_{i,m}} = M_i c_{p_i} ; i = 1,2..k$$

- In multicomponent systems, the specific heat at constant pressure

$$c_p = \sum_{i=1}^{n} Y_i c_{p_i} ; \qquad c_{p,m} = \sum_{i=1}^{n} X_i c_{p_{i,m}}$$

Basic Thermodynamics

Definitions and Equations

- Temperature dependent molar entropy, enthalpy and specific heat can be predicted applying the NASA 7 coefficient poly-nominals (constants of a_i are listed in tables) or can be predicted (using CANTERA)

$$\frac{s_m}{R} = a_1 \ln(T/K) + a_2 (T/K) + a_3 \frac{(T/K)^2}{2} + a_4 \frac{(T/K)^3}{3} + a_5 \frac{(T/K)^4}{4} + a_7 + \ln\left(p/p_0\right)$$

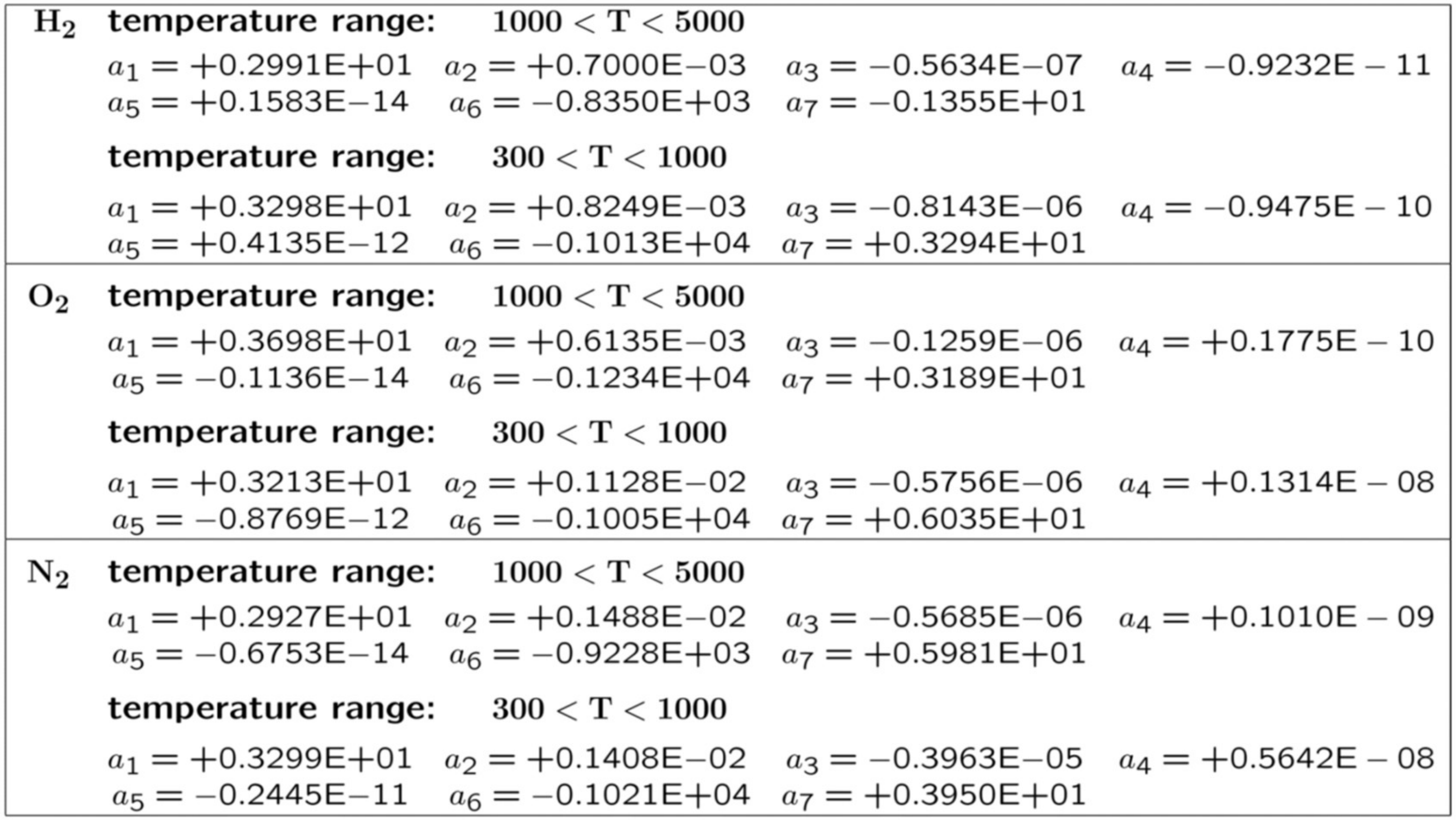
$$\frac{h_m}{RT} = a_1 T + a_2 \frac{1}{2}\frac{T}{K} + a_3 \frac{1}{3}\left(\frac{T}{K}\right)^2 + a_4 \frac{1}{4}\left(\frac{T}{K}\right)^3 + a_5 \frac{1}{5}\left(\frac{T}{K}\right)^4 + a_6 \frac{1}{T/K}$$

$$\frac{c_{p,m}}{R} = a_1 + a_2 \frac{T}{K} + a_3 \left(\frac{T}{K}\right)^2 + a_4 \left(\frac{T}{K}\right)^3 + a_5 \left(\frac{T}{K}\right)^4$$

Basic Thermodynamics

Definitions and Equations

NASA poly-nominal coefficients for hydrogen, oxygen and nitrogen for two temperature ranges and standard pressure (p_0 = 1 atm)



H_2 temperature range: $1000 < T < 5000$

$a_1 = +0.2991E+01$ $a_2 = +0.7000E-03$ $a_3 = -0.5634E-07$ $a_4 = -0.9232E - 11$
$a_5 = +0.1583E-14$ $a_6 = -0.8350E+03$ $a_7 = -0.1355E+01$

temperature range: $300 < T < 1000$

$a_1 = +0.3298E+01$ $a_2 = +0.8249E-03$ $a_3 = -0.8143E-06$ $a_4 = -0.9475E - 10$
$a_5 = +0.4135E-12$ $a_6 = -0.1013E+04$ $a_7 = +0.3294E+01$

O_2 temperature range: $1000 < T < 5000$

$a_1 = +0.3698E+01$ $a_2 = +0.6135E-03$ $a_3 = -0.1259E-06$ $a_4 = +0.1775E - 10$
$a_5 = -0.1136E-14$ $a_6 = -0.1234E+04$ $a_7 = +0.3189E+01$

temperature range: $300 < T < 1000$

$a_1 = +0.3213E+01$ $a_2 = +0.1128E-02$ $a_3 = -0.5756E-06$ $a_4 = +0.1314E - 08$
$a_5 = -0.8769E-12$ $a_6 = -0.1005E+04$ $a_7 = +0.6035E+01$

N_2 temperature range: $1000 < T < 5000$

$a_1 = +0.2927E+01$ $a_2 = +0.1488E-02$ $a_3 = -0.5685E-06$ $a_4 = +0.1010E - 09$
$a_5 = -0.6753E-14$ $a_6 = -0.9228E+03$ $a_7 = +0.5981E+01$

temperature range: $300 < T < 1000$

$a_1 = +0.3299E+01$ $a_2 = +0.1408E-02$ $a_3 = -0.3963E-05$ $a_4 = +0.5642E - 08$
$a_5 = -0.2445E-11$ $a_6 = -0.1021E+04$ $a_7 = +0.3950E+01$

Basic Thermodynamics

Definitions and Equations

- Temperature dependent molar entropy, enthalpy and specific heat can be predicted applying the more recent 9 coefficient NASA poly-nominals (CANTERA)

$$\frac{s_m}{R} = -\frac{a_0}{2}T^{-2} - a_1 T^{-1} + a_2 \ln T + a_3 T + a_4 \frac{1}{2}T^2 + \frac{a_5}{3}T^3 + \frac{a_6}{4}T^4 + a_8$$

$$\frac{h_m}{RT} = -a_0 T + a_1 \frac{\ln T}{T} + a_2 + \frac{a_3}{2}T + \frac{a_4}{3}T^2 + \frac{a_5}{4}T^3 + \frac{a_6}{5}T^4 + \frac{a_7}{T}$$

$$\frac{c_{p,m}}{R} = \frac{a_0}{2}T^{-2} + a_1 T^{-1} + a +_2 a_3 T + a_4 T^2 + a_5 T^3 + a_6 T^4$$

Basic Thermodynamics

Equation of State

Although both, aero-engines and rocket engines operate with liquid propellants, most of the regions in a combustion chamber may be treated with an ideal gas equation of state.

$$p = \sum_{i=1}^{k} p_i;$$

$$p_i = \frac{n_i RT}{V} = \frac{\rho Y_i}{W_i} RT,\ i = 1, 2\ldots..,\ k$$

- However, the presence of droplets requires for any predictive tool models for a cubic equation of state, vaporization and quite often a separate handling of the liquid phase.
- Furthermore, the high combustion chamber pressures and low propellant entry temperatures result in trans-critical conditions which necessitate a special treatment.

Basic Thermodynamics

Equation of State

Soave-Redlich-Kwong cubic EOS

$$p = \frac{RT}{V_m - b} - \frac{a\alpha}{\sqrt{T} V_m (V_m + b)}, \qquad a = \frac{0.42747\, R^2 T_c^2}{p_c};\ b = \frac{0.08664\, RT_c}{p_c}, \qquad R = 8.314\ J/(mol\ K)$$

$$\alpha = \left(1 + \left(0.48508 + 1.55171\,\omega - 0.1563\,\omega^2\right)\left(1 - T_r^{0.5}\right)\right)^2, \quad T_r = \frac{T}{T_c};$$

$$\omega = -\log_{10}[P_r(T_r = 0.7)] - 1$$

ω is the acentric factor

Basic Thermodynamics

Transport Coefficients

Momentum

$$\eta_{ij} = 266.93 \cdot 10^{-8} \left(\frac{\sqrt{2M_i M_j T / (M_i + M_j)}}{\sigma_{ij}^2 \Omega_{ij}^{(2,2)*}(T_{ij}^*)} \right);$$

Heat

$$\lambda_{ij} = 8.3 \cdot 10^{-4} \left(\frac{\sqrt{T(M_i + M_j)/2M_i M_j}}{\sigma_{ij}^2 \Omega_{ij}^{(2,2)*}(T_{ij}^*)} \right);$$

Mass

$$D_{ij} = 26.28 \cdot 10^{-8} \left(\frac{\sqrt{T^3(M_i + M_j)/2M_i M_j}}{p\sigma_{ij}^2 \Omega_{ij}^{(1,1)*}(T_{ij}^*)} \right)$$

Already rather complex but this is for binary mixtures only, for multi-component mixtures no general analytical solution exists.

Basic Thermodynamics

Transport Coefficients

Collision integrals

$$\Omega^{(l,s)*}(T) = \frac{1}{(s+1)!}\int_0^\infty \exp(-E/T)\left(\frac{E}{T}\right)^{s+1} Q^{(l)^*}(E)\,d\left(\frac{E}{T}\right),$$

$$Q^{(l)*}(E) = \frac{1}{\left(1-\dfrac{1+(-1)^l}{2(1+l)}\right)}\int_0^\infty \left(1-\cos^l\chi\right) b\,db\,,$$

$$\chi(E,b) = \pi - 2b\int_{r_m}^\infty \frac{dr}{r^2\sqrt{1-\dfrac{\varphi(r)}{E}-\dfrac{b^2}{r^2}}}$$

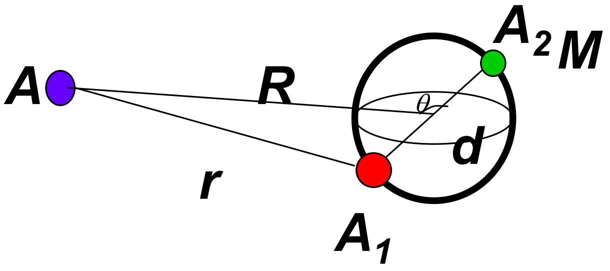
However, the interaction potential ϕ *(r)* is still unknown and therefore approximations (functions) based on experiments with adjustable constants are used.

Basic Thermodynamics

Interaction potential $\varphi_{ij}(r)$

Method of Addition (represent physico-chemical properties of molecule by sum of its structural elements)

$$\varphi(R,\theta)_{A-M} = \sum_i \varphi(r)_{A-A_i^M}$$



Example for two linear molecules:

$$\Phi(r,\overrightarrow{d_1},\overrightarrow{d_2}) = \sum_i^{n_1}\sum_j^{n_2}\left\langle \varphi_{ij}(R)\right\rangle$$

$$\left\langle \varphi_{ij}(R)\right\rangle = \frac{1}{16\pi^2}\int_0^{\pi}\int_0^{2\pi}\sin\theta_2\, d\theta_2\, d\phi_2 \int_0^{\pi}\int_0^{2\pi}\varphi_{ij}\left[r_{ij}(R,d_{1i},d_{2j},\theta_1,\theta_2,(\phi_1-\phi_2))\right]\sin\theta_1\, d\theta_1\, d\phi_1$$

Chemical Reactions

Basic Definitions of Chemical Reactions

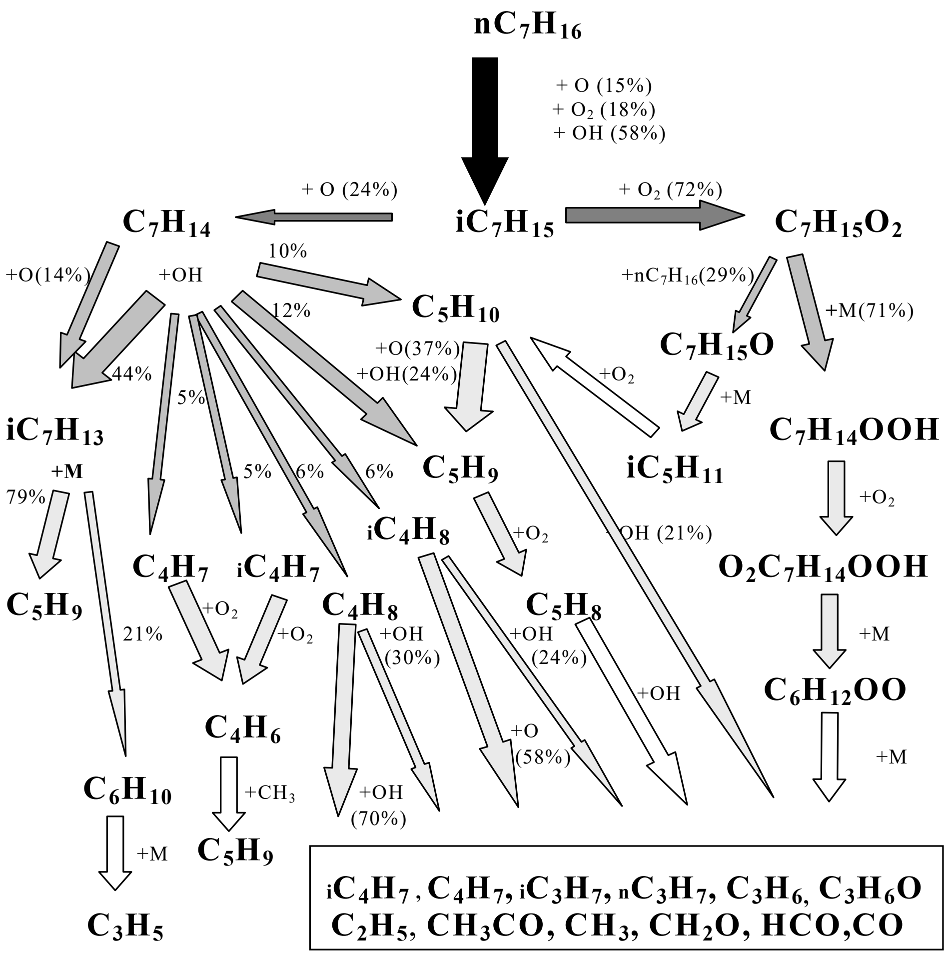
- Elementary Reactions
- Global Reactions
- Reaction Rate
- Stoichiometry and Stoichiometric Coefficients
- Mixture Fraction
- Chemical Equilibrium, Equilibrium Constants
- Chemical Potential
- Fugacity

Chemical Reactions

Elementary Reactions

Main reaction paths for n-heptane

- $T_0 = 730$ K, $P_o = 4$ MPa, and $\phi = 1$,
- at the time when 10% of the initial n-C_7H_{16} are converted.



Chemical Reactions

Elementary Reactions

- Describe actual micro-chemical processes
- Include intermediate species
- Require molecular collisions between reactants to happen
- Reactions velocities can be measured

$$H_2 + O^* \xleftrightarrow{k} H^* + OH^*$$
$$H^* + O_2 \xleftrightarrow{k} O^* + OH^*$$

Double arrow indicates that these reactions can proceed backwards as well,
*Indicates a radical

- Even for simple reactions there are plenty of elementary reaction
- Each reaction can be described in Arrhenius form

$$k = A \cdot e^{(-E_a/RT)};$$

k:	the specific reaction rate constant,
A:	pre-exponential factor
E_a:	activation energy
R:	universal gas constant
T:	temperature

The reaction rate constant is extremely important since it relates the rate of a reaction to the activation energy and the temperature.

Chemical Reactions

Global Reactions

- Relate moles of educts and moles of products
- Doesn't represent chemical intermediate reaction steps and pathways
- Not time-dependent information
- Conservation of elements
- Cumulative balance of many elementary reactions
- Global ratios of amounts of substance

→ **No conservation of the number of moles**

Stoichiometric Coefficients for Reactants ν´ and Products ν´´ and Components $\nu_i = \nu_i'' - \nu_i'$; (holds only for global reactions)

$$\nu'_{C_nH_m} C_nH_m + \nu'_{O_2} O_2 = \nu''_{CO_2} CO_2 + \nu''_{H_2O} H_2O$$

In case of methane/oxygen combustion

$$\nu'_{CH_4} = 1; \nu'_{O_2} = 2; \nu''_{CO_2} = 1; \nu''_{H_2O} = 2$$

→ $CH_4 + 2O_2 = CO_2 + 2H_2O$

In case of hydrogen/oxygen combustion

$$\nu'_{H_2} = 2; \nu'_{O_2} = 1; \nu''_{H_2O} = 2$$

→ $2H_2 + O_2 = 2H_2O$

Chemical Reactions

Global Reactions

Provide both a molar relation and a mass relation:

$2H_2 + O_2 = 2H_2O$

$CH_4 + 2O_2 = CO_2 + 2H_2O$

$4g\ H_2 + 32g\ O_2 = 36g\ H_2O$

$16g\ CH_4 + 64g\ O_2 = 44\ g\ CO_2 + 36g\ H_2O$

Combustion of Hydrocarbons in Oxygen

$$\nu'_{fuel} fuel + \nu'_{O_2} O_2 = \nu''_{CO_2} CO_2 + \nu''_{H_2O} H_2O$$

Sample reaction: Methane + Oxygen

$$\nu'_{CH_4} CH_4 + \nu'_{O_2} O_2 = \nu''_{O_2} CO_2 + \nu''_{O_2} H_2O$$

Stoichiometric coefficients of global reactions are derived from ν'_{CH_4}

Number of Atoms in the fuel:

Carbon **a_C** = 1

Hydrogen **a_H** = 4

Oxygen **a_O** = 0

Balance of Atoms in Global Reactions

- C: $\nu''_{CO_2} = a_C \nu'_{CH_4} = 1$
- H: $\nu''_{H_2O} = a_H \nu'_{CH_4} / 2 = 2$
- O: $\nu''_{O_2} = \nu''_{CO_2} + \nu''_{H_2O} / 2 - (0)\nu'_{CH_4} / 2 = 2$

Chemical Reactions

Global Reactions

Example where oxygen is present in the fuel molecule

$CH_3OH + 1.5O_2 = CO_2 + 2H_2O$

$32g\ CH_3OH + 48g\ O_2 = 44g\ CO_2 + 36g\ H_2O$

Number of Atoms in the fuel:

Carbon $a_C = 1$

Hydrogen $a_H = 4$

Oxygen $a_O = 1$

Balance of Atoms in Global Reactions

- C: $\nu''_{CO_2} = a_C \nu'_{CH_3OH} = 1$
- H: $\nu''_{H_2O} = a_H \nu'_{CH_3OH} / 2 = 2$
- O: $\nu''_{O_2} = \nu''_{CO_2} + \nu''_{H_2O} / 2 - \nu'_{CH_3OH} / 2 = 1.5$

Chemical Reactions

Global Reactions

General reaction: Fuel + Oxygen → Product $\nu_1 F + \nu_2 O = \nu_3 P$

n_1 moles component *1* + n_2 moles component *2* → n_3 moles of component *3*

$$\frac{dn_i}{\nu_i} = \frac{dn_1}{\nu_1}; \quad \frac{dm_i}{\nu_i M_i} = \frac{dm_1}{\nu_1 M_1}; \quad \frac{dY_i}{\nu_i M_i} = \frac{dY_1}{\nu_1 M_1}; \quad (i = 1,2..,n)$$

Relation between fuel and oxygen from the unburnt state (subscript u).

$$\frac{Y_{O_2} - Y_{O_2,u}}{\nu'_{O_2} M_{O_2}} = \frac{Y_F - Y_{F,u}}{\nu'_F M_F}$$

Chemical Reactions

Stoichiometry

Stoichiometric mixture ≡ both fuel and oxidizer are consumed entirely

Example for combustion of an alkane:

C_nH_{2n+2} (subscript f for fuel) or even a more general hydrocarbon fuel C_nH_m

$$\nu'_f C_n H_{2n+2} + \nu'_{O_2} O_2 = \nu''_{CO_2} CO_2 + \nu''_{H_2O} H_2O$$

$$\nu'_f C_n H_m + \nu'_{O_2} O_2 = \nu''_{CO_2} CO_2 + \nu''_{H_2O} H_2O$$

$$\nu'_f = 1,\ \ \nu'_{O_2} = n + \frac{2n+2}{4},\ \nu''_{CO_2} = n,\ \nu''_{H_2O} = \frac{2n+2}{2}$$

$$\nu'_f = 1,\ \ \nu'_{O_2} = n + \frac{m}{4},\ \nu''_{CO_2} = n,\ \nu''_{H_2O} = \frac{m}{2}$$

Let’s check for methane / oxygen combustion: n=1, m=4

$$\nu'_{CH_4} = 1,\ \ \nu'_{O_2} = 2,\ \ \nu''_{\mathrm{CO}_2} = 1,\ \nu''_{H_2O} = 2$$

Chemical Reactions

Stoichiometry

Mole number ratio for stoichiometric conditions

$$\left.\frac{n_{O_{2,u}}}{n_{F,u}}\right|_{st} = \frac{\upsilon'_{O_2}}{\upsilon'_F}$$

or mass fractions

$$\left.\frac{Y_{O_{2,u}}}{Y_{F,u}}\right|_{st} = \frac{\upsilon'_{O_2} W_{O_2}}{\upsilon'_F W_F} = \nu$$

with *ν* the stoichiometric mass ratio which is familiar to the rocket propulsion community, i.e. *ν = 4* for methane/oxygen and *ν* = 7.936 for hydrogen/oxygen.

Chemical Reactions

Propellant Mixtures

Air-breathing people talk about the equivalence ratio which is the ratio between fuel to oxidizer in the unburnt mixture to that of a stoichiometric mixture.

$$\phi = \frac{Y_{f,u} / Y_{O_2,u}}{(Y_{f,u} / Y_{O_2,u})_{st}} = \upsilon \frac{Y_{F,u}}{Y_{O_2,u}}$$

with ν, the stoichiometric mass ratio

In Rocketry, people talk about mixture ratio:

$$r_{of} = \frac{\dot{m}_{oxidizer}}{\dot{m}_{fuel}} = \frac{m_o}{m_f}$$

In rocketry, the combustion in the main chamber will be always fuel-rich while in air-breathing propulsion the standard operation is lean (air-rich).

However, due to the wide operation range, some of the fuel is burnt rich and later the remainder is burnt lean (RQL – concept). During take-off there are can be fuel-rich operation.

Fuel-rich in rocket engine reduces wall heat load and increases performance.

Chemical Reactions

Reaction Rate (Law of Mass Action)

- Rate of Disappearance of a chemical species is proportional to the products of concentrations of reacting chemical species
- Concentrations being raised to the power equal to the corresponding stoichiometric coefficient

$$RR = k \cdot \prod_{i=1}^{N} \left(c_{M\,i}\right)^{\nu_i'};$$

- with *k* , the specific reaction rate constant which is the well-known Arrhenius law

$$k = BT^{\alpha} e^{-\frac{E_a}{RT}};$$

- BT^{α} is often combined to the pre-exponential factor *A* which includes the collision frequency *Z* of the molecules which depends on species concentration, pressure, the steric factor which accounts for the orientation of the colliding molecules and in addition depends as well mildly on temperature.

For a two component reaction (species B and C) *Z* can be written as:

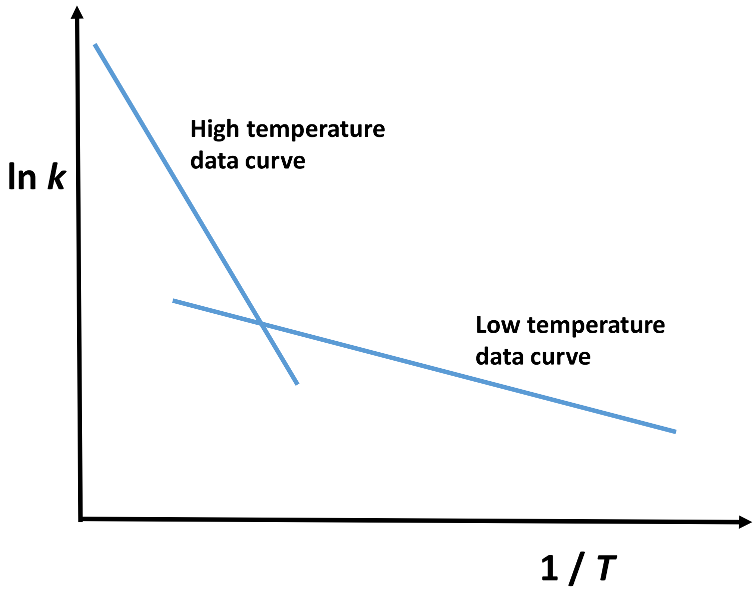
$$Z = \sigma_{BC}^2 \left(\frac{8\pi kT}{\mu}\right) c_B c_c;$$

K	Boltzmann constant,
μ	$(m_b m_c)/(m_b+m_c)$ reduced mass of the molecules
σ_{BC}^2	collision radius of the species
m_b, m_c	masses of the molecules

Chemical Reactions

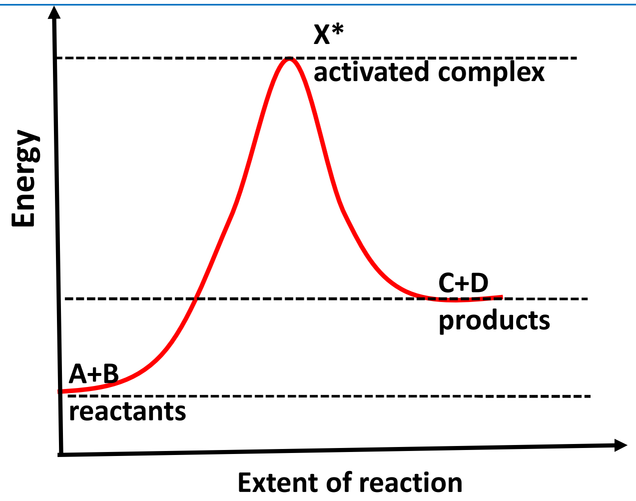
Reaction Rate (Law of Mass Action)

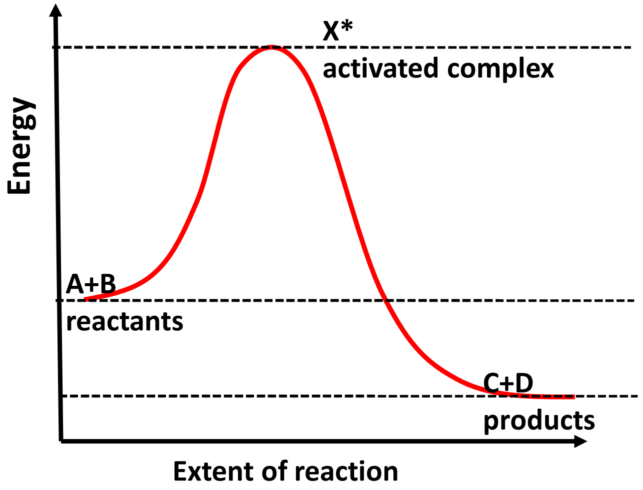
Graphical Illustration of reaction rate dependency on temperature and temperature range



Activation energy for the following reaction where an activated intermediate state is shown

$A+B \leftrightarrow X^* \leftrightarrow C+D$





Chemical Reactions

Mixture Fraction ***Z***

Defined such that it is a conserved scalar (while molecules are consumed or generated, element and their mass fraction in the mixture will be conserved.

$$Z = Z_f = \frac{\nu Y_f - Y_O + Y_{O,2}}{\nu Y_{f,1} + Y_{O,2}}$$

Notation: local quantities without index, educts=1, and index products=2

Let's look at the generic combustion of a hydrocarbon fuel with oxygen

$$\nu_f^{'} C_n H_m + \nu_{O_2}^{'} O_2 = \nu_p products$$

Changes of elements

$$\frac{dn_c}{n \nu_f} = \frac{dn_H}{m \nu_f} = \frac{dn_O}{2 \upsilon_O}$$

Changes of element mass fractions

$$\frac{dZ_C}{\nu_f n W_C} = \frac{dZ_H}{\nu_f m W_H} = \frac{dZ_O}{\upsilon_O W_O}$$

Chemical Reactions

Mixture Fraction *Z*

$$\beta = \frac{Z_C}{\nu'_f n W_C} + \frac{Z_H}{\nu'_f m W_H} - 2\frac{Z_O}{\upsilon'_O W_O}$$

Normalizing such that ***Z = 1*** in the fuel and ***Z = 0*** in oxidizer yields Bilger's definition for a two-component (oxidizer, fuel) problem

$$\boxed{Z = \frac{\beta - \beta_2}{\beta_1 - \beta_2}}$$

with

$$\frac{\nu Y_{f,1}}{Y_{o,2}} = \frac{1 - Z_{st}}{Z_{st}}$$

yields a relation between mixture fraction and equivalence ratio

$$\phi = \frac{Z}{1-Z}\frac{(1-Z_{st})}{Z_{st}}$$

Mixture fraction is an expression for the local equivalence ratio

Chemical Reactions

Example: Combustion with Methane

What do we know: molar masses of O_2 ~ 32 g/mol, N_2 ~ 28 g/mol, CH_4 ~ 16 g/mol

What don't we know: mole fractions and element mass fractions

Air-breathing Application

10 mass % CH_4 + 90 mass % air
(79% vol. fraction of N_2, 21% vol. fraction of O_2)

Mass fractions in air:

$$Y_{O_2(air)} = \frac{M_{O_2} X_{O_2}}{M_{O_2} X_{O_2} + M_{N_2} X_{N_2}} \approx 0.232$$

$$Y_{N_2(air)} = 1 - Y_{O_2} \approx 0.768$$

Mass fraction in mixture:

$$Y_{O_2} = 0.9 Y_{O_2(air)} \approx 0.209, \quad Y_{N_2} = 0.9 Y_{N_2(air)} \approx 0.691, \quad Y_{CH_4} = 0.1$$

Mixture mean molar mass:

$$M = \left(\sum_{i=1}^{3} \frac{Y_i}{M_i} \right)^{-1} \approx 27.9\, g/mol$$

Rocket Application

10 mass % CH_4 + 90 mass % O_2

Mass fraction in mixture:

$$Y_{O_2} = 0.9, \quad Y_{CH_4} = 0.1$$

$$M = \left(\sum_{i=1}^{2} \frac{Y_i}{M_i} \right)^{-1} \approx 29.1\, g/mol$$

Chemical Reactions

Example: Combustion with Methane

Air-breathing Application

Mole fraction of components:

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

$$X_{CH_4} = 0.175, X_{O_2} = 0.182, X_{N_2} = 0.643$$

Mass fraction of elements:

$$Z_j = \sum_{i=1}^{3} \frac{a_{ij} M_j}{M_i} Y_i$$

$Z_H = 0.025$, $Z_C = 0.075$, $Z_O = 0.209$, $Z_N = 0.691$

Rocket Application

Mole fraction of components:

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

$$X_{CH_4} = 0.182, X_{O_2} = 0.818$$

$Z_H = 0.025$, $Z_C = 0.075$, $Z_O = 0.9$

Chemical Reactions

Adiabatic Flame Temperature

In the literature you will find quite often the term adiabatic flame temperature which should characterize a combustion process where no energy is exchanged with the environment → all the bond energy released will increase the energy of the products. Important: Any type of high temperature dissociation reactions are neglected and therefore the adiabatic flame temperature will always be too high.

Example: Calculate the adiabatic flame temperature of the following reaction.

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$$

We can break down this reaction into two steps:

1. $$2H_2(g) + O_2(g) \rightarrow 2H_2O_{(l)} + (2\Delta H^0_{f,H_2O_{(l)}} = -571.9kJ)$$

2. $$2H_2O_{(l)} \rightarrow 2H_2O_{(g)} + (2\Delta H_{\text{vap}} = 87.9kJ)$$

Chemical Reactions

Adiabatic Flame Temperature

Adding these two equations yields

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)} - 484kJ$$

$$484kJ = 2\int_{298}^{T} c_{p,H_2O} dT$$

Assuming constant heat capacity results in an adiabatic flame temperature a little shy of 5000 K. Obviously, this is way too high.

Typically, for H_2/O_2 combustion T_{max} ~ *3500K*.

Chemical Reactions

Adiabatic Flame Temperature

Example: Predict the adiabatic flame temperature of the combustion of methane in air

$$CH_{4(g)} + 15\left(0.21O_{2(g)} + 0.79N_{2(g)}\right) \rightarrow n_{CO_2}CO_2 + n_{H_2O}H_2O + n_{N_2}N_2 + n_{O_2}O_2$$

Atom conservation yields:

C: 1 = n_{CO_2}
O: 15(0.21x2) = $2n_{CO_2} + n_{H_2O} + 2n_{O_2}$
N: 15(0.79x2) = 2 n_{N_2}
H: 4 = 2 n_{H_2O}

$$\Rightarrow \begin{cases} n_{CO_2} = 1 \\ n_{O_2} = 1.15 \\ n_{N_2} = 11.85 \\ n_{H_2O} = 2 \end{cases}$$

Change of enthalpy for an adiabatic process is Zero.

$$\underbrace{\sum_{i=1}^{N} \nu_i'' \Delta H^0_{f,M_i} - \sum_{i=1}^{N} \nu'_i \Delta H^0_{f,M_i}}_{\Delta H_r} - \sum_{i=1}^{N} \nu'_i \left(H_{T,i} - H_{298}\right)_{M_i} + \sum_{i=1}^{N} \nu_i'' \left(H_{T_f} - H_{298}\right)_M = \Delta H = 0$$

Now the 3rd term is zero since T_i = 298 K and we know ΔH_f^0 of O_2 and N_2 = 0;

Chemical Reactions

Adiabatic Flame Temperature

$$\left(1\Delta H^0_{f,CO_2} + 2\Delta H^0_{f,H_2O_{(g)}}\right) - 1\Delta H^0_{f,CH_4} = \Delta H_r = -$$

$$\left[1\left(H_{T_f} - H_{298}\right)_{CO_2} + 2\left(\left(H_{T_f} - H_{298}\right)_{H_2O_{(g)}}\right) + 11.85\left(H_{T_f} - H_{298}\right)_{N_2} + 1.15\left(H_{T_f} - H_{298}\right)_{O_2}\right] = 0$$

$$\Delta H_r = [(-393.5) + 2(-241.8)] - [-74.68] = -803.3J$$

$$= -\left[1\left(H_{T_f} - H_{298}\right)_{CO_2} + 2\left(\left(H_{T_f} - H_{298}\right)_{H_2O_{(g)}}\right) + 11.85\left(H_{T_f} - H_{298}\right)_{N_2} + 1.15\left(H_{T_f} - H_{298}\right)_{O_2}\right]$$

Solution iteratively using table in Annex:

Let's assume	$T_f = 1800\ K$,	then equation above yields	- 972.9 kJ;
If we let	$T_f = 1700\ K$,	then we get	- 782.2 kJ;

By interpolation we receive $T_f \sim 1730\ K$.

However, the assumption of negligible other products holds solely for $T_f < 1200\ K$.

Chemical Reactions

Adiabatic Flame Temperature

Example: for higher temperatures, the reaction may be

$$CH_{4(g)} + 15\left(0.21O_{2(g)} + 0.79N_{2(g)}\right) \rightarrow n_{CO_2}CO_2 + n_{H_2O}H_2O + n_{N_2}N_2 + n_{O_2}O_2$$

$$+ n_{NO}NO + n_H H + n_{OH}OH + n_O O + n_N N + n_{CO}CO + n_{NO^+}NO^+ + n_{e^-}e^- + etc$$

If the reaction is in chemical equilibrium, we can obtain more relations to solve the problem applying the rules of equilibrium constans for each equation.

$$N_2 + O_2 \Leftrightarrow 2NO$$

$$CO + 1/2O_2 \Leftrightarrow CO_2$$

$$O_2 \Leftrightarrow 2O$$

$$N_2 \Leftrightarrow 2N$$

$$H_2O \Leftrightarrow H + OH$$

$$2H \Leftrightarrow H_2$$

$$NO \Leftrightarrow NO^+ + e^-$$